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Summary

The stabilization of neptunium(IV) in alkaline solution by chemical reductants under various conditions was studied. Testing showed that neptunium(V) is slowly reduced to Np(IV) by V(IV) at room temperature in alkaline solutions. Increasing temperature accelerates reduction. Complete reduction of 2×10^{-4} M Np(V) occurs in three hours at 80°C in 1 M NaOH with 0.02 M $VOSO_4$. Under similar conditions, but in 5 M NaOH, only 15 to 20% of the Np(V) was reduced in 5 hours. In all cases, about 98% of the initial neptunium was found in the precipitate. Thus V(IV) acts both as a reductant and as a precipitation carrier. Tests showed Np(V) reduction by hydrazine hydrate could be catalyzed by Pd(II). Reduction increased with temperature and catalyst concentration and decreased with hydroxide concentration.

Reduction of Np(V) also takes place in 1 M NaOH solutions containing 1 M sodium formate and palladium. Increasing temperature accelerates reduction; with three hours' treatment in 5 M NaOH solution at 90°C, about 95% of the initial 2×10^{-4} M neptunium(V) is transformed to Np(IV).

Organic complexants and organic acid anions hinder the decontamination of alkaline solutions from neptunium and plutonium by coprecipitation with d-element hydroxides (the Method of Appearing Reagents). It was found that ethylenediaminetetraacetate (EDTA) and N-(2-hydroxyethyl) ethylenediaminetriacetate (HEDTA) are decomposed by H_2O_2 in alkaline solution in the presence of cobalt compounds with heating and by $Na_2S_2O_8$ at moderate temperatures. Citrate, glycolate, and oxalate are decomposed by $Na_2S_2O_8$ with heating. Oxidant amounts must be increased when $NaNO_2$ also is present in solution.

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Part I. Reduction Reactions of Neptunium(V)

1.0 Introduction

Any technology for treating radioactive alkaline wastes requires the separation of long-lived neptunium, plutonium, and americium isotopes to a small volume fraction of the original waste. Coprecipitation of transuranium elements with carriers obtained in alkaline solutions by the Method of Appearing Reagents is a possible way to decontaminate radioactive alkaline wastes (Krot et al. 1996).

In the development of the Method of Appearing Reagents to treat alkaline radioactive waste solutions, it was shown that coprecipitation of soluble neptunium(V) generally is poor. To achieve better decontamination, reduction of Np(V) to low solubility Np(IV) compounds is necessary. Recent further experiments on neptunium removal by coprecipitation confirm that reduction of neptunium to its tetravalent oxidation state substantially increases the efficiency of neptunium removal (Bessonov et al. 1997). Neptunium(V) can be reduced to Np(IV) by use of strong reductants. For instance, hydrazinium nitrate reduces Np(V) slowly at 20°C and concentrations higher than 0.1 M are required (Shilov et al. 1996). Redox catalysts to increase Np(V) reduction rate were investigated to allow lower hydrazine concentrations to be used.

Hydrazine decomposition by redox reactions is accompanied by evolution of nitrogen gas (N_2). Reductants to produce Np(IV) which do not evolve gaseous products also may be interesting. Compounds of V(IV) and formic acid salts were tested as possible Np(V) reductants. Formate oxidation produces carbon dioxide (CO_2) which transforms in alkaline solution to carbonate. The behavior of Np(V) in 1 to 5 M NaOH solution with V(IV) and with formate in the presence of catalysts was investigated.

In alkaline solution, Np(V) exists as a complex anion $NpO_2(OH)_3^{2-}$. Because activated charcoal adsorbs multicharged ions from solutions of various composition, activated charcoal may adsorb Np(V). The sorption of Np(V) by activated charcoal in pure alkaline solutions also was investigated.

2.0 Experimental Materials and Methods

2.1 Reagents and Equipment

The isotope ^{237}Np was used to investigate Np(V) reduction. Neptunium stock solution was purified by anion exchange. The purified nitric acid solution was evaporated with perchloric acid to dryness. The residue was dissolved in doubly distilled water. To prepare neptunium(V), sodium nitrite ($NaNO_2$) was added to the low-acid Np(VI) solution. The product Np(V) then was precipitated by ammonia and the Np(V) hydroxide precipitate separated by centrifugation, washed with water, and dissolved in a minimum amount of perchloric acid. The neptunium valent forms in the product stock solution were determined spectrophotometrically. The neptunium concentration was determined by complexometric titration with xylenol orange after preliminary reduction of neptunium to the tetravalent state using $NH_2OH \cdot HCl$ in HCl (Smirnov-Averin et al. 1966).

The isotope ^{239}Np (half-life 2.346 days) was used as a radiotracer. It was derived from its mother ^{243}Am (half-life 7,370 years) with which it rapidly achieves secular equilibrium. To separate the ^{239}Np, the dilute perchloric acid solution of ^{243}Am was evaporated with concentrated nitric acid, oxidizing neptunium to the hexavalent state. The residue was dissolved in 0.2 M HNO_3. Americium(III) was separated from solution by precipitation of Am(III) oxalate in 0.1 M HNO_3 and 0.1 M $H_2C_2O_4$. The initial clotted precipitate became compact after 10 to 20 minutes under the supernatant solution. Heating accelerated the process; the Am(III) oxalate precipitate was digested for one hour and was separated by centrifugation. The supernatant solution was heated until it formed moist salts, and nitric and perchloric acids were added to decompose oxalic acid and oxidize neptunium to the hexavalent state. This operation was performed twice to guarantee complete oxalic acid decomposition. The residue was dissolved in 0.01 M HNO_3. To prepare $^{239}Np(V)$, sodium nitrite was added to the low-acid $^{239}Np(VI)$ solution. The tracer was not examined for purity because it is well known that Am(III) oxalate solubility is low (0.3 mg/L).

Preparation of catalysts on anion exchange resin support began with sorption of $PdCl_4^{2-}$ or $PtCl_6^{2-}$ on the macroporous basic anion exchange resin from chloride solutions. This was followed by reduction of Pd or Pt with hydrazine hydrate and heating. Catalysts were then washed with water and dried. Samples of activated charcoal were washed with HCl solution, rinsed with water, and dried.

Standardized sodium hydroxide solutions were used in the experiments. They were prepared by diluting special purity grade 17 M NaOH. Other reagents used ($N_2H_4 \cdot HNO_3$, $N_2H_4 \cdot 2HCl$, $VOSO_4$, HCOONa, $NaNO_2$, $Cu(NO_3)_2$, $CoCl_2$, $PdCl_2$, H_2PtCl_6) had chemical purity grade or p.a. (pro analysis) grades. All solutions were prepared using doubly distilled water. Reagent concentrations were calculated from the weights of corresponding samples or were determined by standard methods.

Experiments were conducted in quartz cuvettes and in glass or polyethylene test tubes. A centrifuge (36 cm diameter, 3000 rpm, separation factor 1750) was used to separate precipitates. Constant temperature was maintained using thermostats. Spectrophotometric measurements were performed using a Shimadzu UV-3101 PC (Japan) spectrophotometer. Radiometric measurements were conducted using a β counter, model PSO2-4 (Russia), with solid plastic scintillator.

2.2 Experimental Methods

Working solutions were prepared by adding 10 mL of neutral 1 x 10^{-3} M ^{237}Np(V) to 20 mL of 4 to 10 M NaOH with intense stirring. The tubes with working solutions were placed in the thermostat, and, after thermal equilibrium was reached, the reductant was added. Periodically, 10 mL of the suspension was removed. After cooling, the precipitates were centrifuged, then washed with small quantity of water and dissolved in 4 M HCl or 4 M $HClO_4$. Neptunium valent states in solutions acidified with HCl were determined by spectrophotometric methods using Np(IV) (at 725 and 962 nm) and Np(V) (at 982 nm) absorption bands.

