Studies on Aqueous Soluble Carbonato Complexes of Mn\textsuperscript{II}, Mn\textsuperscript{III} and Mn\textsuperscript{IV}: Oxidation–Reduction Relationships

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Aqueous carbonato complexes of Mn\textsuperscript{II}, Mn\textsuperscript{III} and Mn\textsuperscript{IV} were prepared and investigated by UV–visible spectrophotometry and electrochemical techniques. Mn\textsuperscript{II} forms soluble anionic carbonato complexes in concentrated carbonate solutions. A complex with two CO\textsubscript{3}\textsuperscript{2–} has been found in 1 M K\textsubscript{2}CO\textsubscript{3} solutions. The value of its conditional formation constant is in the range 10\textsuperscript{5.7±0.3}. The soluble Mn\textsuperscript{II} carbonato complexes are readily oxidized by air to Mn\textsuperscript{III} species. Mn\textsuperscript{IV} complexes were obtained by reduction of MnO\textsubscript{2} ions or by oxidation of Mn\textsuperscript{II} in concentrated carbonate solutions. Insoluble solids, probably oxides, were often produced during the studied oxidation-reduction reactions.

The carbonato complexes of Mn and also of Tc and Re, all elements belonging to the Group VIIIB, have not been thoroughly investigated, except for the almost insoluble MnCO\textsubscript{3}, rhodochrosite,\textsuperscript{1} one of the natural minerals of Mn. An acidic species of Mn\textsuperscript{II} with the formula MnHCO\textsubscript{3}\textsuperscript{+} has been found.\textsuperscript{2} Its formation constant is rather small (log θ = 1.275 at 25 °C)\textsuperscript{3} and by taking into account the presence of such species one introduces only small changes in the solubility product value of MnCO\textsubscript{3}.

A more complete knowledge of the equilibria involving Group VIIIB ions in carbonate solutions is crucial to understanding many natural phenomena involving Mn\textsuperscript{II,III,IV} ions.

In connection with nuclear waste storage safety, it is necessary to investigate the stability of soluble carbonato species of Tc\textsuperscript{V,IV,III,II} which could participate in the transport of radioactive \textsuperscript{99}Tc from storage sites to the biosphere.

The competition between OH\textsuperscript{–}, O\textsubscript{2}\textsuperscript{2–} and CO\textsubscript{3}\textsuperscript{2–} for the coordination sites of ions from Group VIIIB is a key parameter for the stability of carbonato complexes at a given pH. Investigations of Mn complexes might be a useful first approach for the study of the Tc complexes, except for the higher stability of the Tc ions in oxidation states greater than II. In this paper we report the first results dealing with soluble manganese(II, III, IV) carbonato complexes.

**Experimental**

**Products.** MnO\textsubscript{2} was provided by the Institut des Matériaux de Nantes. Its crystallinity was poor, as shown by its X-ray powder diffraction diagram. Only broad lines of the Akthenskite MnO\textsubscript{2} structure (JC-PDS 30-820) were observed. MnCO\textsubscript{3} was an Aldrich product, 37744-9, 99.9% pure. All other chemicals were Prolabo products of analytical grade and were used without further purification.

**Apparatus.**

**Electrochemistry.** A Radiometer Analytical SA set was used. This comprised (1) A Trace Lab 150, which included a polarograph MDE 150 and a solid rotating electrode EDI 101 T. Trace lab 150 permits one to use most electroanalytical methods. It is computer-driven by a program under Windows 3.1 provided by Radiometer. (2) A Volta Lab 32, which includes a galvanpo potentials unit DEA 332 with a programmable interface IMT 101. A Volta Master 2 program, also provided by the manufacturer, was used to drive this unit.

**Spectrophotometry.** A double-beam UV–visible spectrophotometer 21016C from Shimadzu, operating between 190 and 900 nm, was used for the spectrosopic investigations.

**Solid structural investigations.** Some of the solids obtained in this work were analyzed by X-ray powder diffraction techniques, using a Siemens PW 1710 diffractometer. Energy-dispersive X-ray analyses were performed using an EDX microprobe (Oxford

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Instruments) coupled with a Leica Stereoscan 440 scanning electron microscope.

