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Interaction of Ozone with Variable-Valence Metal Ions in Concentrated Silicate Solutions

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Abstract—Spectrophotometric studies have revealed that ozone oxidizes Cr(III) into Cr(VI), Fe(III) into Fe(VI), Mn(VI) into Mn(VII), and Np(VI) into Np(VII) in the concentrated aqueous silicate solutions. Cr(III) oxidation is accelerated in alkaline-silicate and alkaline solutions as compared to neutral silicate solution. Ferrate and permanganate ions are unstable in Na_2SiO_3 solutions (0.5–1.3 mol/L of the silicate). Neptunium(VII) ions formed in the course of ozonation are stable in Na_2SiO_3 solution (1 mol/L) upon drying in air to form solid vitreous mass.

Keywords: chromium, iron, manganese, neptunium, ozone, sodium silicate

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Ozone is considered a promising oxidizer for various processes due to its high oxidizing potential [1] and availability of simple and convenient equipment for ozone production. Therefore, ozone is suitable for water treatment to remove organic and inorganic pollutants [2]. Many metal ions can be converted into higher oxidation states upon interaction with ozone in the aqueous solutions; this is applied to perform catalytic transformation of organic substrates [3]. Oxidation of chromium(III) with ozone in the course of reprocessing of alkaline wastes is of practical importance [4]. A number of anions are found in such wastes, including silicate [5]. Even low concentration of silicate ions can substantially alter metal ions behavior in redox processes. Formation of silicate ion complexes with metal ions in concentrated Na_2SiO_3 solutions has been studied in detail in the cases of silica-alumina compounds [6]. Similar interactions are possible in solutions of variable-valence metals, for instance, Cr(III) or Fe(III); however, they have been scarcely studied so far [7].

pH of concentrated silicate solutions is of 13.5 [8]. The alkaline medium favors oxidation processes and stabilizes the oxidized state of metal ions; however, the presence of silicate ions can have the opposite effect. Oxidation of metal ions in silicate solutions has been practically unexplored. In order to fill in the gap, we have studied ozonation of *d*- and *f*-block elements in their silicate solutions.

Chromium. Upon mixing of 5 mL of Na_2SiO_3 solution (0.7–1.2 mol/L) with 20–100 μL of $Cr(NO_3)_3$ solution (0.5 mol/L), precipitate was initially formed, rapidly dissolving under vigorous stirring. Absorption spectrum of the so formed transparent solution was typical of complex chromium(III) ions: two absorption bands were observed in the visible spectral range (Fig. 1).

The observed absorption bands (619.5 nm [ε = 26.3 L mol^{-1} cm^{-1}] and 440 nm at 1.2 mol/L of Na_2SiO_3) were shifted towards longer wavelength as compared to spectra of aquatic Cr(III) complexes and even to the hydroxo complexes formed in silicate-free alkaline solutions (594 nm {ε = 27.1 L mol^{-1} cm^{-1}} and 425 nm [9]); that confirmed complex formation of Cr(III) with silicate ions. The bands shift occurred slowly, within several hours. The example of spectrum evolution kinetics observed upon mixing of aqueous solution of Na_2SiO_3 (1.2 mol/L) with equal volume of alkaline (0.9 mol/L of NaOH) solution containing 1.2×10^{-2} mol/L of $Cr(NO_3)_3$ in the form of hydroxo complexes is shown in Table 1.

The observed spectral changes were assigned to slow substitution of hydroxyl ligands in Cr(III) coordination sphere with silicate ions.

Upon ozonation of the Cr(III) aqueous silicate solutions, the bands typical of Cr(III) ions disappeared, and a new band at 371 nm appeared, assigned to chromate ion. Noteworthily, absorption due to the presence of chromate ions could not disfigure the above-described spectral changes associated with the complex formation.

The rate of Cr(III) oxidation estimated from change of the long-wavelength absorbance was lower in the case of silicate solutions than that in the alkaline silicate-free solutions (Table 2).

Slowing down of chromium oxidation was due to lower reactivity of silicate complexes towards ozone than that of anionic hydroxo complexes. Oxidation of Cr(III) into Cr(VI) is a three-electron process and likely proceeds via formation of Cr(IV) and Cr(V) ions. Noteworthily, hydrogen peroxide formed in the course of ozone decomposition appeared to oxidize Cr(III) in its silicate solutions; similar reaction has been known for alkaline solutions of chromium(III) [9].

Iron. Colorless homogeneous solutions containing 1–10 mmol/L of Fe(III) could be obtained by mixing $Fe(NO_3)_3$ solution with that of Na_2SiO_3 (0.5–1.2 mol/L). Ozonation of those silicate-containing solutions resulted in partial oxidation of Fe(III) into Fe(VI). Absorption spectra of the ozonized solutions coincided with those of alkaline solutions containing ferrate ions. Addition of iron(III) salts into sodium silicate solutions (above the solubility limit) yielded suspension of various iron(III) compounds. Ozonation of the suspension resulted in formation of ferrate ions as well; addition of alkali enhanced efficiency of iron(III) oxidation and stabilized ferrate ions (increasing their lifetime). The results were poorly reproducible, and therefore the rate of ferrate ions reduction in the presence of sodium silicate could not be precisely determined.

