Radioactive chromium-51, a waste byproduct from operation of nuclear reactors at Hanford, Washington, has been followed down the Columbia River and into the Pacific Ocean. Chemical factors influencing the partitioning of $^{51}$Cr between solution and sediment have been considered.

Chromium-51, in a hexavalent oxyanion when introduced into the Columbia River, largely remains in solution in a hexavalent anion during its passage through the lower river and after its entrance into the Pacific Ocean.

A minor fraction of Hanford-induced $^{51}$Cr becomes attached to suspended particles and bottom sediments. Reduction of Cr(VI) to Cr(III) apparently precedes or accompanies sorption. Iron oxides appear to be the most important sorption substrate. Sediment organic matter acts both as a reducing agent, making $^{51}$Cr less soluble, and as a sorption substrate. Ion exchange on sediment
particles is not important in retention of $^{51}$Cr by Columbia River sediment.

Chromium-51 is a sensitive and unique tracer for Columbia River water at sea and has been used to trace the Columbia River plume up to 525 km away from the mouth of the river.

Dispersion of $^{51}$Cr by the Columbia River system would be adversely affected by: 1) lowered pH; 2) presence of particulate organic wastes; 3) increased temperature; 4) increased biological oxygen demand. These factors would increase the rate of uptake of $^{51}$Cr by sediments and thus increase the steady-state inventory of $^{51}$Cr on the bottom of the river.
CHROMIUM-51 IN THE COLUMBIA RIVER
AND ADJACENT PACIFIC OCEAN

by

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CHROMIUM-51 IN THE COLUMBIA RIVER
AND ADJACENT PACIFIC OCEAN

INTRODUCTION

General Statement

When an artificial radionuclide is introduced into a stream or an ocean, it becomes fractionated among solution, sediment and biological phases. Knowledge of how each radioactive pollutant is partitioned is useful in recognizing potentially hazardous reservoirs of radioactivity and in promoting rapid dispersion of the contaminant. In addition, the behavior of radioactive pollutants in a stream may provide information on geochemical processes or conditions. In general, physical and chemical factors determine which phases contain significant fractions of a radionuclide.

The Columbia River and adjacent Pacific Ocean waters provide a natural laboratory for the observation of the behavior of radioisotopes of several elements. Low level wastes from the operation of plutonium production reactors at Hanford, Washington, have been introduced into the river since the mid-1940's. Chromium-51 from this source is one of the most abundant radionuclides in the Columbia River. Its 27.8-day half-life makes $^{51}$Cr a potentially useful timing tracer for processes occurring over periods of a few days to a few months.
The moderately complicated chemistry of chromium and its extremely low concentration in natural waters make prediction of the fate of radiochromium an interesting and challenging endeavor. The purpose of this work is to determine what conditions and what reactions are effective in fractionation of $^{51}\text{Cr}$ from the Hanford effluent.

**Background Information**

**Chemistry of Chromium**

Chromium occurs naturally in four isotopes of the following average abundance: $^{50}\text{Cr} - 4.31\%$, $^{52}\text{Cr} - 83.76\%$, $^{53}\text{Cr} - 9.55\%$, $^{54}\text{Cr} - 2.38\%$. The only known radioisotope with a half-life greater than a few minutes is 27.8-day $^{51}\text{Cr}$ (Friedlander, Kennedy and Miller, 1964). Chromium-51 can be formed by at least two neutron-capture reactions: $^{50}\text{Cr}(n, \gamma)^{51}\text{Cr}$ and $^{54}\text{Fe}(n, \alpha)^{51}\text{Cr}$. The cross-section for the former reaction with thermal neutrons is 16 barns. In a thermal neutron flux the latter reaction is much less likely than the competing $^{54}\text{Fe}(\gamma)^{55}\text{Fe}$ or $^{54}\text{Fe}(n, p)^{54}\text{Mn}$ reactions.

Elemental chromium is a hard, bluish-white metal which rarely, if ever, occurs naturally. Although compounds and/or complexes containing chromium in all valence states from -2 to +6 have been reported (Cotton and Wilkinson, 1962), only the valence states
+3 and +6 are stable in aqueous solutions. Dipositive chromium is metastable in aqueous solutions isolated from the air but will slowly displace hydrogen from water. Thus it seems important to consider only the +3 and +6 states in natural surface water.

The tripositive state is considered the most stable and important state for chromium. Green Cr(III) aquo ions are present in moderately acidic solutions. At intermediate values of pH, after hydrolysis, a gelatinous, blue-green precipitate containing a variable amount of water forms. Although this solid is often called chromic hydroxide, "hydrous chromic oxide" is probably a better name. This oxide is amphoteric and, provided that it is not dried and ignited, dissolves in basic solution to yield "chromite" solutions of uncertain composition. Cotton and Wilkinson (loc. cit.) suggested that chromite solutions contain the ions $[\text{Cr(OH)}_6]^{3-}$ or $[\text{Cr(OH)}_5\text{H}_2\text{O}]^{2-}$. Garrels and Christ (1965) tabulated thermo-dynamic data for a chromite ion of supposed composition $\text{CrO}_2^{-}(\text{aq})$. Udy (1956) stated that the dissolution of hydrous chromic oxide in basic solutions does not yield anions but rather a peptized negative sol.

One of the most fascinating aspects of Cr(III) chemistry is the formation of thousands of complexes. Apparently Cr(III) always has a coordination number of six. Ligand exchange reactions are often very slow and this factor probably contributes to the large
number of complexes that have been isolated. Kinetic inertness, though often a boon to the preparative chemist, is a severe handicap in the determination of thermodynamic constants. Thus, stability constants are known for only a few chromium (III) complexes.

Hexavalent chromium has a coordination number of four and the most common ligand is oxide. Under very acidic conditions, halides can replace oxide to form oxyhalide ions, \( \text{CrO}_3 \text{X}^- \) (\( \text{X} = \text{F}^-, \text{Cl}^-, \text{Br}^- \) or \( \text{I}^- \)), or chromyl halides (\( \text{CrO}_2 \text{Cl}_2 \) or \( \text{CrO}_2 \text{F}_2 \) only). These all hydrolyze readily in pure water to yield oxyanions. In basic solutions the chromate ion, \( \text{CrO}_4^{2-} \), is the prevalent species. At lower pH, \( \text{HCrO}_4^- \) forms, and, if the total Cr(VI) concentration is high enough, \( \text{Cr}_2\text{O}_7^{2-} \) is produced. The reactions involved:

\[
\text{HCrO}_4^- = \text{H}^+ + \text{CrO}_4^{2-} \quad \text{K}_{a2} = 3.5 \times 10^{-7} \text{ and }
\]

\[
2\text{HCrO}_4^- = \text{Cr}_2\text{O}_7^{2-} + \text{H}_2\text{O} \quad \text{K} = 49,
\]

are readily reversible. In acidic solutions of very high Cr(VI) concentration, further polymerization may occur.

The tetrahedral chromate ion is somewhat similar to the sulfate ion in solution-precipitation behavior. It is precipitated by \( \text{Ba}^{2+}, \text{Pb}^{2+}, \text{Tl}^+, \text{Ag}^+ \) or \( \text{Bi}^{3+} \). Ordinarily, dichromates are more soluble than chromates and the latter often precipitate from solutions where dichromate is the prevalent Cr(VI) species.

Hexavalent chromium is a rather strong oxidant in acidic solution but less so in basic solution.
\[
\begin{align*}
\text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 6\text{e}^- &= 2\text{Cr}^{3+} + 7\text{H}_2\text{O} \quad E^0 = 1.33 \text{ v.} \\
\text{CrO}_4^{2-} + 4\text{H}_2\text{O} + 3\text{e}^- &= \text{Cr(OH)}_3(\text{s}) + 5\text{OH}^- \quad E^0 = -0.13 \text{ v.}
\end{align*}
\]

The Cr(III)-Cr(VI) half-reactions involve three electrons per atom of chromium but redox reactions probably do not have a step in which three electrons are exchanged. As a result, rate laws for these reactions are complicated and reaction mechanisms ordinarily involve the formation of unstable intermediate Cr species. Exchange reactions between Cr(III) and Cr(VI) also appear to involve unstable intermediates and are further complicated by a change in coordination number (Altman and King, 1961). Thus, the exchange is slow (Altman and King, ibid.; Muxart et al., 1947; Aten et al., 1953).

**Chromium as a Bioelement**

Chromium is present in trace amounts in many plants and animals, but has ordinarily not been considered essential for any organisms (Baetjer, 1956; Foster, 1963). Evidence that traces of trivalent chromium may be important in assisting the function of insulin in humans has recently been presented (Glinsmann, Feldman and Mertz, 1966).

Hexavalent chromium is harmful to animals. In sufficient concentration it is a systemic poison. At lower concentrations it is an irritant. When inhaled Cr(VI) may cause cancer of the respiratory tract. Whether the carcinogenic action is due to irritation or to
the production of a carcinogenic agent in the body is unresolved (Baetjer, loc. cit.). The toxicity of Cr(VI) has been attributed to its "high solubility and diffusibility under physiological conditions" (Grogan and Oppenheimer, 1955).

It has long been known that both Cr(III) and Cr(VI) react with proteins. Such interactions are apparently involved in the chrome tanning process (Lollar, 1956). Grogan and Oppenheimer (loc. cit.) report that Cr(III) (like many heavy metal ions) precipitates proteins on the basic side of their isoelectric point and Cr(VI) precipitates proteins on the acid side. Whether or not these interactions might be important in removing dissolved chromium from a system so dilute as natural surface waters is a point yet to be resolved. It would be necessary to learn which specific proteins are involved, their concentration in the system and the solubility of the precipitate.