**Procedures.**

**Dissolution of MnCO₃ into K₂CO₃ solutions.** The solubility of MnCO₃ in carbonate solutions under oxidic and anoxic conditions was investigated. The concentration of Mn was determined by γ-counting of MnCl₂ labelled by ⁵⁴Mn. ⁵⁴Mn disintegrates by electron capture with a 312-day half-life. Counting its 834.84 keV γ-rays served to monitor the Mn concentrations. For these experiments constant ionic strength was calculated by applying the equation

\[ I = \frac{1}{2} \sum \gamma_i c_i \]

and was maintained at I = 4.4 by addition of KCl. The chloride complexes of Mn⁶⁺ are very weak, β₁₁ = 1.5 and play a minor role in the reactions investigated here. At room temperature equilibria were obtained after 100 h. To avoid oxidation of Mn⁶⁺, small amounts of hydrazine 10⁻² M were daily added to the solutions. The oxidation of the Mn⁶⁺ carbonato complexes by O₂, MnO₄²⁻, was carried out and followed by voltammetry at a rotating platinum electrode. The solids obtained during this study were analyzed by X-ray diffraction and electron microscopy.

**Reduction of the MnO₄²⁻ ions by the solvolyte.** The standard potentials of the couples MnO₄²⁻/MnO₄⁻ (0.54 V vs. SHE); and MnO₄⁻/Mn⁶⁺ (0.64 V vs. SHE) at a pH around 12 are higher than the potential of the O₂/H₂O couple (0.51 V vs. SHE). This means that Mn⁶⁺ (MnO₄²⁻) and Mn⁶⁺ (MnO₄⁻) ions are thermodynamically unstable in carbonate solutions at a pH in the range from 11 to 12. This instability is increased if carbonate complexes of Mn⁶⁺ are more stable than the oxide MnO₂. MnO₄⁻ ions were reduced by water when heating their carbonate solutions at temperatures close to 100 °C. For MnO₄⁻ solutions in 5 M K₂CO₃, 0.5 M KHCO₃, 2 h of heating were necessary to observe the complete disappearance of Mn⁶⁺. UV-visible spectrophotometry was used to follow this reduction. As some solids were formed during the reduction the spectra were recorded after careful filtration of the solutions through 0.25 or 0.45 μm millipore filters. Extended reaction times were necessary to achieve reduction of MnO₄⁻, contained in less concentrated carbonate solutions, especially at lower pH.

**Dissolution of MnO₂ into a melted eutectic of K₂CO₃ and Na₂CO₃.** 0.1 g MnO₂ was carefully mixed and ground with 50 g of a K₂CO₃/Na₂CO₃, 0.5 mol fraction. This powder was heated to 800 °C, at which point the melted carbonates rapidly dissolved the MnO₂ to give a red solution. The surface of the melt in contact with air changed color from red to green, indicating the partial oxidation of MnO₂ to MnO₄⁻ ions. After being cooled the solidified salts were dissolved in a 1 M KHCO₃ solution, then the green color disappeared rapidly due to Mn⁶⁺ disproportionation. Finally a red solution was obtained. The UV-visible spectrum showed that it was the same Mn species as obtained by reduction of MnO₄⁻ ions by H₂O.

**Leaching of MnO₄ by aqueous carbonate solutions.** The solutions and the solids obtained by leaching MnO₂ by various carbonate solutions were investigated. The influence of pH, carbonate concentrations, temperature of leaching and agitation was studied.

**Chemical analysis.** The oxidation state of Mn in the solids and the solutions was determined by spectrophotometric analysis of formed Fe⁹⁺ by the oxidation of a deoxygenated solution of FeSO₄ in sulfuric acid mixed with the sample. This procedure is based on the fact that all ions of Mn in higher oxidation states than II are reduced by Fe⁹⁺ into Mn⁰ in an acidic solution of sulfate. The Mn content in the samples was analysed by spectrophotometry after oxidation of all Mn⁰ ions into MnO₄⁻ by sodium persulfate in the presence of catalytic amounts of Ag⁺ ions. This standard procedure is described in Ref. 4.