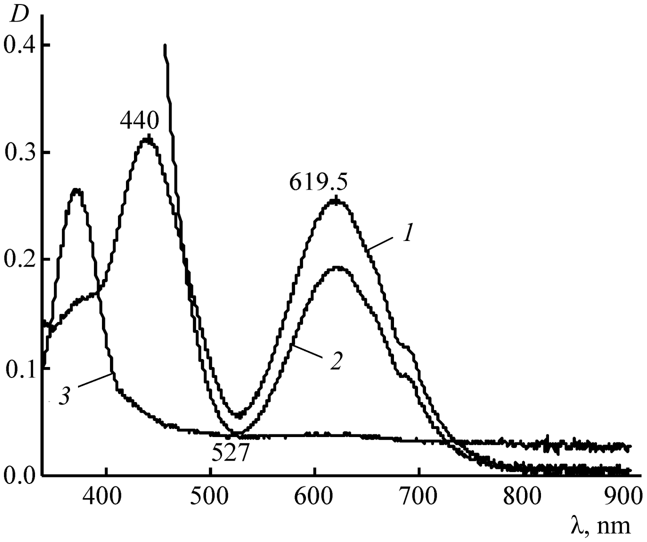

Fig. 1. Evolution of electronic absorption spectrum of $Cr(NO_3)_3$ aqueous solution (9.5×10^{-3} mol/L) in the presence of 1.2 mol/L of Na_2SiO_3 in the course of oxidation with ozone. (*1*) Initial solution; (*2*) the same solution after partial oxidation of Cr(III); (*3*) partially oxidized solution, 50-fold diluted with solution of Na_2SiO_3 (1.2 mol/L).

Manganese. Being relatively stable in alkaline solutions, in the presence of 1.2 mol/L of sodium silicate permanganate ions (initial concentration of 5×10^{-4} mol/L of $KMnO_4$) were reduced to manganate ions within 1 h. Ozonation resulted in rapid oxidation of manganate ions back to permanganate ones, and such reverse oxidation-reduction could be performed repeatedly. Positions of absorption bands in the solutions spectra coincided with those in the known spectra of alkaline solutions of manganates and permanganates. Easiness of the redox processes suggested that Mn(VI) and Mn(VII) ions existed in the free form in concentrated silicate solutions.

In the presence of silicate, manganate ions were more stable than permanganate ones. Absorption bands typical of manganate ions disappeared within 1 week; simultaneously, UV-range absorption became stronger.

Table 1. Changes of maxima of absorption bands (nm) of chromium(III) ions in the spectrum of the solution containing 0.6 mol/L of Na_2SiO_3, 0.45 mol/L of NaOH, and 6×10^{-3} mol/L of $Cr(NO_3)_3$

Time after mixing	0	60 min	191 min	251 min	2 days
Band 1, nm	431	438	440	440	440
Band 2, nm	600	615	617	619	619

Table 2. Rate of Cr(III) oxidation with ozone in alkaline-silicate solutions at 22°C

Na_2SiO_3, mol/L	NaOH, mol/L	$Cr(NO_3)_3$, mol/L (initial)	r, mol min^{-1} L^{-1}
1.2	–	5×10^{-3}	0.2×10^{-3}
0.6	0.45	5×10^{-3}	0.84×10^{-3}
–	0.9	5×10^{-3}	1.2×10^{-3}

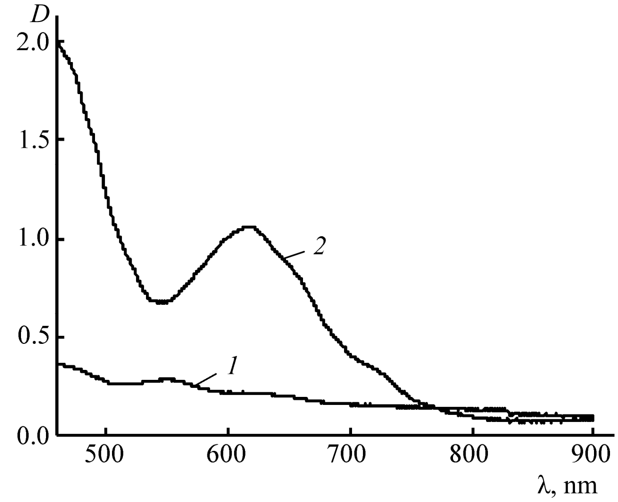

Fig. 2. Electronic absorption spectrum of solution of Na_2SiO_3 (1 mol/L) containing 2.6×10^{-3} mol/L of $NpO_2(ClO_4)_2$ before ozonation (*1*) and after 10 min of ozone treatment (*2*).