Trivalent and hexavalent chromium are highly fractionated in human blood with Cr(VI) entering the red blood cells and Cr(III) binding to plasma proteins. This fractionation is so complete that simultaneous determinations of red cell mass and plasma volume have been made using \(^{51}\)Cr-labeled sodium chromate and chromic chloride (Gray and Frank, 1953).

Among marine organisms the greatest accumulators of chromium appear to be green algae (Black and Mitchell, 1952).
Similarly, the highest apparent concentration factor for $^{51}$Cr in Columbia River organisms is that for green algae (Foster, 1963). The concentration mechanism is unknown. Radiochromium is not accumulated in marine organisms above the first trophic level (Osterberg, Pearcy and Curl, 1964). Stevenson, Ufret and Diecidue (1965) reported rather high concentration factors (400,000 to 900,000 for marine animals and 10,000 to 300,000 for benthic algae). However they did not determine the Cr concentration in the seawater from which their samples were taken. Instead, they used a value reported for Cr in seawater by Goldberg (1957). It is worth noting that Goldberg's value (0.05 micrograms Cr/liter) is at the lower end of a range of reported values that spans two orders of magnitude. Until it has been demonstrated that Cr is uniformly distributed in the sea, concentration factors should be reported only when the element has been measured both in the organisms and in their surrounding medium.

**Geochemistry and Mineralogy of Chromium**

Chromium is usually in the tripositive state in nature. It occurs in many silicate minerals as a substitute for Fe(III) or Al(III) (Thayer, 1956). Thayer considers "the monoclinic amphiboles, pyroxenes and chlorites" to be "the most important chromium-bearing silicates." The only mineral of economic significance
is chromite, a spinel represented by the formula \((\text{Mg, Fe})(\text{Cr, Al, Fe})_2\text{O}_4\).

The earth's crust contains an average of 200 ppm of chromium (Barth, 1952). The element is ordinarily associated with ultramafic rocks and economic deposits are always in ultramafic rocks (Thayer, loc. cit.). Turekian and Carr (1960), reporting abundance of Cr in various units of the earth's crust, listed a markedly higher concentration in the 'ultramafic' unit (1600 ppm) than in any other unit. The next highest units were 'schists' (174 ppm) and 'basaltic' (170 ppm). The fractionation pattern of chromium in the Skaergaard Intrusion is also illustrative. The rocks in this body, crystallized from a basaltic magma, vary from early, Mg-rich, \(\text{SiO}_2\)-poor rocks to late, \(\text{K}_2\text{O}\)-rich, \(\text{SiO}_2\)-rich rocks (Mitchell, 1964). The chromium concentration in the earliest rocks is 2000 ppm and in the latest, only 5 ppm. Thayer (loc. cit.) believes that all economically interesting primary chromium deposits are of early magmatic origin and that hydrothermal processes are not responsible for ore deposits.

Meteoritic matter contains an average of 0.34% chromium (Mason, 1960). The element is ordinarily a lithophile but Mason points out that in the absence of oxygen, \(\text{Cr}\) becomes a chalcophile. However, the sulfo-spinel, daubreelite (\(\text{FeCr}_2\text{S}_4\)), is known only from meteorites. The silicate phase of meteorites contains an average
0.36% Cr while the troilite (sulfide) phase contains only 0.12% 
average (Mason, ibid.).

Hexavalent chromium minerals are rare. Crocoite (PbCrO₄) 
is sometimes found in the oxidized portions of lead deposits. (Asso-
ciated minerals are cerussite and anglesite.) This mineral is of 
historic interest because chromium was first discovered in crocoite 
specimens (Hurlbut, 1959). Dietzite (Ca(IO₃)₂CaCrO₄) and tar-
apacaite (K₂CrO₄) are found in certain niter deposits in Chile 
(Barth, 1952). These rare deposits also contain other highly oxid-
ized species such as iodates and perchlorates.

Chromium in Seawater

The concentration of chromium in seawater is low. The 
reported values range from 10⁻² to a few micrograms per liter 
(Table 1). Krauskopf (1956) estimated that sufficient chromium 
has been weathered from rocks during geologic time to produce a 
concentration of 120 milligrams per liter in the oceans. However 
it is likely that only a small fraction of the weathered chromium 
has been dissolved. Although chromium-bearing silicates are 
readily decomposed, spinels such as chromite are highly resistant 
to weathering.
Table 1. Concentration of Cr in seawater

<table>
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<tr>
<th>Analytical Method</th>
<th>Concentration found micrograms/liter</th>
<th>Reference</th>
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</thead>
<tbody>
<tr>
<td>Spectrographic</td>
<td>1 - 2.5</td>
<td>Black and Mitchell (1952)</td>
</tr>
<tr>
<td>Spectrographic</td>
<td>0.2</td>
<td>Noddack and Noddack (1940)</td>
</tr>
<tr>
<td>Spectrophotometric</td>
<td>0.13 - 0.25</td>
<td>Loveridge et al. (1960)</td>
</tr>
<tr>
<td>Spectrophotometric</td>
<td>0.04 - 0.07</td>
<td>Ishibashi (1953) cited by Loveridge et al. (1960)</td>
</tr>
<tr>
<td>Spectrophotometric</td>
<td>0.46</td>
<td>Chuecas and Riley (1966)</td>
</tr>
</tbody>
</table>

The oxidation state of Cr in seawater is important in determining its reactions. Thermodynamic considerations indicate that \( \text{CrO}_4^{2-} \) should be the predominant species. Krauskopf (1955) applied stability-field or Eh-pH diagrams to the aqueous chromium system. A diagram of this type is shown in Figure 1. (Construction and interpretation of Eh-pH diagrams is discussed in the appendix.) Harvey (1960) stated that the pH of open ocean waters seldom varies beyond 8.00 or 8.30 and Cooper (1938) gave an experimental value of Eh for seawater of 0.43 volt. Under these conditions \( \text{CrO}_4^{2-} \) is the predominant ion at equilibrium. This observation led Krauskopf (1956) to postulate "Chromium in aerated seawater would exist as
Figure 1. Stability-field diagram for chromium.
It should be noted that the thermodynamic significance of measured Eh values, particularly in aerated waters, has been questioned. The reader is referred to the appendix. While the Eh-pH diagram provides a readily seen qualitative estimate of the equilibrium species under wide ranges of oxidation potential and pH, the method used by Sillén (1960) gives a quantitative ratio of activities of any pair of species for a given Eh and pH. Thus for the reaction between the most probable trivalent and hexavalent species the activity ratio of Cr(III) to Cr(VI) at equilibrium is $10^{-21.9}$. This calculation and a set of similar calculations for other Cr ions is included in the appendix along with a discussion of the method.

The prediction of predominant chemical forms in natural water systems from thermodynamic data alone is probably a rough approximation at best. The importance of kinetic factors can be great, particularly in a dilute system. Therefore it is conceivable that an element such as chromium, with a short residence time in the sea ($t=350$ years, Goldberg, 1965), simply may not ever reach chemical equilibrium.

Krauskopf (1956) concluded that Cr(VI) should not be precipitated by cations present in seawater at their usual concentration. He added "massive" quantities of $K_2Cr_2O_7$ to seawater and observed no precipitate. On the other hand, Arrhenius (1963) found that authigenic celestobarite (Ba, SrSO$_4$) crystals from equatorial North Pacific
sediments contained 1400 ppm of chromium. He suggested that \( \text{CrO}_4^{2-} \) substituted for \( \text{SO}_4^{2-} \) in these crystals. Chow and Goldberg (1960) stated that surface waters in the equatorial Pacific are not saturated with \( \text{BaSO}_4 \) but that saturation may be reached in deeper waters owing to an increase in barium concentration with depth. Thus it appears that Cr concentration may be controlled in the sea by coprecipitation of \( \text{CrO}_4^{2-} \) with \( \text{BaSO}_4 \) at depth. It does not seem likely that Cr(III) would be more concentrated in \( \text{BaSO}_4 \) than in other sediments. Therefore, Arrhenius' observations are evidence that chromium in seawater is hexavalent. Chuecas and Riley (1966) concluded from experimental results that Cr in seawater is trivalent. However, they acidified and stored their samples prior to determining the oxidation state. Possibly Cr(VI) could have been reduced during storage in an acidic solution.