To test heterogenous catalysts, alkaline solutions of Np(V) were passed through a thermostatted column (inner diameter 0.8 cm) filled with the anion exchange resin previously coated with 2% Pt or 1% Pd. After passing the alkaline solution, the column was washed with 2 M HCl followed by water to remove the adsorbed Np(IV). Alkaline and acidic solutions collected from the column were combined, and the spectra of the resulting solutions were recorded.

To investigate the sorption of Np(V) on activated charcoal from strong alkaline solution, 1 gram of charcoal and a 10-mL aliquot of alkaline solution containing 1 x 10^{-4} M ^{237}Np(V) traced with ^{239}Np(V) were placed in a glass vessel and agitated on a reciprocal shaker. Periodically, 0.3 mL aliquots were removed and filtered through a polymeric filter. Two quantitative 0.1 mL aliquots of the resulting solutions were deposited on special stainless steel targets, and, after drying, radiometric measurements were made.

3.0 Results and Discussion

The potential of the Np(V)/Np(IV) couple in 1 M NaOH solution is 0.13 V (Shilov and Yusov 1997). This value was obtained by investigation of the equilibrium of the reaction

$$Np(IV) + Np(VI) \rightleftarrows 2\ Np(V) \qquad (3.1)$$

The potential decreases with increasing NaOH concentration. Recently, the reactions of Np(V) with various reductants in alkaline media were studied (Shilov et al. 1996). However, additional information about Np(V) behavior was needed to improve reduction to tetravalent neptunium in alkaline media.

3.1 Reduction of Np(V) by Hydrazine in Alkaline Solutions Containing Catalysts

It is known that the reaction between N_2H_4 and O_2 is accelerated in weakly alkaline solutions in the presence of Cu(II), Pd(II), and other d-element compounds. Experiments were performed to determine whether the reaction between Np(V) and hydrazine also may be accelerated in the presence of d-element salts.

Tests showed that the extent of Np(V) reduction depends on the anion in the starting hydrazinium compound. The reduction of Np(V) is observed only with $N_2H_4 \cdot HNO_3$. Other hydrazinium salts; $N_2H_4 \cdot H_2O$, $N_2H_4 \cdot 2HCl$, $N_2H_4 \cdot H_2SO_4$, $N_2H_4 \cdot CH_3COOH$; were not effective. A mixture of $N_2H_4 \cdot H_2O$ and $NaNO_3$ in concentrations up to 1 M into alkaline solution also was found ineffective. Based on these experiments, it was concluded that the active reductant is formed in the initial hydrazinium nitrate. Hydrazoic acid, HN_3, is one such compound. To confirm this supposition, a slow flow of argon gas was passed through concentrated $N_2H_4 \cdot HNO_3$ solution and then through Fe(III)/HNO_3 solution. After some time, the color of the Fe(III) solution became red, corresponding to formation of the $Fe(N_3)_3$ complex. Thus, the initial hydrazinium nitrate contained HN_3. To obtain NaN_3 solution, hydrazinium nitrate with added HNO_3 was heated with argon bubbling. The gas flow was passed through NaOH solution. Analysis showed N_3^- accumulated in alkaline solution. The alkaline solution of N_3^- was added to an alkaline Np(V) solution. The reduction of Np(V), however, was not observed; thus, some other intermediate product is present in $N_2H_4 \cdot HNO_3$ solution that is an effective reductant of Np(V) in alkaline media.

Experiments on Np(V) reduction by hydrazine were conducted at 22 to 25°C in 2 M NaOH solutions initially containing 2×10^{-4} M Np(V), 0.1 M $N_2H_4 \cdot HNO_3$, and 5×10^{-4} M Co(II), Cu(II), Pd(II), and Pt(IV) salts as catalysts. None of these additives accelerated Np(V) reduction by hydrazinium nitrate. Addition of heterogeneous catalysts resulted in slow Np(V) adsorption on their surfaces.

Further experiments with catalytic reduction of Np(V) by hydrazine hydrate were performed at elevated temperatures. Catalysts tested were Pd(II), Pt(IV), and Cu(II). For palladium, it is believed that Pd(II) first is reduced to Pd^0. The dispersed Pd^0 metal then adsorbs Np(V) and reductant on its surface and the reduction occurs there. Spectrophotometric analyses of the $HClO_4$-dissolved product sediments were used to determine the extent of Np(V) reduction.

Experimental results (Table I.3.1) show that Np(V) reduction to Np(IV) increases with temperature and catalyst concentration and decreases with hydroxide concentration. Tests confirm that Cu(II) and Pt(IV) also catalytically reduce Np(V) to Np(IV) at 60°C and 2 M LiOH.

Table 1.3.1. Reduction of Np(V) by Hydrazine with Pd(II) in LiOH Solution

$5x10^{-4}$ M Np(V); 0.05 M $N_2H_4 \cdot HNO_3$

[LiOH], M	[Pd(II)], M	T, °C	t, Minutes	Np(IV)/Np(V)^0, %
2	0.0001	40	60	6
2	0.0002	40	60	9
2	0.0005	40	60	18
2	0.00075	40	60	32
2	0.001	40	60	41
1	0.0001	60	100	36
2	0.0001	60	100	30
3	0.0001	60	100	24
4	0.0001	60	100	12
2	0.0001	80	100	82
4	0.0001	80	100	50

3.2 Reduction of Np(V) by Vanadium(IV) in Alkaline Solution

The potential of the V(V)/V(IV) couple in 1 M NaOH, -0.93 volts, makes V(IV) a suitable reagent for Np(V) reduction. Because the transformation of Np(V) to Np(IV) occurs with reorganization of structure, this reaction likely is slow.

Experiments have shown that excess V(IV) transforms Np(V) to Np(IV). Some typical results are given in Table I.3.2.

Table I.3.2. Reduction of Np(V) by V(IV) in NaOH Solution

2×10^{-4} M Np(V)

[NaOH], M	[V(IV)], M	T, °C	t, hours	Np in Precipitate, %	
				Np(IV)	Np(V)
1	0.02	20	22	62	20
2	0.02	20	22	53	20
3	0.02	20	22	43	14
4	0.02	20	22	32	10
5	0.02	20	22	22	8
1	0.02	40	3	15	15
3	0.02	40	3	12	10
5	0.02	40	3	11	8
1	0.02	60	3	39	12
2	0.02	60	3	31	10
3	0.02	60	3	27	8
4	0.02	60	3	21	7
5	0.02	60	3	15	5
1	0.001	80	3	0	0
3	0.001	80	3	0	0
5	0.001	80	3	0	0
1	0.02	80	3.3	98	2
2	0.02	80	3.3	80	20
3	0.02	80	3.3	65	35
4	0.02	80	3.3	40	60
5	0.02	80	3.3	15 - 20	80 - 85

As these data show, Np(V) reduction is slow. Increasing temperature accelerates the process. Neptunium(IV) precipitates and captures part of the Np(V). In 3 to 5 M NaOH, the V(IV) compounds also may act as carriers.