**Results and discussion.**

Manganese(II). The solubility of MnCO₃ at room temperature in potassium carbonate at a constant pH of 11.6 and an ionic strength of 4.4 as a function of carbonate concentration is plotted in Fig. 1 on a bilogarithmic scale. The slope of the straight line is close to 1. That means that one CO₃²⁻ ion is added to the insoluble MnCO₃ to form a soluble dicarbonato species. The formation constant of this species, \( β_{12} = \frac{\text{Mn}^2+\text{CO}_3^{2-}}{\text{Mn}^2+} \cdot \frac{\text{CO}_3^{2-}}{\text{Mn}^2+} \cdot \frac{\text{Mn}^2+}{\text{CO}_3^{2-}} \), can be evaluated in the presence of solid MnCO₃ by taking into account the value of MnCO₃ solubility product, \( K_{sp} = 10^{-9.68} \) at an ionic strength of 3, allowing the concentration of Mn²⁺ to be calculated, with the result \( β_{12} = 10^{2.7} \). As was observed, the value of the experimental solubility product values are sensitive to the degree of the insoluble solid crystallinity: an error of ±0.3 log units in \( β_{12} \) could be easily made using this solubility method. The UV-visible spectrum of the colorless solution obtained by dissolving MnCO₃ in deaerated aqueous 4 M in K₂CO₃ and 1 M in KHCO₃ is shown in Fig. 2a. This spectrum has been

![Fig. 1. Solubility of Mn⁰ in potassium carbonate solutions as a function of CO₃²⁻ ion concentrations. Ionic strength, I = 4.4.](image-url)
attributed to Mn$^{II}$, after checking the oxidation state of manganese by the spectrophotometric titration of Fe$^{III}$, following the procedure described in the Experimental section. The addition of small quantities of hydrazine \((\text{NH}_2\text{NH}_2)\) maintained manganese in the divalent state, even in the presence of air. The species of manganese(II) observed in these conditions are probably anionic carbonate species with formula \(\text{Mn} (\text{CO}_3)_2(\text{OH})_{(4+\gamma-2)}\). The number of \(\text{OH}^-\) ions will be considered later after the investigation of the pH influence upon the Mn$^{II}$ solubility.

**Manganese(III).** In contact with air, the colorless solutions of Mn$^{II}$ darkened and their UV–visible spectrum changed as shown in Fig 2b. Two new bands, with maximum absorption at 274 and 450 nm, appeared. After several hours a black solid precipitated. Its X-ray powder diagram, reproduced in Fig. 3, accords with the JCPDS 42-1317 reference file diagram, corresponding to \(\text{K}_0.5\text{Mn}_2\text{O}_4\cdot1.5\text{H}_2\text{O}\). The small crystallite size, 10–13 nm, calculated by applying the Scherrer formula, showed that the sample was poorly crystallized. A Mn : K ratio close to 4 was determined by an energy-dispersive X-ray analysis, statistically performed on the grains of the sample using an EDX microprobe Oxford instrument coupled with a Leica Stereoscan 440 scanning electron microscope. Apparently, at a pH around 10.8, the final state of the Mn$^{II}$ carbonate complexes in the presence of oxygen is a Mn$^{IV}$/Mn$^{III}$/K mixed oxide. The soluble Mn$^{III}$ carbonate complexes are metastable species which can be observed for several days. At a pH close to 11, however, $\text{O}_2^-$ ions seem to be able replace the carbonate ligand in the first coordination sphere of Mn$^{III}$. The formation of the \(\text{K}_0.5\text{Mn}_2\text{O}_4\cdot1.5\text{H}_2\text{O}\) is probably due to the occurrence of a thermodynamic sink which favors the partial oxidation of Mn$^{III}$ into Mn$^{IV}$ by oxygen. As potassium ions are contained in the solid and participate to the structure stability, it is premature to conclude that this behavior is general, because a change in the potassium concentration or its replacement by another cation may change the reaction path and the nature of the final products.

The voltamgram at the rotating platinum electrode, of a potassium carbonate solution, \(5 \times 10^{-4} \text{ M in Mn}^{III}\), in contact with air for two days, is shown in Fig. 4. It can be seen that the Mn$^{III}$–Mn$^{II}+\gamma$ couple in the carbonate medium looks reversible at the platinum electrode. Its formal potential in 5 M $\text{K}_2\text{CO}_3$ and 0.5 M $\text{KHC}_2\text{O}_3$ is +0.07 V vs. the Ag/AgCl electrode, which yields +0.29 V vs. the normal hydrogen electrode. A slope analysis of the voltamperometric curve, by plotting $\log I/I_0-I$ as a function of the potential, yields 0.065 V. This indicates that one has to deal with an one electron quasi-reversible reaction. One may therefore conclude.