Krauskopf (1956) also studied the sorption of Cr(VI) from seawater on \( \text{MnO}_2 \cdot n\text{H}_2\text{O} \), \( \text{Fe}_2\text{O}_3 \cdot n\text{H}_2\text{O} \), apatite, "clay", and "plankton". Of these, only \( \text{MnO}_2 \cdot n\text{H}_2\text{O} \) was effective in removing Cr(VI) from his solutions. It would seem reasonable, then, that chromium might be enriched in manganese nodules. This is decidedly not the case. While Goldberg and Arrhenius (1957) reported an average of 82 ppm of Cr in Pacific pelagic sediments, the element is conspicuously absent from reported analyses of manganese nodules (Riley and Sinhaseni, 1958; Menard and Shipek, 1958; Willis and Ahrens, 1962).
Krauskopf (1956) suggested that Cr concentration in the sea is controlled by local reduction and precipitation as the "hydroxide". Probably the hydrous oxide would not precipitate, but rather Cr(III) might be removed by sorption to any available solid phase. Curl, Cutshall and Osterberg (1965) found that $^{51}$Cr(III) is actively adsorbed on living and dead plankton or on glass beads at all pH values normal for seawater. Such sorption could occur, of course, with chromium originally present as Cr(III) or produced by local reduction of Cr(VI). It is likely that hydrous chromic oxide is too soluble to precipitate at the Cr concentration and pH of seawater. From Figure 1 it appears that the most probable trivalent Cr ion at a pH of 8.0 is $\text{Cr(OH)}_2^+$. The precipitation of this ion might be: $\text{Cr(OH)}_2^+ + \text{H}_2\text{O} = \text{Cr(OH)}_3(s) + \text{H}^+$, for which log $K = -1.76$. Assuming $\text{H}_2\text{O}$ and $\text{Cr(OH)}_3$ have unit activity, the minimum activity of $\text{Cr(OH)}_2^+$ required for precipitation at a pH of 8.0 would be about $6 \times 10^{-7}$ M. Neglecting the activity coefficient (which would make the computed concentration even higher), this corresponds to a saturation concentration of 33 micrograms Cr/liter. Since the highest reported value for Cr in seawater is 2.5 micrograms/liter, it is apparent that seawater is not saturated with respect to $\text{Cr(OH)}_3$ even if Cr is trivalent. This does not rule out the possibility that Cr(III), if it is present, may enter a solid phase. Iron oxides might be expected to adsorb (coprecipitate) Cr(III) since $\text{Cr}_2\text{O}_3$ and $\text{Fe}_2\text{O}_3$ form a
complete solid solution series.

Fukai (1965) leached sediments from the Bay of Roquebrune with various concentrations of hydrochloric acid and analyzed the leachates for Cr and Fe. The parallel behavior of these two elements was striking. This would be expected if the chromium were associated with iron oxide. Fukai cautioned that he was working with shallow-water sediments and that sediments from the open ocean might be quite different. Bonatti and Joensuu (1966) observed that chromium was lower in iron and manganese oxide rocks than in basalt fragments taken in a single dredge haul in the South Pacific. They believe their iron and manganese oxide rocks were precipitated locally from hydrothermal solutions and that Cr is deficient because it is oxidized in seawater and remains in solution as $\text{CrO}_4^{2-}$.

Chromium in Rivers

Durum and Haffty (1963) reported the median concentration of Cr in large North American rivers to be 5.8 micrograms/liter and the range 0.72 to 84 micrograms/liter. They noted that rivers draining into the Atlantic Ocean were usually above the median while those entering the Pacific were usually below the median. Chromium concentrations in the Columbia River ranged from below 0.8 to 9 micrograms/liter in four-month composites of weekly samples taken in 1961-62 (U.S. Department of Health, Education and Welfare, 1962).
The oxidation state of Cr in river waters is not known. Whetten (1966) found 50 ppm in sediments from each of three locations in the lower Columbia River.

In summary, the cycle of chromium in rivers and oceans is not known well enough to permit a priori prediction of the fate of $^{51}$Cr with great confidence.
EXPERIMENTAL

Radioanalysis

All measurements of radioactivity were made by gamma-ray spectrometry. Theory and practice of this rather new method are discussed by Crouthamel (1960), Heath (1964), Baird-Atomic Incorporated (1960) and by Perkins (1958). Briefly, gamma-rays emitted from a sample cause a detector to scintillate. The scintillations are converted to current pulses by a photomultiplier tube and the pulses are measured and recorded in a multichannel analyzer. In practice an individual system is experimentally calibrated using known amounts of radioactive nuclides. Data from the analyzer are reduced by making corrections for interferences and efficiency. More specific information on the systems used for this work is given by Osterberg (1964) and Perkins (1958).

Chromium-51 in the Columbia River

Source and Associated Radionuclides

Sodium dichromate is added to reactor coolant water at Hanford, Washington, (Figure 2) to inhibit corrosion (Perkins, Nelson and Haushild, 1966). Chromium-50, a stable isotope, undergoes radiative neutron capture to yield 27.8-day $^{51}$Cr. The coolant
Figure 2. Map of lower Columbia River.
water, carrying $^{51}$Cr, is eventually returned to the Columbia River. Many other radionuclides are also induced in the coolant water but most of these decay below detectable levels before reaching the river and only a few of them reach the ocean. Some of the longer-lived radionuclides that do reach the ocean are: $^{54}$Mn, $^{65}$Zn, $^{46}$Sc and $^{60}$Co. These four were often found in samples analyzed for $^{51}$Cr.

Although the principal concern of this work is $^{51}$Cr, the other radionuclides will be occasionally mentioned for contrast and comparison with chromium. Zinc-65 and scandium-46 in the Columbia River are probably almost entirely derived from the Hanford plant (as is $^{51}$Cr). Manganese-54 and cobalt-60, on the other hand are probably contributed both by the Hanford plant and by fallout from atmospheric nuclear detonations. Occasionally, radioactive fission products, particularly $^{95}$Zr-$^{95}$Nb, $^{106}$Ru and $^{144}$Ce, were also observed. These too may be from fallout or from fuel element ruptures at Hanford. These fission products were most commonly found in sediments and were very unevenly distributed (Cutshall and Osterberg, 1964).

Sorption of Chromium-51 to Solid Phases

A fraction of the $^{51}$Cr from Hanford becomes associated with suspended and bottom sediment particles. Perkins, Nelson and Haushild (1966) filtered samples of reactor effluent water and
Columbia River water taken between Hanford and Vancouver, Washington through 0.3-micron membrane filters and determined the fraction of $^{51}$Cr associated with filterable particles. In reactor effluent, 2.4% was filtered out. At Pasco, Washington, Hood River, Oregon and Vancouver, the filters retained 6.4%, 4.0% and 7.6% respectively. Similar measurements were made in March, 1966 between Vancouver and Astoria, Oregon, aboard the R/V *Yaquina* (Table 2). Although the "percent particulate" values are a complicated function of the suspended load, hence stream velocity and immediate past history of the water, such measurements demonstrate that the bulk of $^{51}$Cr is transported in a non-filterable state.

Table 2. "Percent particulate" $^{51}$Cr between Vancouver and Astoria. (0.45-micron filters; March, 1966)

<table>
<thead>
<tr>
<th>Approximate distance upstream from Astoria, n. m.</th>
<th>Location</th>
<th>Percent particulate Chromium-51</th>
</tr>
</thead>
<tbody>
<tr>
<td>75</td>
<td>Vancouver Lower Range</td>
<td>3.66</td>
</tr>
<tr>
<td>67</td>
<td>Henrici Range</td>
<td>3.68</td>
</tr>
<tr>
<td>53</td>
<td>Kalama Lower Range</td>
<td>4.17</td>
</tr>
<tr>
<td>38</td>
<td>Stella Range</td>
<td>4.83</td>
</tr>
<tr>
<td>32</td>
<td>Eureka Channel</td>
<td>4.90</td>
</tr>
<tr>
<td>21</td>
<td>Puget Island Range</td>
<td>5.94</td>
</tr>
<tr>
<td>11</td>
<td>Pillar Rock Lower Range</td>
<td>6.30</td>
</tr>
<tr>
<td>7</td>
<td>Harrington Point Range</td>
<td>5.23</td>
</tr>
<tr>
<td>0</td>
<td>Astoria Range</td>
<td>5.33</td>
</tr>
</tbody>
</table>
While it appears that, under present conditions, particles play a small role in the distribution of $^{51}$Cr, the abundance of this nuclide, as compared to other radionuclides in the river, causes the inventory of $^{51}$Cr in bottom sediments between Pasco and Vancouver to be the highest of the ten artificial nuclides studied by Perkins, Nelson and Haushild (1966). Thus $^{51}$Cr is of considerable interest in the study of radionuclides in Columbia River sediments. Two approaches have been employed in analyzing the $^{51}$Cr-sediment interaction: 1) uptake of spikes has been observed in the laboratory; 2) $^{51}$Cr has been removed from river sediments by a variety of means.

**Uptake Experiment**

Uncontaminated sediment from above the reactors (Priest Rapids reservoir) was exposed to solutions of $^{51}$Cr and the isotope remaining in solution was observed at various times. Four uptake runs were made under the following conditions: 1) $^{51}$Cr(III) spike on air-dried sediment; 2) $^{51}$Cr(III) spike on $\text{H}_2\text{O}_2$-treated, air-dried sediment; 3) $^{51}$Cr(VI) spike on air-dried sediment; 4) $^{51}$Cr(VI) on $\text{H}_2\text{O}_2$-treated, air-dried sediment. In the $\text{H}_2\text{O}_2$ treatment the sediments were moistened with water and 30% hydrogen peroxide was added slowly. When the initial, vigorous reaction subsided the slurry was gently heated and more $\text{H}_2\text{O}_2$ solution was added. This
process was continued for several hours until the addition of peroxide solution to a near boiling suspension apparently caused only the decomposition of $\text{H}_2\text{O}_2$.

Ten grams of sediment were suspended in 50 ml of distilled water to which $^{51}\text{Cr}$ tracer had been added. Stable chromium carrier concentration was 80 micrograms/liter. The sample tubes were shaken vigorously for timed intervals after which the tubes were placed in a centrifuge and the sediment spun down. A 1-ml portion of the supernatant solution was withdrawn for counting and the sediment immediately resuspended. The activity withdrawn as a function of time is shown in Figure 3.