3.3 Reduction Np(V) by Formate in Alkaline Solutions Containing Catalysts

The standard potential in acid for the reaction

$$HCOO^- + H_2O \rightleftarrows CO_3^{2-} + 3\ H^+ + 2\ e^- \qquad (3.2)$$

is 0.227 V. Recalculation to 1 M NaOH solution gives a potential of about -1 V. Thus, formate is capable of reducing Np(V) according to the reaction

$$2\ Np(V) + HCOO^- + 3\ OH^- \rightleftarrows 2\ Np(IV) + CO_3^{2-} + 2\ H_2O \qquad (3.3)$$

Such redox reactions can often be heterogeneously catalyzed if one or, better still, both redox couples are electrochemically reversible on the metal catalyst. However, in this case, the reduction process is complicated because structural rearrangement of neptunium coordination must occur. In addition, two-electron reductants (such as formate) usually react slowly with oxidants.

The kinetics of 2×10^{-4} M Np(V) reduction by formate were studied in 1 to 5 M NaOH. This reaction did not occur within five hours at measurable rates in 60 to 90°C solutions containing 0.1 to 1.0 M HCOONa. Many other redox reactions of this type exist which, for kinetic rather than thermodynamic reasons, do not proceed. However, in 3 M NaOH solutions containing 1×10^{-3} M $Cr(NO_3)_3$, 1 M HCOONa, and 2×10^{-4} M Np(V), all neptunium coprecipitated as Np(V) at 90°C in 150 minutes.

Reduction of Np(V) in alkaline media occurs in the presence of palladium. The extent of Np(V) reduction after three days at 22°C was 25% in 1 M NaOH containing 1 M HCOONa and 5×10^{-4} M Pd(II). Neptunium precipitated with metallic Pd. An increase in temperature and the initial amount of palladium compound accelerated Np(V) reduction. In 5 hours' reaction at 90°C, 90 and 95%, respectively, of the Np(V) reduced to Np(IV) in 1 and 3 to 5 M NaOH containing 1 M HCOONa and 2×10^{-3} M Pd(II). The mechanism of the process includes reduction of palladium ions by formate to form metallic palladium. The dispersed palladium accelerates Np(V) reduction.

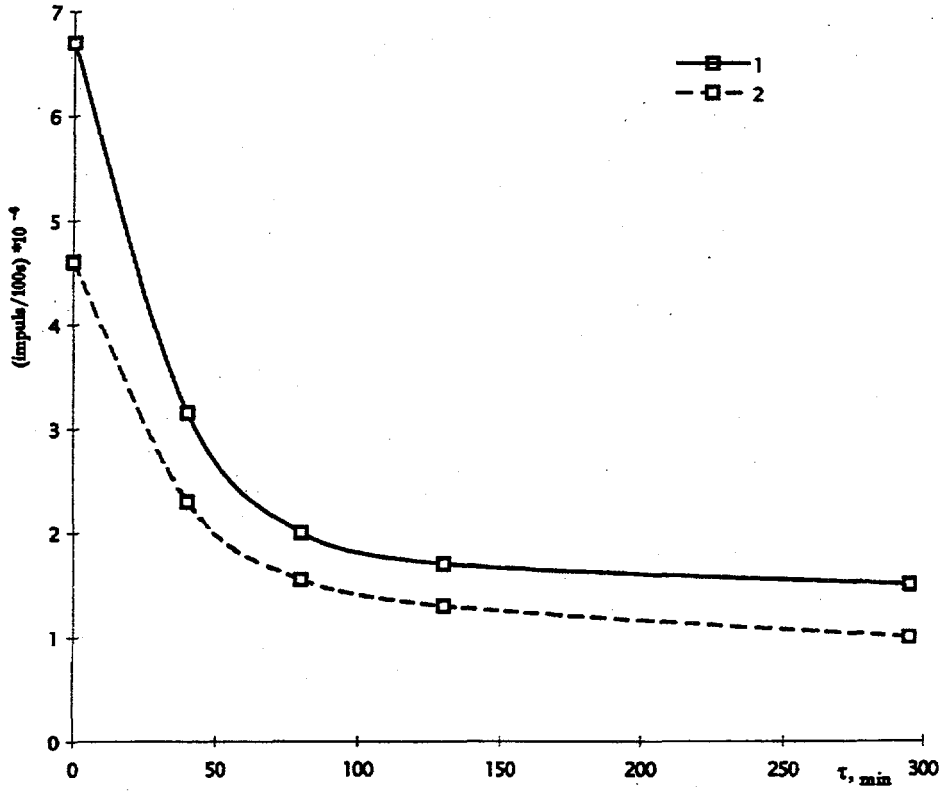
Platinum compounds have less effect on neptunium reduction by formate. Neptunium(V) reduction was 20% in 5 M NaOH containing 1×10^{-3} M platinum compound and 1 M HCOONa in 5 hours' reaction at 90°C.

The reduction of Np(V) on metallic palladium and platinum coated on anion exchange resin was studied. Solutions of 2 to 5 M NaOH, containing 2×10^{-4} M Np(V) and 1 M sodium formate, were slowly passed through thermostatted columns of anion exchange resin coated with metallic palladium or platinum. In 1 hour of contact at 80°C, almost 80% neptunium reduction was achieved.

Neptunium behavior in alkaline solution containing sodium oxalate was studied. No sorption was observed when these solutions were passed through an anion exchange column coated by metallic palladium or platinum, and neptunium remained in the pentavalent state.

3.4 Sorption of Np(V) by Activated Charcoal from Alkaline Solution

The kinetics of adsorption of Np(V) by activated charcoal (trademark, BAU; Russian manufacture) from 1.7 and 3.4 M NaOH is shown in Figure I.3.1. At room temperature, 50% and 80% of the Np(V) adsorbed after 40 and 120 minutes, respectively. No further change was noted at three hours. Five types of charcoal were tested, and all results were similar.



[NaOH], M 1 - 1.7
2 - 3.4

Figure I.3.1. Adsorption of 1 x 10^{-4} M [^{237}Np(V) + ^{239}Np(V)] by Activated Charcoal in NaOH Solution at 25°C as a Function of Time

4.0 Conclusions

Interactions of Np(V) in alkaline media with various reductants were studied in the presence and absence of catalysts. Neptunium(V) was reduced by hydrazium nitrate (but no other hydrazinium salt) without catalysts and by hydrazine hydrate in the presence of Pd(II). Neptunium(V) was reduced by vanadium(IV) at 20 to 80°C. Slow reduction of Np(V) was observed in solutions containing formate and palladium. Increasing temperature accelerates reduction.

Neptunium(V) sorption from alkaline solutions on activated charcoal was studied. From 50% to 80% of the Np(V) was adsorbed at ratio of solid (in grams) and liquid (mL) phases of 1:10 after 40 minutes and 2 hours, respectively.

Part II. Decomposition of Complexants and Organic Acid Anions

1.0 Introduction

Alkaline radioactive wastes accumulated during military plutonium production on the Hanford Site contain NaOH, Na_2CO_3, $NaNO_3$, $NaNO_2$, organic complexants, uranium fission products, and the long-lived isotopes of neptunium, plutonium, and americium (Delegard et al. 1994). The purification of alkaline solutions from neptunium, plutonium, and americium can be performed by a technique of coprecipitation of transuranium elements with carriers generated in alkaline solution by the Method of Appearing Reagents (Krot et al. 1996). Recent studies have shown that the presence of complexants—ethylenediaminetetraacetate (EDTA), hydroxyethylethylenediaminetriacetate (HEDTA), and anions of organic acids—glycolate, citrate, and oxalate—hinders the removal of actinides from such solutions (Bessonov et al. 1997). Consequently, it is necessary to develop procedures for the destruction of these organic substances in alkaline solutions. Complete oxidation to CO_2 and H_2O is not required to eliminate their deleterious influences; it is only required that their complexing ability be eliminated. Results are described of experiments using common suitable oxidants such as hydrogen peroxide and sodium persulfate to destroy waste organic complexants. Experiments on the use of transition metal salts as redox catalysts also are described.