**Fig. 3.** X-Ray diffraction pattern of the solid precipitated from 0.001 M Mn$\text{CO}_3$ in 4 M $\text{K}_2\text{CO}_3$ and 1 M KHCO$_3$ after 8 days of contact with air, compared with the JCPDS42-1317 reference file of $\text{K}_0.5\text{Mn}_2\text{O}_4\cdot1.5\text{H}_2\text{O}$.

**Fig. 4.** Voltammogram of a $5 \times 10^{-4} \text{ M MnCO}_3$ in 4 M $\text{K}_2\text{CO}_3$ and 1 M KHCO$_3$ after 2 days of contact with air (rotating platinum electrode 1000 r.p.m.).
that the Mn$^{II}$/Mn$^{III}$ couple is close to reversible at the platinum electrode in carbonate–bicarbonate solutions around a pH of 11.2. The strong shift of the Mn$^{III}$/Mn$^{II}$ formal potential to lower values when replacing an acidic medium [$E_\text{o}(\text{Mn}^{III}/\text{Mn}^{II}) = 1.51$ V vs. NHE] by a carbonate medium shows clearly that the carbonate complexes of Mn$^{III}$ are more stable than the corresponding Mn$^{II}$ complexes. However, because of the O$^{2-}$/OH$^-$ competition for the Mn$^{III}$ coordination sites being apparently favorable to the oxides ions, the Mn$^{II}$ carbonato complexes are more easily observed at high pH. The electrochemical evidence for the oxidation of Mn$^{III}$ carbonato complexes into soluble Mn$^{IV}$ carbonato complexes shown in Fig. 4 was corroborated by UV-visible spectrophotometry. The absorption bands of aged solutions of Mn$^{II}$ carbonato species in contact with air, shown in Fig. 2b, can be attributed to Mn$^{II}$ because further oxidation of Mn with MnO$_2$ gave rise to a new spectrum, attributed to manganese(IV) or a species of Mn$^{IV}$ other than MnO$_2$$^-$, which possesses a completely different UV-visible spectrum. The highly intense bands appearing in the spectra of the ions at higher oxidation state than II ($E_\text{m} = 10^4$) are probably due to charge transfer rather than d-d transitions. The spectrum of Mn$^{III}$ changes with the pH of the solution, even for small changes in the carbonate concentration, indicating that mixed hydroxo-carbonato complexes are formed. The relative intensity of the absorption bands at 450–724 nm (Table 1), decreases with pH, showing that the 450 nm band is probably due to the presence of hydroxo groups in the first coordination sphere of manganese(III). The UV band at 274 nm is probably due to CO$_2$$^2-$–Mn$^{III}$ charge-transfer transitions, and the band at 450 nm could be attributed to some Mn$^{III}$-Mn$^{II}$ electron transfer, the two metal ions being present in a polymeric species in which the metal ions are linked by OH bridges. The red shift for the electron transfer bands when some CO$_2$$^2-$ ions are replaced by OH$^-$ has already been observed in UV-visible hydroxocarbonato complexes.

Manganese(IV). Soluble manganese(IV) carbonato complexes were obtained through three procedures: by boiling KMnO$_4$ in carbonate solutions, by oxidizing Mn$^{II}$ by MnO$_2$ ions or by dissolving MnO$_2$ into K$_2$CO$_3$–Na$_2$CO$_3$ eutectic at 800°C and then dissolving the cooled solidified melt into an aqueous solution of HKCO$_3$.

**Table 1.** Effect of pH on the optical density ratio (R) at 274–450 nm bands in the UV-visible spectra of various 10$^{-3}$ M Mn$^{III}$ carbonato complexes.

<table>
<thead>
<tr>
<th>K$_2$CO$_3$ /mol L$^{-1}$</th>
<th>KHCO$_3$ /mol L$^{-1}$</th>
<th>pH</th>
<th>R</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>0</td>
<td>&gt;12.5</td>
<td>1.6</td>
</tr>
<tr>
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<td>0.33</td>
<td>11.3</td>
<td>6.5</td>
</tr>
<tr>
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<td>0.5</td>
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<td>8.9</td>
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</tr>
<tr>
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<td>2</td>
<td>9.2</td>
<td>28</td>
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**Fig. 5.** UV-visible absorption spectrum of a 5 x 10$^{-4}$ M KMnO$_4$ solution in 5 M K$_2$CO$_3$ and 0.5 M KHCO$_3$. Mn$^{IV}$ was reduced by boiling for 2 h.