Uptake of $^{51}\text{Cr(III)}$ was much too rapid to be observed by this crude experiment. Essentially all the radioisotope was associated with either air-dried or $\text{H}_2\text{O}_2$-treated, air-dried sediment within six minutes. After a rapid initial uptake of about 30%, $^{51}\text{Cr(VI)}$ reacted more slowly. There was a significant difference in the rate of uptake of Cr(VI) on the two sediments, with the reaction on peroxide-treated sediment being slower. Two explanations seem plausible. First, the peroxide treatment may have destroyed the substrate on which Cr(VI) is adsorbed. Second, the sorption of Cr(VI) may be preceded or accompanied by reduction to Cr(III) and the peroxide treatment impaired the reducing ability of the sediment. These possibilities will be mentioned again in a later section.
Figure 3. Curves showing loss of Cr(VI) from solutions in contact with Columbia River sediment.

- x = air dried sediment
- * = H₂O₂-treated, air-dried sediment
One thing is readily evident--if $^{51}$Cr(VI) is reduced to $^{51}$Cr(III) in the river, the reduced portion will not long remain in solution.

**Desorption Experiments**

Johnson (1966) conducted the first desorption experiments with Columbia River sediments. He leached fresh sediment samples with a variety of solutions: 1 N ammonium acetate, seawater, 0.05 M solutions of CuSO$_4$, MnSO$_4$, and CoCl$_2$.

The first two solutions are capable of displacing ions held by cation exchange while the transition metal solutions displace specifically sorbed cations. "Specific sorption" is used to designate an exchange reaction in which transition metals are capable of displacing one another, but NH$_4^+$ or ions of alkali metals or alkaline earths have little or no effect. Among divalent transition metals, the Irving-Williams order of stability of complexes ($\text{Mn}^{2+} < \text{Fe}^{2+} < \text{Co}^{2+} < \text{Ni}^{2+} < \text{Cu}^{2+} > \text{Zn}^{2+}$) is paralleled by specific sorption preference. That is, metals whose complexes are more stable (thermodynamically) are preferentially sorbed. It would appear that coordinate bonding is involved in specific sorption. None of the solutions used by Johnson displaced $^{51}$Cr from sediment. Johnson, Cutshall and Osterberg (n. d., in press) concluded that $^{51}$Cr is not bound to Columbia River sediment by cation exchange. Since its ligand exchange reactions are so slow, Cr(III) might be specifically sorbed,
but not displaced sufficiently rapidly to have been detected.

Electrodialysis

Samples of mud from the bottom of McNary Dam reservoir (Lake Wallula) were subjected to electrodialysis in an attempt to remove radionuclides. It was hoped the removal of $^{51}\text{Cr}$ might be accomplished without oxidation or reduction of Cr and that Cr(VI) (anionic) might be distinguished from Cr(III) (cationic). These experiments were only partly successful. Cr(VI) and Cr(III) could, indeed, be readily separated by electrodialysis, but they could not be displaced from the sediment. Samples were placed in the center chamber of the apparatus shown in Figure 4 and a voltage applied across the electrodes. Anions migrated from the center cell through the anion exchange membrane (immobile positive charges) into the anode chamber. Cations, likewise, migrated to the cathode compartment. (Ionac MC-3142 cation exchange membrane and MA-3148 anion exchange membrane were used. Ionac Chemical Company, Birmingham, New Jersey.) Electrolysis of water in the end compartments caused an increase in pH in the cathode chamber, while the pH in the anode chamber decreased. During a run the pH in each of these chambers was maintained between 2 and 5 by adding HCl or NaOH as required. The pH in the center chamber remained at about 7.
Figure 4. Electrodialysis cell

ANODE CHAMBER

SAMPLE CHAMBER

CATHODE CHAMBER

Pt

+ ________fT_____

anion exchange membrane

ANIONS

cation exchange membrane

CATIONS

Pt

TO POWER SUPPLY
Preliminary trials were made with solutions of $^{51}$Cr(III) and $^{51}$Cr(VI) to assure that they could be separated. Good separation was obtained (Table 3). A previously frozen sediment from McNary Dam was thawed and placed in the center chamber and a 50 ma current was passed for 25 hours. If larger currents were passed for very long, excessive heating resulted and the sample dried out. Virtually no $^{51}$Cr was removed by this treatment (Table 4). On the other hand, considerable fractions of $^{60}$Co, $^{65}$Zn and $^{54}$Mn were removed. Scandium-46, like chromium-51, was not extracted. Cobalt and zinc in the sediments are presumably divalent cations while Mn may be a divalent cation or tetravalent as MnO$_2$. Scandium is trivalent. Sediments that had been spiked with $^{51}$Cr as Cr(III) and as Cr(VI) were also electrodialyzed. Neither of these yielded any $^{51}$Cr.

Although the electrodialysis experiments did not produce the desired result, some conclusions can be drawn. Chromium-51, sorbed to sediment under either laboratory or natural conditions, is tightly held in comparison to divalent radionuclides. This holds for Cr sorbed from either Cr(III) or Cr(VI) solutions. Trivalent $^{46}$Sc is also held more tightly than the divalent metals.

**Sediment Fractionation Experiments**

Evidently rather vigorous chemical treatment is required to remove $^{51}$Cr from Columbia River sediment. Accordingly the
Table 3. Results of electrodialysis of $^{51}$Cr-labelled solutions

<table>
<thead>
<tr>
<th>Form of $^{51}$Cr added</th>
<th>Percent of $^{51}$Cr recovered from each chamber</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Anode</td>
<td>Center</td>
</tr>
<tr>
<td>Cr(III)</td>
<td>2.6</td>
<td>0.2</td>
</tr>
<tr>
<td>Cr(III)</td>
<td>1.2</td>
<td>1.2</td>
</tr>
<tr>
<td>Cr(VI)</td>
<td>90.7</td>
<td>0.3</td>
</tr>
<tr>
<td>Cr(VI)</td>
<td>92.3</td>
<td>0.5</td>
</tr>
<tr>
<td>Cr(VI)</td>
<td>96.1</td>
<td>0.9</td>
</tr>
</tbody>
</table>

Table 4. Results of electrodialysis of McNary dam sediments. (Percent recovery was determined by comparison with an untreated subsample. Lower self-absorption of gamma-rays in the solutions than in the sediments accounts for the apparent recovery of more than 100%.)

<table>
<thead>
<tr>
<th>Nuclide</th>
<th>Percent recovered in each chamber</th>
<th>Apparent total</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cathode</td>
<td>Not removed</td>
</tr>
<tr>
<td>$^{60}$Co</td>
<td>80.4</td>
<td>31.2</td>
</tr>
<tr>
<td>$^{46}$Sc</td>
<td>1.1</td>
<td>106.7</td>
</tr>
<tr>
<td>$^{65}$Zn</td>
<td>78.4</td>
<td>27.6</td>
</tr>
<tr>
<td>$^{54}$Mn</td>
<td>54.1</td>
<td>52.9</td>
</tr>
<tr>
<td>$^{51}$Cr</td>
<td>1.3</td>
<td>97.9</td>
</tr>
</tbody>
</table>
following scheme was devised. The sediment was considered to consist of the following components:

1. An ion exchange substrate--This phase of the work was conducted concurrently with Johnson's (1966) research and his results were not yet available. Many minerals are known to have a cation exchange ability. Exchangeable cations can be displaced by leaching with a solution of 1 N ammonium acetate (Bear, 1964).

2. Organic (biological) particles--The remains of plants and animals may accumulate in sediments. Since organic particles are usually less dense than minerals, a density gradient separation should separate the two. The bromoethanol method of Lammers (1963) was adapted.

3. Organic coatings on minerals--Organic material adsorbed to mineral grains might not be separated from the minerals by density methods. This material was destroyed with hydrogen peroxide.

4. Iron oxide coatings on minerals--Oxides of iron are commonly found as coatings on mineral grains. These are quantitatively removed by treatment with sodium dithionite in the presence of citrate buffer (Aguilera and Jackson, 1953).

5. Inorganic grains--The bulk of a sediment is comprised of grains weathered from rocks. These may be individual minerals, rock fragments or fragments of volcanic glass.
Although the last-named component probably constitutes a very large weight-fraction of the sediment, the potential reactivity and surface availability of the other components make them worthy of consideration. The flow sheet in Figure 5 indicates the course of treatment of the samples. Each step was repeated two to four times and the radioactivity removed with each step was measured. Twelve such separations were made. The first set of four separations included two samples of Priest Rapids sediment spiked with $^{51}$Cr(III) and a duplicate pair of McNary Dam sediments. The second set of eight samples consisted of the sediments used for the $^{51}$Cr uptake experiment plus four samples from different depths in a McNary core. Results of these experiments are given in Tables 5 and 6.

In the second series the ammonium acetate treatment was replaced by leaching with 5% acetic acid. This was perhaps an unfortunate choice in that the removal of radionuclides with this solvent cannot be interpreted within the limits of the proposed sediment model.

The fraction of $^{51}$Cr removed by ammonium acetate was, of course, small; in fact, too small for detection. Of the five nuclides measured only $^{54}$Mn was appreciably removed (about 10%). One or two percent of $^{65}$Zn was displaced. These results agree rather well with those of Johnson (1966).

The density gradient separations were made by carefully introducing the sediment in a water slurry over bromoethanol.
Figure 5. Flow sheet for sediment fractionation experiments. (Numbers in parentheses indicate the number of times each step was performed.)
Table 5. Results of sediment fractionation experiments with chromium-51 spiked Priest Rapids sediment. Percent removed with each component calculated from the amount of isotope put on the sediment.