2.0 Materials and Experimental Methods

2.1 Reagents and Equipment

Titrated NaOH solutions obtained by dilution of special purity 17 M NaOH were used in these experiments. Hypochlorite and hypobromite solutions were prepared by gaseous chlorine absorption and liquid bromine dissolution, respectively, in cooled alkali solutions. Gaseous chlorine was formed by interaction of hydrochloric acid with potassium permanganate. Other reagents, H_2SO_4, HNO_3, EDTA, Na_3HEDTA, Na_3citrate, $HOCH_2COOH$ (glycolic acid), $K_2C_2O_4$, H_2O_2, $Na_2S_2O_8$, $NaNO_2$, $CoCl_2$, $Cu(NO_3)_3$, $PdCl_2$, H_2PtCl_6, $PbCl_2$, $MnCl_2$, $Ni(NO_3)_2$, chromotropic acid, Na_2SO_3, $N_2H_4 \cdot HNO_3$, $Ca(NO_3)_2$, and xylenol orange, were pure for analysis or chemically pure grade and were used without additional purification. All solutions were prepared using distilled water. Reagent concentrations were calculated from the weights of corresponding materials or were determined by standard methods.

The catalysts in some cases were added to complexant solutions before addition of NaOH solution. With this technique, homogeneous solutions containing cobalt compounds were obtained. However, for solutions containing iron, manganese, or bismuth, precipitates formed anyway. In strongly alkaline solution, copper, palladium, and lead form soluble hydroxocomplexes and are not precipitated from complexant solutions.

To obtain Co(III), H_2O_2 was added dropwise to $CoCl_2$ solution in 1 M $NaHCO_3$ cooled with ice water; 2 moles of H_2O_2 were required per mole of $CoCl_2$. The resulting green solution was clarified through a sintered glass filter. Solid $Co(NH_3)_6Cl_3$ was added to the transparent filtrate, forming a precipitate; addition continued until the solution above the precipitate acquired an orange shade. The precipitate $[Co(NH_3)_6Co(CO_3)_3]$ was separated by a glass filter, washed several times with water, and dried in a desiccator. Most of the laboratory equipment used in this study was described in Part I.

2.2 Experimental Methods

The alkaline organic acid salt solutions were held in stoppered test tubes and kept in thermostats to reach thermal equilibrium. Oxidant solutions were quickly added, with stirring, to the organic salt solutions. Periodically, 0.5- to 1-mL aliquots were withdrawn and quickly diluted with a few milliliters of cold water to quench the redox reactions. Residual unreacted oxidants were eliminated by adding appropriate amounts of reductants such as sodium sulfite or hydrazine. In some cases, aqueous KI solutions were used to remove unreacted KClO or KBrO; the evolved I_2 was then removed with $Na_2S_2O_3$.

The extent of complexant decomposition and the process kinetics were studied by a complexometric titration method with xylenol orange as indicator. Both EDTA and HEDTA solutions were titrated with $Th(NO_3)_4$ solutions after acidification of test solutions to pH 2; a similar technique was used with $Bi(NO_3)_3$ solutions at pH 1. Scoping experiments showed that moderate amounts of sulfur dioxide or hydrazine do not greatly influence HEDTA concentration determination by complexometric titration with xylenol orange.

To determine residual oxalate, $Ca(NO_3)_2$ solution was added to test solution aliquots. The CaC_2O_4 precipitate was separated, washed, and dissolved in aqueous sulfuric acid. The oxalic acid was titrated with standard $KMnO_4$ solution. Citrate concentrations were determined spectrophotometrically following neutralization of alkaline test aliquots by the decrease of optical density of La(III)-xylenol orange complexes in a urotropin buffer media.

Studies of glycolate decomposition were complicated by residual oxidants or reductants that could considerably distort absorbance measurements based on the reaction of glycolic acid with chromotropic acid in concentrated sulfuric acid. Therefore, excess sodium sulfite was added to the test solutions. After 15 to 20 minutes, the test aliquots were acidified with sulfuric acid and were evaporated to damp salts with mild heating. The residues obtained were dissolved in 0.4 mL of aqueous 5% chromotropic acid solution, mixed with 4 mL of concentrated sulfuric acid, and heated in a water bath for 15 to 20 minutes. The analytical test tubes were then put into cooled water, stopping the coloration reaction. The absorbances of the analytical test solutions were measured in the visible region of the spectrum relative to a blank solution. This procedure was performed each time with the same initial solutions only without the tested oxidant. The measured absorbances were used to determine the extent of glycolate decomposition.

3.0 Results and Discussion

Results of organic oxidation tests in alkaline media are presented for the five tested organic acid anions: EDTA, HEDTA, citrate, glycolate, and oxalate.

3.1 EDTA Decomposition

The EDTA anion is relatively stable in alkaline solution and is not destroyed by hydrolysis or oxidation with O_2. Consequently, strong oxidants such as H_2O_2, $S_2O_8^{2-}$, ClO^-, or BrO^- must be used to destroy this complexant.

3.1.1 Decomposition by H_2O_2

In 1 M NaOH, the potentials of the reactions

$$O_2 + H_2O + 2\ e^- \rightleftarrows HO_2^- + OH^- \qquad (3.1)$$

and

$$HO_2^- + H_2O + 2e^- \rightleftarrows 3\ OH^- \qquad (3.2)$$

are -0.065 V and +0.867 V, respectively (Bratsch 1989). Therefore, hydrogen peroxide can act either as a reductant or oxidant, depending on the other reactant. Reactions involving hydrogen peroxide in alkaline media also may be complicated by hydrogen peroxide self-decomposition through disproportionation.

In 0.5 to 5.0 M NaOH, 0.02 M EDTA was found not to decompose at 25 and 80°C during 48 and 5.5 hours, respectively. Studies on EDTA decomposition in reaction with H_2O_2 then were conducted in the presence of 5×10^{-4} M V(V), Mn(II), Fe(III), Co(II), Ni(II), Cu(II), Mo(VI), Bi(III), Pb(II), and $K_3Fe(CN)_6$. The results showed that EDTA did not decompose at 25°C in 48 hours or at 40°C in 5 hours, although H_2O_2 vigorously decomposed, evolving O_2. It may be concluded from these experiments that O_2 also does not oxidize EDTA in the presence of the listed catalysts.

Further experiments were performed at 80°C with stepwise addition of hydrogen peroxide solution. In these tests, a 0.2 mL aliquot of 1.1 M H_2O_2 was added to 10 mL of the heated EDTA solution. Twenty minutes after the addition, 0.5 mL of test solution was withdrawn for analysis. A final aliquot of H_2O_2 was added, the mixture given 40 minutes to react, and a 1 mL sample withdrawn for analysis. For tests with Co(II), a third and fourth step-addition of H_2O_2 and sampling were performed with 20-minutes' reaction for the first three steps and 40 minutes for the fourth step. Test results are presented in Table II.3.1.