Reduction of KMnO$_4$ by H$_2$O$_2$. 5 x 10$^{-4}$ to 2 x 10$^{-3}$ M solutions of KMnO$_4$ into 5 M K$_2$CO$_3$–0.5 M KHCO$_3$ solutions were heated in a boiling water bath. After 2 h the rose color of permanganate vanished and was replaced by a brown to yellow color. The UV visible spectrum is shown in the Fig. 5. The oxidation state of manganese was determined using the procedure described in the Experimental section, and a value close to 4 was found. Solids are formed from the yellow–brown solutions during the reduction of MnO$_2$$^-$ ions by the solvent. If boiling is pursued the color of the solution disappears and all the manganese is precipitated. Unfortunately, these solids were amorphous, and XRD was not useful for their identification. The voltammogram of a carbonate solution of Mn$^{IV}$ is shown in Fig. 5. It can be seen that this curve corresponds to one or several irreversible electrochemical steps. Owing to this irreversibility, it was not possible to assign a number of electrons for this reduction, probably involving polymeric species. Oxidation of Mn$^{III}$ in Mn$^{IV}$ was not seen in the voltammogram of a Mn$^{III}$/Mn$^{IV}$ mixture, shown in Fig. 3. This indicates that the reversible formal oxidation potential of the Mn$^{III}$/Mn$^{IV}$ couple is probably higher than the solvent oxidation potential. Unlike the Mn$^{III}$ complex the UV-visible spectra of carbonate solutions of Mn$^{IV}$ were not useful to distinguish the various species being present because only very broad bands were detected.

Reduction of KMnO$_4$ by MnCO$_3$. By mixing gradually, at room temperature, a 10$^{-3}$ M solution of MnCO$_3$ with a 10$^{-3}$ M solution of KMnO$_4$ into 4.5 M K$_2$CO$_3$ plus 1.5 M KHCO$_3$, MnO$_2$ is first reduced to a Mn$_2$CO$_3$ carbonate species which has a UV-visible spectrum as shown in Fig. 2b. Further oxidation led to a solution of which the UV–visible spectrum is similar to the spectrum shown in Fig. 5. The voltammogram of this last solution is close to that of the Mn$^{IV}$ solutions voltammograms represented Fig. 6. Thus it can be concluded that we dealt with the reactions

4 Mn$^{II}$ + Mn$^{IV}$ + 5 Mn$^{IV}$
and

$$3 \text{Mn}^{\text{III}} + \text{Mn}^{\text{VII}} \rightleftharpoons 4 \text{Mn}^{\text{IV}}$$

**Reaction of MnO₂ with aqueous carbonate solutions and the melted K₂CO₃–Na₂CO₃ eutectic.** The reaction of MnO₂ with aqueous carbonate solutions at room temperature or at 100 °C led to very dilute Mn⁴⁺ carbonato species of which the UV–visible spectrum is similar to the Mn⁴⁺ spectrum obtained by the procedure described above. The X-ray diffraction of the amorphous solid from the reaction was not informative. However, as we started with a poorly crystallized sample of MnO₂, Akhtenskite–JCPDS reference file 30-820, the loss of crystallinity and the detection of small amounts of soluble Mn⁴⁺ indicate a chemical reaction. The probable thermodynamic sink for Mn in potassium carbonate solution is the mixed oxide which is formed by partial reduction of MnO₂ by the solvent via the formation of soluble Mn⁴⁺ carbonato complexes.

MnO₂ is dissolved rapidly into melted K₂CO₃–Na₂CO₃, 1/1 eutectic, at 800 °C. It gives a deep red melt. In the presence of air some color change from red to green is observed at the surface of the melt, which indicates partial conversion of the Mn⁴⁺ carbonato species into Mn⁴⁺O₂²⁻ ions. The solidified melt was dissolved into a KHCO₃ solution. The voltammogram and the UV–visible spectrum of the solution showed that Mn⁴⁺ carbonato was obtained. The concentration of Mn and its stability in solution was higher than for the Mn⁴⁺ solutions prepared by other procedures. Increased stability with increased concentrations in manganese can be due to the presence of polymeric species, probably mixed hydroxocarbonate complexes, in which the metals are linked by hydroxo bridges. After several months a black solid could be isolated from the solution.