<table>
<thead>
<tr>
<th>Fraction</th>
<th>Treatment</th>
<th>First Series</th>
<th>Second Series</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(a)</td>
<td>(b)</td>
<td>(c)</td>
</tr>
<tr>
<td>exchangeable cations</td>
<td>ammonium acetate</td>
<td>0.3</td>
<td>0.4</td>
</tr>
<tr>
<td>extracted at pH = 3</td>
<td>acetic acid</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>particulate organic density</td>
<td>density gradient</td>
<td>62.8</td>
<td>57.6</td>
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<tr>
<td>organic coatings</td>
<td>hydrogen peroxide</td>
<td>22.1</td>
<td>28.3</td>
</tr>
<tr>
<td>iron oxide coatings</td>
<td>dithionite</td>
<td>8.7</td>
<td>7.7</td>
</tr>
<tr>
<td>extracted at pH = 2</td>
<td>hydrochloric acid</td>
<td>0.4</td>
<td>0.3</td>
</tr>
<tr>
<td>not removed</td>
<td>0.5</td>
<td>0.2</td>
<td>0.3</td>
</tr>
<tr>
<td>percent recovered</td>
<td>94.8</td>
<td>94.4</td>
<td>99.9</td>
</tr>
</tbody>
</table>

A dash indicates the treatment was not performed on that sample.

(a) Cr(III) spiked sediment.
(b) Cr(III) spiked duplicate of (a).
(c) Cr(III) spiked, air-dried sediment.
(d) Cr(III) spiked, air-dried, H₂O₂-treated sediment.
(e) Cr(VI) spiked air-dried sediment.
(f) Cr(VI) spiked, air-dried, H₂O₂-treated sediment.
Table 6. Removal of radionuclides from McNary sediments by fractionation experiment
(Numbers are % removed with each component calculated by assuming the sum of all components is 100%)

<table>
<thead>
<tr>
<th>Fraction</th>
<th>Treatment</th>
<th>Nuclide</th>
<th>First Series</th>
<th>Second Series</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>a</td>
<td>b</td>
</tr>
<tr>
<td>exchangeable</td>
<td>NH₄Ac</td>
<td>5¹Cr</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>46Sc</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5⁴Mn</td>
<td>10.5</td>
<td>10.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>65Zn</td>
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<tr>
<td></td>
<td></td>
<td>6⁰Co</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>extracted</td>
<td>~5% acetic</td>
<td>5¹Cr</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>at pH = 3</td>
<td>acid</td>
<td>46Sc</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5⁴Mn</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td></td>
<td></td>
<td>65Zn</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td></td>
<td></td>
<td>6⁰Co</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>particulate</td>
<td>density</td>
<td>5¹Cr</td>
<td>18.1</td>
<td>24.1</td>
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<tr>
<td>organic</td>
<td>gradient</td>
<td>46Sc</td>
<td>2.5</td>
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<td></td>
<td></td>
<td>5⁴Mn</td>
<td>33.5</td>
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<td>65Zn</td>
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<td>81.4</td>
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<td>H₂O₂</td>
<td>5¹Cr</td>
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<td>coatings</td>
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<td></td>
<td></td>
<td>5⁴Mn</td>
<td>5.8</td>
<td>4.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td>65Zn</td>
<td>4.7</td>
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<td></td>
<td></td>
<td>6⁰Co</td>
<td>10.0</td>
<td>5.6</td>
</tr>
<tr>
<td>iron</td>
<td>dithionite</td>
<td>5¹Cr</td>
<td>41.9</td>
<td>33.8</td>
</tr>
<tr>
<td>oxides</td>
<td></td>
<td>46Sc</td>
<td>56.4</td>
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<tr>
<td></td>
<td></td>
<td>5⁴Mn</td>
<td>17.6</td>
<td>21.1</td>
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<td></td>
<td></td>
<td>65Zn</td>
<td>7.7</td>
<td>6.9</td>
</tr>
<tr>
<td></td>
<td></td>
<td>6⁰Co</td>
<td>2.7</td>
<td>2.4</td>
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Table 6. (Continued)

<table>
<thead>
<tr>
<th>Fraction</th>
<th>Treatment</th>
<th>Nuclide</th>
<th>First Series</th>
<th>Second Series</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>a</td>
<td>b</td>
</tr>
<tr>
<td>extracted at pH-2</td>
<td>0.01 N HCl</td>
<td>$^{51}$Cr</td>
<td>3.3</td>
<td>2.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$^{46}$Sc</td>
<td>11.1</td>
<td>2.9</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$^{54}$Mn</td>
<td>14.8</td>
<td>2.4</td>
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<td>$^{65}$Zn</td>
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<tr>
<td></td>
<td></td>
<td>$^{60}$Co</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>Not removed</td>
<td>$^{51}$Cr</td>
<td>21.3</td>
<td>20.1</td>
<td>5.5</td>
</tr>
<tr>
<td></td>
<td>$^{46}$Sc</td>
<td>14.9</td>
<td>15.5</td>
<td>5.0</td>
</tr>
<tr>
<td></td>
<td>$^{54}$Mn</td>
<td>17.8</td>
<td>29.1</td>
<td>9.1</td>
</tr>
<tr>
<td></td>
<td>$^{65}$Zn</td>
<td>4.8</td>
<td>4.5</td>
<td>3.1</td>
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<tr>
<td></td>
<td>$^{60}$Co</td>
<td>12.7</td>
<td>13.6</td>
<td>13.7</td>
</tr>
</tbody>
</table>

+ depth in core from which sample was taken
-- indicates this step was omitted
* H$_2$O$_2$ removed some $^{95}$Zr-$^{95}$Nb which prevented accurate analysis of $^{54}$Mn
(specific gravity = 1.77) in a centrifuge tube. The tube was placed in a centrifuge and spun. Particles more dense than bromoethanol sank to the bottom of the tube while less dense particles remained on the surface (or in the bromoethanol-water gradient). The "float" fraction was decanted and the process repeated. After the fourth treatment, the sediment was rinsed once in distilled water in preparation for the next operation. Bromoethanol removed sizeable portions of $^{60}\text{Co}$, $^{65}\text{Zn}$, $^{54}\text{Mn}$ and $^{51}\text{Cr}$ from McNary sediments. The weight fraction of material that floated was very small. No floating particles were observed. (Total weight loss for the entire separation scheme was only 8%.)

Chromium-51 spiked Priest Rapids sediments yielded a larger fraction of this nuclide to bromoethanol than did natural sediments. Either the laboratory sorption reaction was different from that occurring in the river or there is a change in retention with time in the natural sediments. (The natural sediments have presumably been in contact with $^{51}\text{Cr}$ longer than the Priest Rapids sediments.) Furthermore, pre-oxidized, spiked sediments yielded more $^{51}\text{Cr}$ to bromoethanol than did untreated spiked sediments. This result is most surprising since pre-oxidation was intended to destroy at least some of the material that is supposed to float in bromoethanol. Very likely hydrogen peroxide does not destroy all the organic material present in the sediment. Possibly, fairly stable oxidation
intermediates, such as polycarboxylic acids, could have been formed and these could be involved in sorption of transition metals. Such an explanation is not very satisfying. A more probable explanation is that the bromoethanol reacted chemically with the sediment-sorbed radionuclides or their substrates. The initially colorless bromoethanol turned bright red during centrifugation with sediments. This is probably indicative of decomposition with the production of red bromine. Bromine is a fairly powerful oxidant and may have been responsible for much of the observed desorption. A better choice of heavy liquid than bromoethanol could have been made.

The bromoethanol separations were followed by oxidation with hydrogen peroxide. The treatment was carried out essentially as described previously for the Priest Rapids sediments. None of the \( ^{60}\text{Co} \), \( ^{65}\text{Zn} \), \( ^{54}\text{Mn} \) or \( ^{46}\text{Sc} \) was removed by hydrogen peroxide. A highly variable, sometimes large (3-57\%) fraction of \( ^{51}\text{Cr} \) was removed. This desorption could have occurred either because the substrate to which \( ^{51}\text{Cr} \) was sorbed was destroyed or because \( ^{51}\text{Cr(III)} \) was oxidized to \( ^{51}\text{Cr(VI)} \) and thus made soluble. The latter explanation seems more likely.

When the iron oxide coatings were removed, most of the remaining \( ^{51}\text{Cr} \) was desorbed. Usually, the largest fraction of \( ^{51}\text{Cr} \) was removed from natural sediments with this treatment. About 20\% of \( ^{54}\text{Mn} \) and up to 89\% of \( ^{46}\text{Sc} \) were also removed. In another
experiment the dithionite treatment was performed before oxidizing the sediment with \( \text{H}_2\text{O}_2 \). Considerably larger fractions of \(^{60}\text{Co}, ^{65}\text{Zn}, ^{54}\text{Mn}\) and \(^{51}\text{Cr}\) were removed by dithionite if it preceded the removal of "organic" material (Table 7). Apparently there are portions of these nuclides that could be removed either with dithionite treatment or bromoethanol extractions.

Table 7. Comparison of amounts of radionuclides removed along with "iron oxide component" before and after removal of "organic" matter. Percent of each nuclide removed. (Sediments were replicate subsamples from a McNary core. (a) and (b) are duplicates, as are (c) and (d).)