Table II.3.1. Extent of 0.02 M EDTA Decomposition in the Presence of d-Elements with Stepwise Addition of H_2O_2 Solution

1 M NaOH; 80°C

Additive	[Additive], M	EDTA Decomposition, %				Total Time, Minutes
		1 Step	2 Step	3 Step	4 Step	
Co(II)	1×10^{-5}	2	2.5	3	3	100
Co(II)	1×10^{-4}	14	22	29	35	100
Ni(II)	1×10^{-4}	3	4	-	-	60
Cu(II)	1×10^{-4}	3	3	-	-	60
Fe(III)	1×10^{-4}	2.5	1	-	-	60
Cr(III)	1×10^{-4}	3	2	-	-	60
Mn(II)	1×10^{-4}	3	2	-	-	60

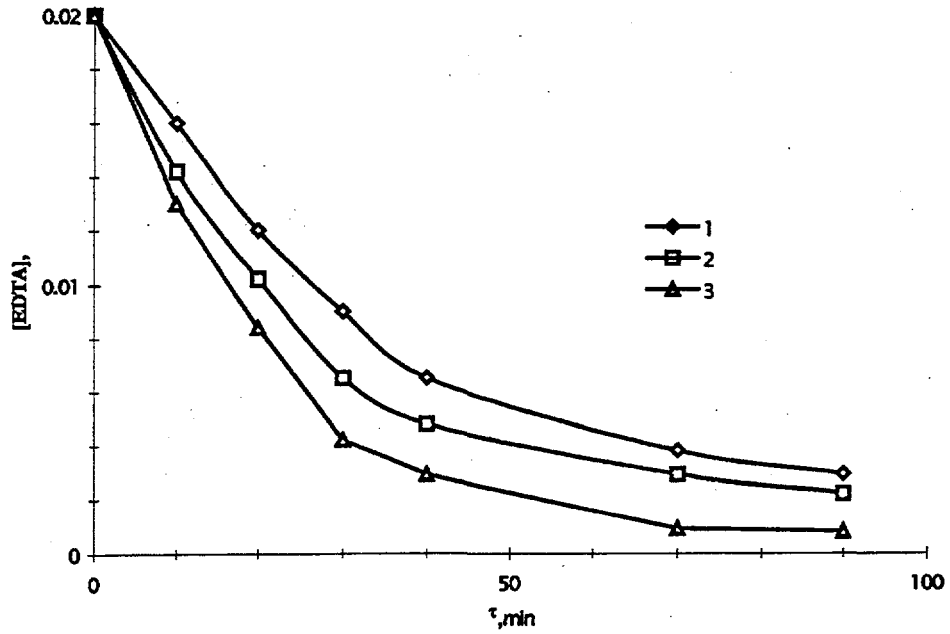
As shown in Table II.3.1, the only effective catalyst for EDTA decomposition is cobalt. Further studies with cobalt used another experimental method. In these tests, 0.2 mL aliquots of 1.1 M H_2O_2 were added every 10 minutes without sampling for analysis. Ten minutes following the last addition, a portion for analysis was withdrawn. A second portion was withdrawn for analysis 30 minutes after the last addition. Test results are given in Table II.3.2.

Table II.3.2. Extent of 0.02 M EDTA Decomposition in the Presence of Co(II) with Stepwise Addition of H_2O_2 Solution

[NaOH], M	[Co(II)], M	T,°C	Number of Additions	EDTA Decomposition, %		Total Time, Minutes
				10 Minutes	30 Minutes	
1.0	5×10^{-5}	60	4	4	5.5	100
1.0	1×10^{-4}	60	4	9	10	100
1.0	2×10^{-4}	60	4	14	16	100
1.0	2×10^{-4}	80	1	18	26	50
1.0	2×10^{-4}	80	2	25	40	70
1.0	2×10^{-4}	80	6	54	61	100
0.1	2×10^{-4}	80	4	95	95	70
0.25	2×10^{-4}	80	4	56	75	70
0.5	2×10^{-4}	80	4	41	52	70

These data show that decomposition increases as temperature increases from 60 to 80°C. At 80°C, increasing the number of H_2O_2 additions from one to six increased EDTA decomposition from 26% to 61%. Decomposition increased when NaOH concentration decreased to 0.1 M from 0.25 and 0.5 M.

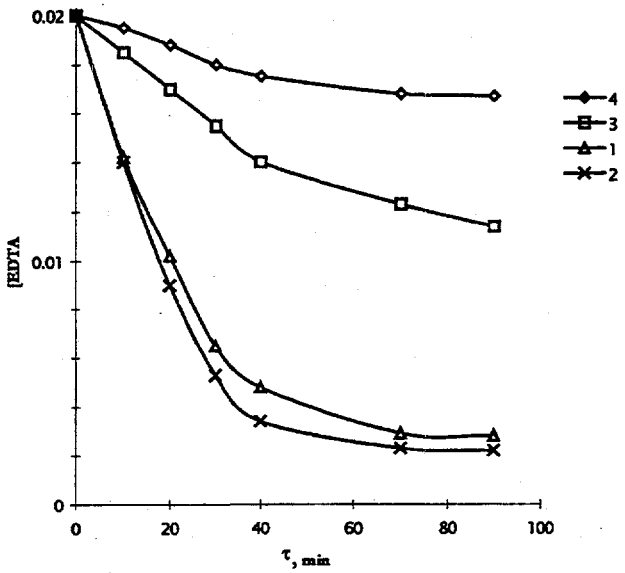
In another series of experiments, the influences of cobalt concentration (Figure II.3.1), NaOH concentration (Figure II.3.2), and temperature (Figure II.3.3) were studied. The H_2O_2 was added as 0.2 mL portions of 1.1 M solution at 0, 10, 20, 30, 40, and 70 minutes. The extent of decomposition increases with increasing cobalt concentration (from 1×10^{-4} to 4×10^{-4} M) and temperature (from 80 to 90°C) but decreases with NaOH concentration (from 1 to 6 M).



0.02 M EDTA (initial); 1 M NaOH; 80°C

[Co(II)], M: 1 - 1.0×10^{-4}, 2 - 2.0×10^{-4}, 3 - 4.0×10^{-4}

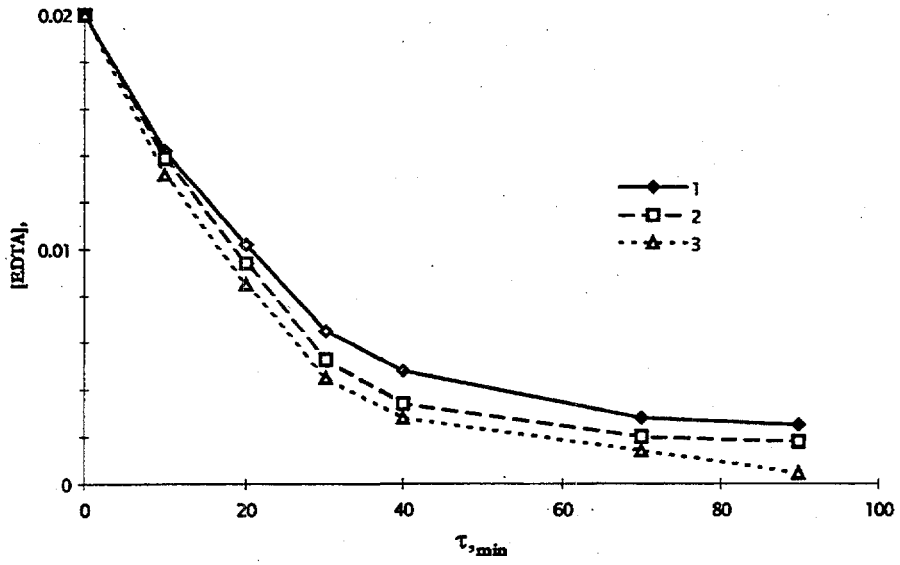
Figure II.3.1. EDTA Decomposition Kinetics by Stepwise Addition of H_2O_2 as a Function of Co(II) Concentration