Ozonation of such incubated transparent yellow solution during 75 min did not result in appearance of absorption bands of manganate ions. Addition of NaOH did not result in precipitation of MnO_2. Ozonation of the alkaline-silicate solutions was not accompanied with appearance of manganate or permanganate ions absorption bands as well. Basing on those observations we suggest that ions of manganese higher oxidation states were reduced to Mn(IV) and incorporated into silicate polymeric and colloid particles. Apparently, silicate surrounding prevented Mn(IV) oxidation with ozone.

Neptunium. Addition of neptunium(VI) perchlorate to solution of 1 mol/L of Na_2SiO_3 yielded suspension. After its centrifugation, the supernatant was pale-yellow, as neptunium(VI) silicates were poorly soluble in concentrated silicate solution. Ozonation of the suspensions resulted in complete dissolution of the precipitate, and the solution turned green. Absorption spectrum of the ozonized neptunium-containing Na_2SiO_3 solution (1 mol/L of the silicate) was similar to those of Np(VII) solutions in alkaline [10] and silicate (0.1 mol/L of Na_2SiO_3) [11] media (Fig. 2). The ozonized solution spectrum shape evidenced about existence of neptunium in the anionic form.

In the solutions containing about 1 mol/L of Na_2SiO_3, complete oxidation of Np(VI) into Np(VII) occurred within 10 min. From redox potentials of the O_3/O_3^- (0.9 V) [1], $O_3^-/O_2,OH^-$ (1.6 V [1]), and Np(VII)/Np(VI) (≈ 0.5 V [1]) pairs, we concluded that Np(VI) was oxidized with both ozone and ozonide ions [Eqs. (1) and (2)].

$$\mathrm{Np(VI)} + O_3 \rightarrow \mathrm{Np(VII)} + O_3^-, \tag{1}$$

$$\mathrm{Np(VI)} + O_3^- \rightarrow \mathrm{Np(VII)} + O_2 + 2OH^-. \tag{2}$$

Simultaneously, reactions (3)–(6) occurred at pH > 13.

$$OH^- + O_3 \rightarrow HO_2^- + O_2, \tag{3}$$

$$HO_2^- + O_3 \rightarrow HO_2 + O_3^-, \tag{4}$$

$$HO_2^- + OH^- \rightarrow H_2O + O_2^-, \tag{5}$$

$$O_2^- + O_3 \rightarrow O_2 + O_3^-. \tag{6}$$

Previously, similar mechanism was suggested to describe ozonation of Np(VI) compounds in their alkaline solutions [12]; ozone interaction with manganate ions possibly followed that mechanism as well. Incubation of Np(VII) solutions in 1 mol/L of Na_2SiO_3 during 3 weeks led to formation of green vitreous solid; the specimen spectrum was not changed upon incubation. The different stability of Mn(VII) and Np(VII) in concentrated silicate solutions was of special interest. In the alkaline medium, standard redox potential of those elements are close: 0.58 V in the case of Np(VII/VI) and 0.56 V in the case of Mn(VII/VI) [1]. Apparently, structural dissimilarity of $NpO_4(OH)_2^{3-}$ ion and neptunium(VI) silicate complexes prevented electron transfer; on the other hand, structural similarity of MnO_4^- and MnO_4^{2-} favored permanganate ions reduction.

To conclude, behavior of the studied compounds upon ozonation in silicate solution is as follows. Chromium(III) exists in the form of complexes with silicate in concentrated silicate solutions; interaction of such complexes with ozone yields stable chromate ions. Ozonation of silicate solutions containing iron(III) and manganese(VI) leads to formation of instable ferrate and permanganate ions, respectively. Oxidation of neptunium(VI) is more efficient and gives stable $NpO_4(OH)_2^{3-}$ ions in silicate solutions.

EXPERIMENTAL

^{237}Np compounds were prepared as described elsewhere [13, 14]. Bidistilled water was used for solutions preparation. $Na_2SiO_3 \cdot 9H_2O$, $Fe(NO_3)_3 \cdot 9H_2O$, $Cr(NO_3)_3 \cdot 9H_2O$, and $KMnO_4$ (all of "analytical pure" grade) were used as received. The ozonation experiments were preformed as follows: ozone-oxygen mixture containing 4 vol % of ozone (80 mg of O_3 per

1 L) was passed through a glass bubbler containing 5 mL of the studied solution at 10–15 L/h. Transparent solutions to be used for further investigation were prepared from the ozonized mixture by centrifugation at 1750*g*. Electronic absorption spectra were recorded with the Shimadzu UV 3100 spectrophotometer (Japan). In order to determine Cr(III) concentration in the initial solution, 0.03–0.1 mL of it was diluted with 3 mL of $HClO_4$ solution (2 mol/L), and absorbance at 574 was measured. The concentration was them calculated using the molar absorptivity of 13.4 L mol^{-1} cm^{-1} [15]. The molar absorptivity of Cr(III) in its silicate solutions was determined in this work separately.

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