**Conclusion**

This study has shown that all ions of Mn, from II to IV, can form carbonate species soluble in aqueous solutions. In the high-pH range investigated here, species can lead to insoluble compounds, probably oxides. Only one has been identified as K₀.₅Mn₃O₄·1.₅H₂O. It is the final product of Mn⁴⁺(CO₃)₂⁻, oxidation by air, first into Mn⁴⁺ soluble carbonato species, followed by a further oxidation to the identified insoluble product. Mn⁴⁺ gives mixed hydroxocarbonato species when in contact with concentrated carbonate solutions. When K⁺ ions are present the precipitation of K₀.₅Mn₃O₄·1.₅H₂O is favored. The determination of the quantitative relationships between these species will be an important piece of work because of the numerous parameters which govern the competition between the ligands: OH⁻, O²⁻, CO₃²⁻ for bonding to the metal. Solubility products of simple oxides, hydroxides and insoluble carbonates must be known. Oxidation–reduction reactions in which the solvent and dissolved oxygen can play a role must be precise. The pH of the medium is obviously an important parameter, as it influences the values of all the other parameters. As mentioned in the Introduction, solid Mn⁴⁺CO₃, isomorphous with calcite, is the only known carbonate of Group VII B metallic ions. It dissolves into carbonate solutions to give one anionic carbonato or hydroxocarbonato species which possesses two CO₃²⁻ ions.

Mn⁴⁺, like Fe⁴⁺, is not known to form stable carbonate species because of its high tendency to be hydrolysed. However, the carbonato complexes of Mn⁴⁺ have been identified in this work, at least as intermediate species, during the oxidation of Mn⁴⁺ carbonate complexes by oxygen. In nature some rare minerals contain carbonate and Mn⁴⁺, for example, desautelsite, Mg₉Mn₄(OH)₁₀(CO₃)₄·4H₂O.⁹

Mn⁴⁺ is also found with carbonate ions in rare minerals like journavskite, Ca₄Mn⁴⁺(OH)₁₀CO₃·SO₄·12H₂O, but the structure of this natural Mn⁴⁺ compound has shown that the Mn⁴⁺ ions are surrounded by six OH⁻ ions.¹⁰ In the present study it has been found that soluble Mn⁴⁺ carbonato species can be obtained in solution as the result of several reactions: reduction of MnO₄²⁻ ions, oxidation of Mn⁴⁺ ions and dissolution of MnO₂ in molten salts. Here again the stability of these carbonato species toward the oxo or hydroxo species in aqueous solutions has to be investigated more completely to tell if they are transient or thermodynamically stable species. The identification of all solids being in equilibria with the solutions has not been achieved completely because most of them were amorphous. The speciation of the soluble complexes is not complete. However, the occurrence of several carbonated species has been established. One remaining task is that of investigating the carbonato complexes in a larger pH range. Most of the present work was carried out in the pH range 10–11.5, in which the concentrations of CO₃²⁻ ions are the highest and are favorable for the formation of carbonate species. However, a more complete investigation must be undertaken to determine precisely the existence of mixed OH⁻/CO₃²⁻ ligand complexes. Our present understanding of the reactions taking place in potassium carbonate media, in the pH range from 10.5 to 11.5, in oxidic environments is shown schematically in Fig. 7. The mixed
Mn valence oxide III/IV (K₃₃Mn₂O₇·1.5H₂O) presents a well in which all the species of all the oxidation states are transformed, after a more or less long period of time, by reduction with water or oxidation by oxygen.

Coming back to the purpose for which this investigation was undertaken, the transportation of Tc via soluble species obtained in the presence of carbonates, we must take into account the very low concentration range of the metal, where the solubility product of the solids might not be reached and where the occurrence of soluble species and sorption on the surfaces are the predominant features.

However, the present investigation is a strong incentive for the research of the soluble carbonates of Tc in a large pH range. Their stability toward insoluble oxides or complexes with humic acid must be specified. Oxidation into very mobile TcO₄⁻ is also a key factor for the environmental behavior of Tc. For all these reactions kinetic factors will play a more important role than the for the equivalent MnV reactions.

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