0.02 M EDTA (initial); 2 x 10^{-4} M Co(II); 80°C

[NaOH], M: 1 - 1.0, 2 - 2.0, 3 - 4.0, 4 - 6.0

Figure II.3.2. EDTA Decomposition Kinetics by Stepwise Addition of H_2O_2 as a Function of NaOH Concentration



0.02 M EDTA (initial); 1 M NaOH; 2 x 10^{-4} M Co(II)

T,°C 1 - 80, 2 - 85, 3 - 90

Figure II.3.3. EDTA Decomposition Kinetics by Stepwise Addition of H_2O_2 as a Function of Temperature

The chemical mechanism probably includes the oxidation of Co(II) to Co(III) by H_2O_2, leading to the following sequence of reactions:

$$Co(OH)_2 + HO_2^- \rightarrow CoO(OH) \cdot H_2O + OH + OH^-$$

$$OH + OH^- \rightarrow O^- + H_2O$$

$$O^- + O_2 \rightarrow O_3^-$$

$$EDTA + O_3^- \rightarrow R + O_2 + OH^- \qquad (3.3)$$

Like ozonide (O_3^-), the Co(III) produced by peroxide oxidation also can oxidize the EDTA anion

$$EDTA + CoO(OH) \cdot H_2O \rightarrow Co(OH)_2 + H_2O + Products \qquad (3.4)$$

The following experiments were conducted to examine the participation of Co(III) compounds in EDTA oxidation. First, $Co(NH_3)_6Cl_3$ was added, to 0.02 M concentration, to a stock solution containing 1 M NaOH and 0.02 M EDTA. Simultaneously, in a second sample, $Co(NH_3)_6Co(CO_3)_3$, to 0.04 M total Co(III), was added to a similar NaOH/EDTA stock solution. Both samples were heated in a thermostat at 80°C for two hours. After heating, the EDTA concentrations in both solutions were determined. It was found that 26% of the initial EDTA was decomposed in both the first and second samples. Apparently, Co(III) compounds, produced by slow hydrolysis of $Co(NH_3)_6^{3+}$ in both tests, could oxidize EDTA. At the same time, rapid hydrolysis of $Co(CO_3)_3^{3-}$ in the second sample occurred. However, the Co(III) species formed in this reaction did not influence EDTA decomposition.

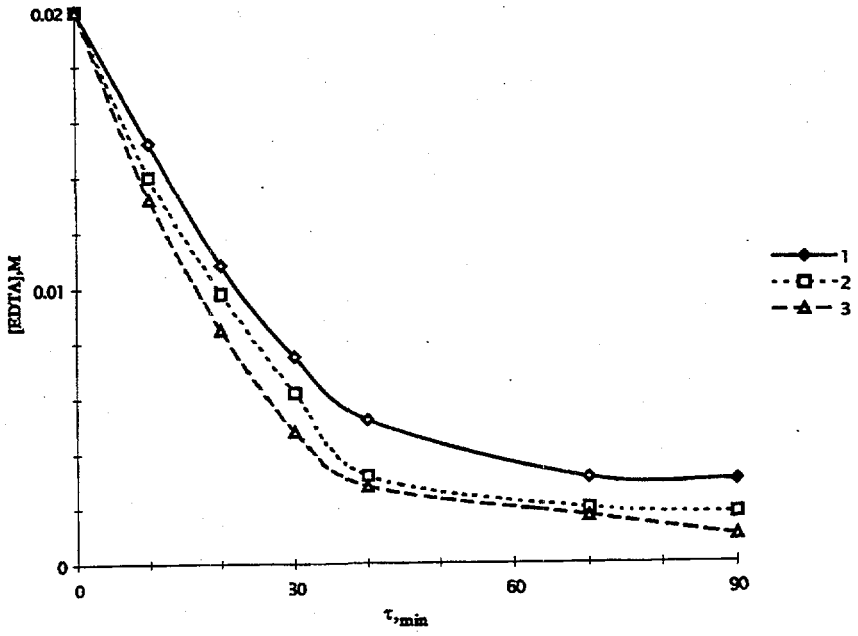
The effect of $NaNO_2$ on EDTA decomposition was studied by the stepwise addition of H_2O_2 to NaOH solutions containing cobalt compounds. Hydrogen peroxide was added in 0.2 mL aliquots of 1.1 M H_2O_2 at 0, 10, 20, 30, 40, and 70 minutes. The results are shown in Figure II.3.4. The extent of decomposition decreased only slightly in the presence of 0.1 M $NaNO_2$. Increasing $NaNO_2$ concentration to 1.0 M had practically no effect on EDTA decomposition.

3.1.2 Decomposition by $Na_2S_2O_8$

The standard potential for persulfate

$$S_2O_8^{2-} + 2\ e^- \rightleftarrows 2\ SO_4^{2-} \qquad (3.5)$$

is 2.01 V (Bratsch 1989). Under various conditions, persulfate can react with reductants either directly or after decomposition to SO_4^- radicals. The SO_4^- radicals oxidize water and hydroxide to OH radicals in alkaline solution. Alkali also causes the catalytic decomposition of persulfate.



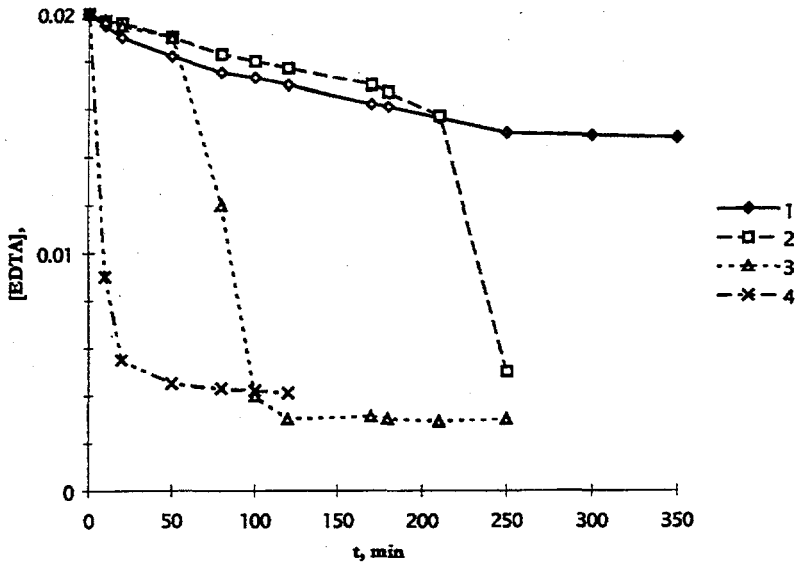
0.02 M EDTA (initial); 1 M NaOH; 2 x 10^{-4} M Co(II); 90°C

[$NaNO_2$], M: 1 - 0.1, 2 - 1.0, 3 - 0

Figure II.3.4. EDTA Decomposition Kinetics by Stepwise Addition of H_2O_2 as a Function of $NaNO_2$ Concentration

Studies of EDTA decomposition by reaction with persulfate were conducted in 0.5 to 5.0 M NaOH. Typical kinetic curves for this process are presented in Figures II.3.5, II.3.6, and II.3.7. It is apparent that EDTA decomposition in most cases does not begin immediately upon mixing the reactants, but only after an induction period. The induction period depends on the composition and temperature of the solution. The induction period decreases with increasing NaOH concentration and temperature. The induction period also decreases when the initial EDTA concentration is two times lower. After the induction period, EDTA decomposition proceeds with a moderate rate, not dependent on NaOH concentration.