<table>
<thead>
<tr>
<th>Order of removal</th>
<th>(^{51}\text{Cr})</th>
<th>(^{46}\text{Sc})</th>
<th>(^{54}\text{Mn})</th>
<th>(^{65}\text{Zn})</th>
<th>(^{60}\text{Co})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Iron oxide before organic</td>
<td>(a) 67.2</td>
<td>58.8</td>
<td>65.7</td>
<td>48.8</td>
<td>67.0</td>
</tr>
<tr>
<td></td>
<td>(b) 66.1</td>
<td>58.9</td>
<td>71.5</td>
<td>48.7</td>
<td>67.6</td>
</tr>
<tr>
<td>Organic before iron oxide</td>
<td>(c) 41.9</td>
<td>56.4</td>
<td>17.6</td>
<td>7.7</td>
<td>2.7</td>
</tr>
<tr>
<td></td>
<td>(d) 33.8</td>
<td>53.3</td>
<td>21.1</td>
<td>6.7</td>
<td>2.4</td>
</tr>
</tbody>
</table>

Thus, iron oxides appear to be the most important single sediment component in the retention of \(^{51}\text{Cr}\). Organic matter may also play an important role both as a sorption surface and as a reducing agent. It seems likely that sorption is accompanied by reduction of \(^{51}\text{Cr(VI)}\) to \(^{51}\text{Cr(III)}\).
Chromium-51 in Seawater

When Columbia River water enters the Pacific Ocean, new possibilities for chemical reactions are encountered. Flocculation of fine-grained sediment material occurs as the surfaces of the particles are affected by dissolved salts. Many ions are more abundant in seawater than in river water and chemical precipitation of elements dissolved in the river may be possible. In short, the tendency of $^{51}$Cr to remain in solution while in the river may change upon contact with seawater.

Early efforts to recover radionuclides produced at Hanford from seawater samples taken off Oregon made use of carrier isotopes and gathering with hydrous iron oxide precipitated in the sample solution (Chakravarti et al., 1964). That is, ZnCl$_2$, MnCl$_2$, CoCl$_2$ and CrCl$_3$ were added to samples to assure recovery of $^{65}$Zn, $^{54}$Mn, $^{60}$Co and $^{51}$Cr, respectively. Although this process has often been called coprecipitation (Chakravarti et al., 1964; Cutshall, Johnson and Osterberg, 1966), in the strictest sense of the word it is not. Laitinen (1960) recommended that the term "coprecipitation" be used only where an ion is recovered in a precipitate under conditions where it is soluble. Where two or more substances are precipitated together under conditions such that both are insoluble he suggested the term "gathering".
Gamma-ray analysis of similarly made precipitates collected off Oregon indicate the presence of $^{124}$Sb (Figure 6b). In an effort to maximize recovery of this nuclide, SbCl$_3$ was added to a duplicate sample. Although no great increase in $^{124}$Sb recovery occurred, a striking gain in $^{51}$Cr recovery was seen (Figure 6a). It was suggested that Sb(III) had reduced $^{51}$Cr(VI) to $^{51}$Cr(III) and that Cr(III) was more efficiently recovered by hydrous ferric oxide. Chromium (VI) could be recovered in hydrous ferric oxide by adsorption while Cr(III) would be coprecipitated or, with high enough Cr(III) concentration, be gathered. The reaction appears thermodynamically possible:

$$\begin{align*}
\text{CrO}_4^{2-} + 3e^- + 6H^+ &= \text{Cr(OH)}_2^+ + 2H_2O & E^o &= 1.27 \text{ volt} \\
2\text{SbO}^+ + 3H_2O &= \text{Sb}_2\text{O}_5^- + 6H^+ + 4e^- & E^o &= -0.58 \text{ volt}
\end{align*}$$

$$4\text{CrO}_4^{2-} + 6H^+ + 6\text{SbO}^+ + H_2O = 4\text{Cr(OH)}_2^+ + 3\text{Sb}_2\text{O}_5^-$$

$E^o = 0.69 \text{ volt.}$

Also, As(III), another group V element, is known to reduce Cr(VI).

The following experiments were designed to resolve this point. In the laboratory $^{51}$Cr spikes, as Cr(III), were added to filtered seawater, and the yield checked with and without carriers. This was repeated for $^{51}$Cr added as Cr(VI), plus additional tests with Sb(III) and Sn(II) reducing agents. Results (Table 8) show that recovery of Cr(III) by coprecipitation with hydrous ferric oxide was
essentially complete, whether carrier was added or not. Addition of Cr(VI) carrier had no effect on recovery of $^{51}\text{Cr(III)}$. In the case of $^{51}\text{Cr(VI)}$ spikes, recovery was incomplete and erratic when no carrier or only Cr(III) carrier was used. Carrier Cr(VI) consistently reduced the yield. However, either reducing agent was effective in giving complete recovery. It should be pointed out that the reaction between the reducing agent and Cr(VI) is probably not direct. Most likely the reducing agent reacts with Fe(III) to yield Fe(II) which in turn reduces the Cr(VI).

Similar results were obtained at sea with proportionately larger samples and precipitates (Table 9). Laboratory and shipboard precipitates were made with 45 mg of Fe(III) and 0.64 ml of 28% $\text{NH}_4\text{OH}$ per liter of solution. Similarly, carriers and reducing agents were added in the same proportion to the 250-ml laboratory tests and to the 560-liter shipboard samples (5.3 mg of chloride salts or $\text{K}_2\text{Cr}_2\text{O}_7$ per liter). Aboard the U.S. Coast Guard Cutter Modoc, in June, 1965, sampling was extended over an 18-hour period, during which the ship drifted through waters of varying salinity. It was therefore necessary to rectify the counts to allow for the changing fraction of Columbia River water in the samples. All counts were corrected to a salinity of 29.2 per mil.

To obtain truly duplicate samples, the tests were repeated in August, 1965, aboard the R/V Yaquina. Levels of $^{51}\text{Cr}$ were
much lower because the tongue of low-salinity water observed in June (Osterberg, Cutshall and Cronin, 1965) had spread greatly and become saltier. Rectification of these data was not required since salinity values did not vary during the tests.

In every case maximum yield of $^{51}$Cr from seawater occurred when a reducing agent was added prior to precipitation. Evidently Hanford-induced $^{51}$Cr remains principally in the hexavalent oxidation state in the ocean. This conclusion is supported by the "hold-back" effect of Cr(VI) carrier in the absence of a reducing agent. Since the $^{51}$Cr measured off Newport has been in contact with seawater for weeks or even months, it appears that reduction of $^{51}$Cr(VI) to $^{51}$Cr(III) must occur only very slowly if at all.

Chromium-51 is effectively recovered from seawater by the following procedure. Ferric chloride solution (122 gm of FeCl$_3$·6H$_2$O in 500 ml of H$_2$O) is added to 560 liters of seawater while stirring. Stirring this large volume can be readily accomplished by introducing compressed air at the bottom of the tank. Carrier (plus reducing agent) solution is added immediately (3 gm each of CrCl$_3$·6H$_2$O and SnCl$_2$·2H$_2$O in 500 ml of H$_2$O). The solution is stirred for 30 minutes, after which 360 ml of 28% NH$_4$OH is slowly added, followed by 500 ml of 0.05% Separan NP10 solution, after which stirring is ceased. (Separan NP10 is a Dow Chemical flocculating agent.) The precipitate is allowed to settle for one to two hours and the supernatant
is siphoned off and discarded. The precipitate slurry can be counted directly or processed further if desired.

Table 8. Recovery of $^{51}$Cr spikes from seawater by Fe(OH)$_3$ precipitates in the laboratory. (percent)

<table>
<thead>
<tr>
<th>Carrier added</th>
<th>Cr(III)</th>
<th>Cr(VI)</th>
</tr>
</thead>
<tbody>
<tr>
<td>None</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chromium(III) spike</td>
<td></td>
<td></td>
</tr>
<tr>
<td>98.3</td>
<td>99.1</td>
<td>98.1</td>
</tr>
<tr>
<td>98.3</td>
<td>95.2</td>
<td>99.1</td>
</tr>
<tr>
<td>Chromium(VI) spike</td>
<td></td>
<td></td>
</tr>
<tr>
<td>72.4</td>
<td>38.4</td>
<td>1.9</td>
</tr>
<tr>
<td>27.3</td>
<td>15.9</td>
<td>2.2</td>
</tr>
</tbody>
</table>

99.5 Sb(III)
99.6 Sn(II)

Table 9. Chromium-51 recovered from seawater samples by Fe(OH)$_3$ precipitates. (Picocuries/liter. All locations were at 44° 39'N.)

<table>
<thead>
<tr>
<th>Carrier added</th>
<th>Cr(III)</th>
<th>Cr(VI)</th>
</tr>
</thead>
<tbody>
<tr>
<td>None</td>
<td></td>
<td></td>
</tr>
<tr>
<td>June, 1965; 125° 12' W</td>
<td></td>
<td></td>
</tr>
<tr>
<td>13.4</td>
<td>24.7</td>
<td>4.7</td>
</tr>
<tr>
<td>8.2</td>
<td>53.3 Sb(III)</td>
<td></td>
</tr>
<tr>
<td>August, 1965; 125° 38' W</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5.8</td>
<td>2.0</td>
<td>9.2 Sb(III)</td>
</tr>
<tr>
<td>August, 1965; 125° 02' W</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.9</td>
<td>23.5 Sb(III)</td>
<td></td>
</tr>
</tbody>
</table>
Figure 6. Gamma-ray spectra of precipitates from 560-liter samples of seawater collected off Newport, Oregon, June, 1965. a) SbCl$_3$ was added; b) no SbCl$_3$ was added.
DISCUSSION

Chromium-51 as a Radioactive Tracer

Chromium-51 has been used as a radioactive tag for Columbia River water after it enters the sea. Gross, Barnes and Riel (1965), using an in situ detector, traced $^{51}$Cr to about 115 km from the mouth of the river. Osterberg, Cutshall and Cronin (1965) used a chemical concentration at sea and laboratory radioanalysis to follow the plume 350 km away from the river mouth. Their concentration methods were discussed by Cutshall, Johnson and Osterberg (1966) and elsewhere in the present work. Chemical concentration and shipboard radioanalysis were combined by Frederick (1966) to provide a system capable of detecting one part of Columbia River water in about 250 parts of seawater (neglecting radioactive decay) with a four-hour processing time. Samples from the latter process are later analyzed at the laboratory in Corvallis with even greater sensitivity.