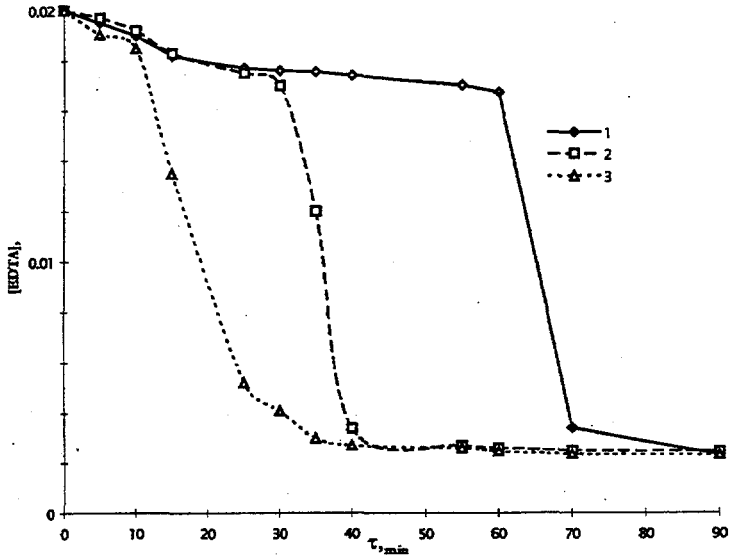
However, about 10% of the initial EDTA remained at the end of process because of insufficient oxidant. Therefore, experiments with 0.2 and 0.4 M $Na_2S_2O_8$ concentrations were performed. Under these conditions, the induction period decreased and no detectable EDTA remained. Kinetic curves of EDTA decomposition in solutions initially containing 0.4 M $Na_2S_2O_8$ and 0.02 M EDTA are shown in Figure II.3.8.



0.02 M EDTA (initial)

[NaOH], M: 1 - 0.5, 2 - 1.0, 3 - 2.0, 4 - 5.0

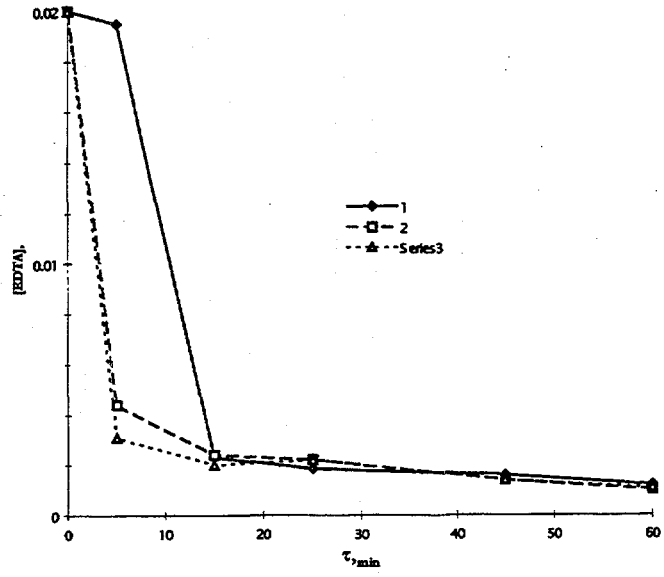
Figure II.3.5. EDTA Decomposition Kinetics by 0.1 M $S_2O_8^{2-}$ as a Function of NaOH Concentration at 25°C



0.02 M EDTA (initial)

[NaOH], M: 1 - 0.5, 2 - 1.0, 3 - 2.0

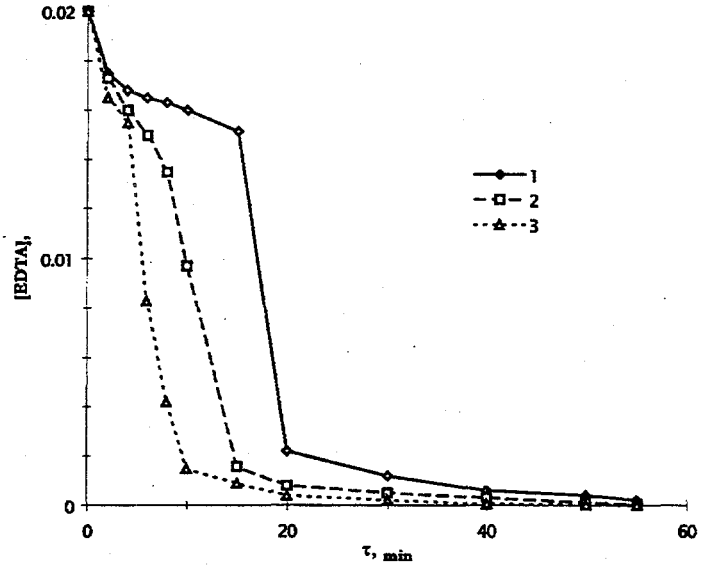
Figure II.3.6. EDTA Decomposition Kinetics by 0.1 M $S_2O_8^{2-}$ as a Function of NaOH Concentration at 40°C



0.02 M EDTA (initial)

[NaOH], M: 1 - 0.5, 2 - 1.0, 3 - 2.0

Figure II.3.7. EDTA Decomposition Kinetics by 0.1 M $S_2O_8^{2-}$ as a Function of NaOH Concentration at 60°C



0.02 M EDTA (initial)

[NaOH], M: 1 - 0.5, 2 - 1.0, 3 - 2.0

Figure II.3.8. EDTA Decomposition Kinetics by 0.4 M $S_2O_8^{2-}$ as a Function of NaOH Concentration at 34°C

Various candidate catalysts were studied in 0.5 to 2.0 M NaOH solution to decrease the induction time for EDTA decomposition. Compounds of V(V), Mn(II), Fe(III), Co(II), Ni(II), Cu(II), Mo(VI), Pd(II), Ag(I), Pb(II), Bi(III), and $K_4Fe(CN)_6$ with (1 to 5) x 10^{-4} M concentrations were tested. The test results are shown in Table II.3.3.

The observed induction period is because persulfate itself does not react with the EDTA anion at a measurable rate, but the sulfate radical (SO_4^-) does. Thermal dissociation of persulfate occurs with a low rate at 25°C. The rate constant (k) for the reaction

$$S_2O_8^{2-} \rightarrow 2\ SO_4^- \qquad (3.6)$$

Table II.3.3. Influence of Candidate Catalysts on the Induction Period of EDTA Decomposition by $S_2O_8^{2-}$ in Alkaline Solution

[NaOH], M	Additive	Induction Period, Minutes
0.5	--	>300
0.5	V(V)	>300
0.5	Mn(II)	>300
0.5	Ni(II)	>300
0.5	Cu(II)	>300
0.5	Fe(III)	>300
0.5	Pb(II)	>300
0.5	Pd(II)	270
0.5	Co(II)	250
0.5	Bi(III)	140
0.5	Mo(VI)	135
0.5	Ag(I)	<5
0.5	$Fe(CN)_6^{4-}$	0
1.0	--	200
1.0	Bi(III)	130
1.0	Ag(I)	0
1.0	$Fe(CN)_6^{4-}$	0
2.0	--	50
2.0	Ag(I)	0
2.0	$Fe(CN)_6^{4-}$	0

in 0.1 M NaOH at 50°C is 6 x 10^{-5} min^{-1} (Kolthoff and Miller 1951). With an activation energy of 33.5 kcal/mol (140 kJ/mol), the rate constant, k, at 25°C is 7.3 x $10^{-7}min^{-1}$. In 0.1 M $S_2O_8^{2-}$, the rate of SO_4^- formation is 1.46 x 10^{-7} M-min^{-1}.