If another parameter indicative of Columbia River water is measured simultaneously with $^{51}$Cr, the decay of the radioisotope can be used to calculate the relative times since different samples entered the ocean. Osterberg, Cutshall and Cronin (1965) used salinity to correct for dilution of their samples with seawater and
calculated an average flow rate for the core of the plume. Since salinity can be lowered by fresh water from other rivers or from rainfall, another parameter might be more useful for identifying Columbia River water. Park (1966) suggested that specific alkalinity is a qualitative tool for identifying Columbia River water but this does not appear to offer sufficient resolution for quantitative estimates. Another radionuclide from Hanford, 60-day $^{124}$Sb, appears to remain in solution and move with the plume waters. If this nuclide is conservative, the ratio of $^{51}$Cr to $^{124}$Sb may be the best indicator of the relative "ages" of plume samples. Sensitivity for $^{124}$Sb analysis will have to be improved, however, since very little of this nuclide is present in the river. One possibility might be the use of multidimensional gamma-ray spectrometry (Perkins, 1965).

Chromium-51 is probably not a suitable tracer for naturally-occurring stable chromium in the Columbia River and plume system. The radioisotope is introduced into the river in the +6 oxidation state and appears to remain hexavalent, for the most part. Mineral chromium is principally trivalent. Attainment of isotopic equilibrium is slow. Hexavalent $^{51}$Cr would probably be a good tracer for Cr(VI) in industrial wastes.

Radioactive Waste Disposal Considerations

Since $^{51}$Cr is present in the Columbia River as a radioactive
waste, it is appropriate to discuss factors that determine the efficiency of disposal. Rapid dilution and wide dispersion are desirable while concentration and immobilization are undesirable. Biological concentration and food-chain transmission do not appear significant for $^{51}$Cr. In fact, under present conditions, $^{51}$Cr is a well-behaved waste that remains in solution and is eventually diluted in the vast Pacific Ocean. A portion is concentrated on particles and remains in bottom sediments. Knowledge of factors involved in the sorption and retention should be useful in maximizing dispersion rates.

If $^{51}$Cr(VI) is reduced to $^{51}$Cr(III) it rapidly sorbs to particles. Krauskopf (1956) concluded that local reduction and "precipitation" controls the concentration of Cr in seawater. Jennings (1966) observed that $^{51}$Cr: $^{65}$Zn ratios in sediments in Youngs River increase for some distance upstream from where it enters the Columbia. He suggested that the Youngs River sediments were reducing and taking up $^{51}$Cr. Gross (1966) suggested a similar mechanism to explain surprisingly high $^{51}$Cr concentrations in certain Willapa Bay sediments. Reducing conditions in sediments "are brought about by the activities of microorganisms acting upon the organic material in the deposit" (Sverdrup, Johnson and Fleming, 1942). Therefore an increase in particulate organic waste from domestic or industrial sources would probably cause increased retention of $^{51}$Cr by sediments. Since microbial decomposition
rates generally increase with higher temperatures, an increase in water temperature should also cause increased retention and slower dispersion.

Reactions for reduction of Cr(VI) to Cr(III) consume several hydrogen ions per atom of chromium so that a decrease in pH markedly favors reduction. The pH of the Columbia averages about 7.9 in the upper reaches (U.S. Department of Health, Education and Welfare, 1962). At Clatskanie, on the lower end of the river, the pH is usually slightly lower—about 7.5. Probably the more acidic Willamette River is partly responsible for the drop. No evidence is yet available to show that increased sorption does occur following the pH decrease. Of course, under extremely acidic conditions (pH less than 3) \(^{51}\text{Cr}\) would probably be leached from the sediments. However it is unlikely that such conditions would occur naturally in the river.

In general, the characteristics that are desirable from a water quality standpoint: clarity, low temperature and low biological oxygen demand, are also desirable for rapid and complete dispersion of chromium-51.


Loveridge, B. A. et al. 1960. The determination of copper, chromium, lead and manganese in sea water. 42 p. (United Kingdom Atomic Energy Authority. AERE-R-3323)


Riley, J. P. 1966. Professor, University of Liverpool, Dept. of Oceanography. Personal communication.


APPENDIX
APPENDIX

_Application of Thermodynamic Data to Natural Water Systems_

Thermodynamic data have been used to predict the state of various elements in natural waters or models of natural waters. Two approaches have been used. In the first, a stability field or Eh-pH diagram is constructed. Then, with Eh and pH values for the system, the most abundant species at equilibrium can be predicted. This method is applicable over wide ranges of Eh and pH but provides only a qualitative estimate. The second approach has been the construction of an equilibrium model similar to the system of interest and computation of the relative abundance of various pairs of species for the model. The former approach has been practiced by Krauskopf (1955) and has been described by Garrels and Christ (1965). The latter method was used by Sillén (1961). Each method will be described and certain difficulties will be mentioned.

_Symbols_

\[ \Delta F^O_r = \text{Free energy change in a reaction} \]

\[ \Delta F^O_f = \text{Free energy of formation} \]

\[ R = \text{Gas constant} \]

\[ T = \text{Absolute temperature} \]
\( \ln x \) = Natural logarithm of \( x \)

\( \log x \) = Base 10 logarithm of \( x \)

\( (x) \) = Activity of \( x \)

\( K \) = Equilibrium constant

\( \mathcal{F} \) = Faraday constant

\( n \) = Number of moles of electrons specified by the half-reaction used

\( E^0 \) = Standard electrode potential

**Equations**

\[ \Delta F^0_r = \Sigma (\Delta F^0_f \text{ for products}) - \Sigma (\Delta F^0_f \text{ for reactants}) \]

\[ \Delta F^0_r = -RT \ln K = -n \mathcal{F} E^0 \]

\[ Eh = E^0 - \frac{RT}{n\mathcal{F}} \ln K' \]

\[ pH = -\log (H^+) \]

\[ pE = -\log (e^-) \]

**Free Energy of Formation of Selected Species at 25°C**

(Taken from tables in Garrels and Christ, 1965)

<table>
<thead>
<tr>
<th>Formula</th>
<th>( \Delta F^0_f ), Kcal/mole</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{H}_2\text{O} )</td>
<td>-56.7</td>
</tr>
<tr>
<td>( \text{H}^+ )</td>
<td>0.0</td>
</tr>
<tr>
<td>( \text{Cr}^{2+} )</td>
<td>-42.1</td>
</tr>
<tr>
<td>( \text{Cr}^{3+} )</td>
<td>-51.5</td>
</tr>
</tbody>
</table>
Eh-pH Diagrams

The construction of Eh-pH diagrams has the following pattern.

A reaction or half-reaction is written and log K or $E^0$ is computed.

The activity of a reactant and a product are assumed to be equal and an expression for $Eh = f(E^0, pH)$ or $pH = f(log K)$ is derived. The expression thus derived is the equation of a line in the diagram.

**Examples**

1. Reactions involving both $H^+$ and $e^-$.  

$$CrO_4^{-2} + 3e^- + 6H^+ = Cr(OH)^+_2 + 2H_2O \quad \Delta F^0_r = -88.5$$

$$E^0 = \Delta F^0_r/(-nF) = -88.5/(-3 \times 23.06) = 1.27 \text{ volts}$$

$$Eh = E^0 - \frac{0.059}{3} \log \frac{(Cr(OH)^+_2)(H_2O)^2}{(CrO_4^{-2})(H^+)^6}$$

Assume $(H_2O) = 1$ and $(Cr(OH)^+_2) = (CrO_4^{-2})$.

then

$$Eh = E^0 - \frac{0.059}{3} \times 6 \text{ pH}$$

$$Eh = 1.27 - 0.118 \text{ pH}$$

This is the equation of line 1 on Figure 7.
2. Reactions involving $e^-$ but not $H^+$.

\[ \text{Cr}^{3+} + e^- = \text{Cr}^{2+} \quad \Delta F^o = 9.4 \]

\[ E^o = \frac{\Delta F^o}{-n} = 9.4/(-1 \times 23.06) = -0.41 \text{ volts} \]

\[ E_h = E^o - \frac{0.059}{1} \log \frac{\text{Cr}^{2+}}{\text{Cr}^{3+}} \]

Assume \((\text{Cr}^{3+}) = (\text{Cr}^{2+})\),

then \( E_h = E^o \)

\[ E_h = -0.41 \text{ volts} \]

This is the equation of line 2 on Figure 7.

3. Reactions involving $H^+$ but not $e^-$.

\[ \text{HCrO}_4^- = H^+ + \text{CrO}_4^{2-} \quad \Delta F^o = 8.8 \]

\[ \log K = -\frac{\Delta F^o}{RT \ln 10} = -\frac{8.8}{1.36} = -6.45 \]

\[ \log K = \log \frac{(\text{CrO}_4^{2-})}{(\text{HCrO}_4^-)} + \log (H^+) \]

Assume \((\text{CrO}_4^{2-}) = (\text{HCrO}_4^-)\),

then \( \log K = -\text{pH} \)

\[ \text{pH} = 6.45 \]

This is the equation of line 3 on Figure 7.

These steps are repeated for possible reactions between all species considered. Figure 7 (page 11) is the product of the three example calculations plus the following.

\[ \text{Cr}^{3+} + \text{H}_2\text{O} = \text{CrOH}^{2+} + \text{H}^+ \quad \Delta F^o = 5.2 \]
\[ \text{pH} = 3.81 \]
\[ \text{CrOH}^{2+} + \text{H}_2\text{O} = \text{Cr(OH)}_2^+ + \text{H}^+ \quad \Delta F_r^o = 8.5 \]

\[ \text{pH} = 6.23 \]
\[ \text{Cr(OH)}_2^+ = \text{CrO}_2^- + 2\text{H}^+ \quad \Delta F_r^o = 23.2 \]

\[ \text{pH} = 8.5 \]
\[ \text{HCrO}_4^- + 3\text{e}^- + 7\text{H}^+ = \text{Cr}^{3+} + 4\text{H}_2\text{O} \quad \Delta F_r^o = -93.4 \]
\[ \text{Eh} = 1.35 - 0.138 \text{ pH} \]
\[ \text{HCrO}_4^- + 3\text{e}^- + 6\text{H}^+ = \text{CrOH}^{2+} + 3\text{H}_2\text{O} \quad \Delta F_r^o = -88.2 \]
\[ \text{Eh} = 1.27 - 0.118 \text{ pH} \]
\[ \text{HCrO}_4^- + 3\text{e}^- + 5\text{H}^+ = \text{Cr(OH)}_2^+ + 2\text{H}_2\text{O} \quad \Delta F_r^o = -79.7 \]
\[ \text{Eh} = 1.15 - 0.099 \text{ pH} \]

\[ \text{CrO}_4^{2-} + 3\text{e}^- + 4\text{H}^+ = \text{CrO}_2^- + 2\text{H}_2\text{O} \quad \Delta F_r^o = -65.3 \]
\[ \text{Eh} = 0.94 - 0.079 \text{ pH} \]
\[ \text{CrOH}^{2+} + \text{e}^- + \text{H}^+ = \text{Cr}^{2+} + \text{H}_2\text{O} \quad \Delta F_r^o = 4.2 \]
\[ \text{Eh} = -0.18 - 0.059 \text{ pH} \]
\[ \text{Cr(OH)}_2^+ + \text{e}^- + \text{H}^+ = \text{Cr}^{2+} + 2\text{H}_2\text{O} \quad \Delta F_r^o = -4.3 \]
\[ \text{Eh} = 0.10 - 0.118 \text{ pH} \]

That equilibrium conditions are determined by Eh and pH is implicit in the calculations. Sets of Eh and pH for which two species have the same activity correspond to the lines drawn. If Eh and pH are such that the point of interest falls on a line, the species on either side of that line will have the same activity. If the point of interest falls in a "field" one species will have greater activity than all others. Thus, when Krauskopf (1956) considered the Eh and pH
Figure 7. Partially constructed Eh–pH diagram.
of seawater (no values given), he found that the activity of \( \text{CrO}_4^{2-} \) should be greatest of all species considered. (Actually Krauskopf apparently considered fewer possible forms than are included in the above calculations.) Therefore he concluded that Cr in seawater should exist mainly as chromate.

Eh-pH diagrams are valid only for the species considered in their construction. If important species are omitted the conclusions drawn from the diagrams may be trivial. For example if a Cr(III) complex with ligands other than \( \text{H}_2\text{O} \) or \( \text{OH}^- \) contains most of the total Cr in seawater, the predominance of \( \text{CrO}_4^{2-} \) over \( \text{Cr(OH)}_2^+ \) has very little significance. It is also possible that Cr(III) may be contained in neutral \( \text{Cr(OH)}_3 \) species analogous to Sillén's (1961) suggested neutral \( \text{Fe(OH)}_3 \) for iron. Unfortunately, free energy data for these species are lacking.

A major problem in the application of Eh-pH diagrams arises when experimental Eh and pH are used. pH can be measured with fair reliability. Eh, however, can be very difficult, if not impossible to measure. The Eh of aerated seawater is determined by the amount of \( \text{O}_2 \) present (Sillén, 1966). The reversible reaction, \( \text{O}_2 + 4\text{H}^+ + 4e^- = 2\text{H}_2\text{O} \) has an \( E^0 \) of 1.23 volts, but this can be measured only in very pure solutions. Watanabe and Devanathan (1964) reported an exchange current for this reaction of \( 10^{-10} \text{ amp/cm}^2 \). The presence of impurities in the solution or on the Pt electrode apparently leads to other electrode reactions with higher exchange currents but which are irreversible. Sillén (1966) cited the data gathered by Baas Becking, Kaplan and Moore (1960) which show a rather constant pH
for marine sediments but a highly variable Eh. He suggested that
the spread in Eh values may be due to catalysis of the \( \text{O}_2\text{-H}_2\text{O} \) reac-
tion by oxides of manganese. The thermodynamic interpretation of
a system implies equilibrium and control by reversible reactions.
Morris and Stumm (1966) concluded that Eh measurements may or
may not have thermodynamic significance depending on the system.
Similarly, Hayes, Reid and Cameron (1958), cited Wartenburg's
conclusion in 1935 that correlations between measured Eh values and
soil properties are due to special circumstances and particular
methods and are not explainable by true theoretical considerations.
This problem has led Sillén to avoid experimental Eh values entirely
and to assume that for an equilibrium system the reversible oxygen
reaction controls redox potential at \( \text{Eh} = 1.23 - 0.059 \text{ pH} \). In fact,
he prefers to express oxidation power of a system as \( \text{pE} = -\log (e^-) = \text{Eh}/0.059 \), thus avoiding the temptation to use experimental values.

**Equilibrium Model Approach**

Sillén (1961) computed \( \text{pE} = 12.5 \) for a seawater model in equi-
librium with air at \( 25^\circ \text{C} \) and at \( \text{pH} = 8.2 \). This corresponds to
\( \text{Eh} = 0.74 \) volts, a value considerably higher than the usual experi-
mental value for seawater (0.43 volt). Thus, in certain cases, the
calculated value might predict an oxidized state while the exper-
imental value might predict a reduced state. This is not the case
for chromium; both methods predict \( \text{CrO}_4^{2-} \). A set of calculations
made by Sillén's method follows.
Trivalent Chromium Species

\[
\text{Cr}^{3+} + \text{H}_2\text{O} = \text{CrOH}^{2+} + \text{H}^+ \quad \Delta F_r^0 = 3.81
\]

\[
\log \left( \frac{\text{CrOH}^{2+}}{(\text{Cr}^{3+})} \right) = \log K + \text{pH} \\
= -3.81 + 8.2 = 4.4
\]

\[
\text{CrOH}^{2+} + \text{H}_2\text{O} = \text{Cr(OH)}_2^{+} + \text{H}^+ \quad \Delta F_r^0 = 8.5
\]

\[
\log \left( \frac{\text{Cr(OH)}_2^{+}}{(\text{CrOH}^{2+})} \right) = \log K + \text{pH} \\
= -6.2 + 8.2 = 2.0
\]

\[
\text{Cr(OH)}_2^{+} = \text{CrO}_2^{-} + 2\text{H}^+ \quad \Delta F_r^0 = 23.2
\]

\[
\log \left( \frac{\text{CrO}_2^{-}}{(\text{Cr(OH)}_2^{+})} \right) = \log K + 2\text{pH} \\
= -17.0 + 16.4 = -0.6
\]

Thus, the activity of \(\text{Cr(OH)}_2^{+}\) at equilibrium will be greatest of the four trivalent species considered.

Hexavalent Chromium Species

\[
\text{HCrO}_4^- = \text{CrO}_4^{2-} + \text{H}^+ \quad \Delta F_r^0 = 8.8
\]

\[
\log \left( \frac{(\text{CrO}_4^{2-})}{(\text{HCrO}_4^-)} \right) = \log K + \text{pH} \\
= -6.5 + 8.2 = 1.7
\]

Thus, the activity of \(\text{CrO}_4^{2-}\) is greater than that of \(\text{HCrO}_4^-\) at equilibrium.
Cr(VI) - Cr(III) Reaction

\[ \text{CrO}_4^{2-} + 3e^- + 6H^+ = \text{Cr(OH)}_2^+ + 2H_2O \quad \Delta F_r^0 = -88.5 \]

\[
\log \left( \frac{\text{Cr(OH)}_2^+}{\text{CrO}_4^{2-}} \right) = \log K - 6 \text{pH} - 3 \text{pE}
\]

\[
= 64.8 - 6(8.2) - 3(12.5)
\]

\[
= -21.9
\]

Thus, at equilibrium, the activity of \( \text{Cr(OH)}_2^+ \), the most probable trivalent species, is only \( 10^{-21.9} \) of the activity of \( \text{CrO}_4^{2-} \).

The following points are critical in the use of thermodynamic data to interpret natural water systems:

1. If important species are not considered, the conclusions may be immaterial.
2. The system must be at equilibrium. This may not be true for seawater.
3. Pressure and temperature effects on equilibria are usually not taken into account.
4. The formation of solid solutions or adsorption is usually not considered.

Riley (1966) stated, "I feel that one has to be very cautious in drawing hard and fast conclusions about the ionic species in the sea, owing to the number of unknown factors involved."