Thus, Ag(I), Bi(III), $Fe(CN)_6^{4-}$ (Table II.3.3), and OH^- (Figures II.3.5, II.3.6, and II.3.7) accelerate the formation of oxidative radicals. The reaction is illustrated with $Fe(CN)_6^{4-}$.

The first step

$$Fe(CN)_6^{4-} + S_2O_8^{2-} \rightarrow Fe(CN)_6^{3-} + S_2O_8^{3-} \qquad (3.7)$$

is followed by the sequence

$$S_2O_8^{3-} + OH^- \rightarrow 2\ SO_4^{2-} + OH$$

$$OH + OH^- \rightarrow O^- + H_2O$$

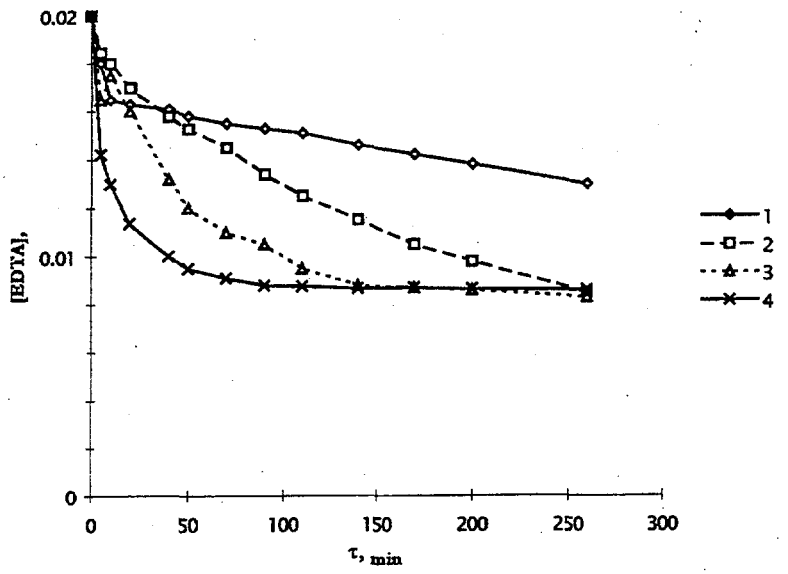
$$O^- + O_2 \rightarrow O_3^-$$

$$EDTA + O_3^- \rightarrow R_1 + O_2 + OH^-$$

$$Fe(CN)_6^{3-} + R_1 \rightarrow Fe(CN)_6^{4-} + R_2$$

$$S_2O_8^{2-} + R_1 \rightarrow S_2O_8^{3-} + R_3 \qquad (3.8)$$

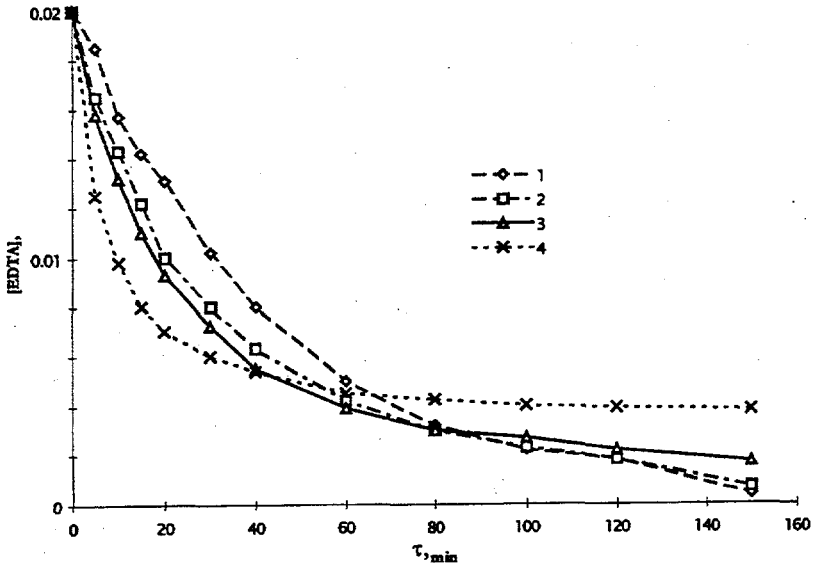
Nitrite can react with persulfate in alkaline solution and hinder the EDTA decomposition. Therefore, EDTA destruction was studied in solutions with various concentrations of $NaNO_2$. Kinetic curves for EDTA decomposition by persulfate in alkaline solution containing 0.5 M $NaNO_2$ are presented in Figure II.3.9. Induction periods were not observed in solutions containing 0.5 M $NaNO_2$; 60% EDTA decomposition is found in 1 to 5 M NaOH solutions containing 0.1 M $Na_2S_2O_8$. The extent of EDTA decomposition increases to 95%, 90%, and 80% by 0.4 M $Na_2S_2O_8$ in solutions containing 0.5 to 1.0, 2.0, and 5.0 M NaOH, respectively (Figure II.3.10).



0.02 M EDTA (initial); 25°C

[NaOH], M: 1 - 0.5, 2 - 1.0, 3 - 2.0, 4 - 5.0

Figure II.3.9. EDTA Decomposition Kinetics by 0.1 M $S_2O_8^{2-}$ in the Presence of 0.5 M $NaNO_2$ as a Function of NaOH Concentration



0.02 M EDTA (initial); 25°C

[NaOH], M: 1 - 0.5, 2 - 1.0, 3 - 2.0, 4 - 5.0

Figure II.3.10. EDTA Decomposition Kinetics by 0.4 M $S_2O_8^{2-}$ in the Presence of 0.5 M $NaNO_2$ as a Function of NaOH Concentration

Gas evolution as a result of reaction of EDTA with persulfate was studied at room temperature. No gas was obtained in 0.5 M NaOH containing 0.02 M EDTA, 0.2 M $Na_2S_2O_8$, and (5 to 10) x 10^{-4} M $K_4Fe(CN)_6$. About 5 mL gas per mmole EDTA decomposed formed in 5 M NaOH solution containing 0.02 M EDTA and 0.2 M $S_2O_8^{2-}$.

3.1.3 Decomposition by ClO^-

The formal oxidation potential for the reaction

$$ClO^- + H_2O + 2\ e^- \rightarrow Cl^- + 2\ OH^- \qquad (3.9)$$

is 0.89 V in 1 M NaOH (Bratsch 1989). Therefore, hypochlorite can oxidize EDTA. However, the process will be complicated by the disproportionation and decomposition of ClO^-.

The kinetics of EDTA decomposition by ClO^- were studied in 0.5 to 5.0 M NaOH at 30 to 60°C. At 30°C, EDTA decomposition at 90 minutes was 50 and 45%, respectively, in 0.5 and 5.0 M NaOH containing 0.02 M EDTA and 0.1 M KClO. No further reaction occurred after this time. Decomposition of EDTA after 90 minutes increased to 65 and 50%, respectively, for 0.5 and 5.0 M NaOH when KClO concentration increased to 0.18 M.

The extent of EDTA decomposition does not increase when temperature increases to 40 or 60°C because both ClO^- self-decomposition and the reaction of ClO^- with EDTA accelerate with increasing temperature. At 25°C, 65% EDTA decomposition was observed in 0.5 M NaOH containing 0.18 M KClO and 5 x 10^{-4} M $Ni(NO_3)_2$ or $Co(NO_3)_2$. Salts of Mn(II), V(V), Fe(III), Cu(II), Cr(III), Mo(VI) have no effect on EDTA decomposition by hypochlorite.

At 25°C, stepwise addition of oxidant to 0.5 M NaOH increases EDTA decomposition to 85%. The total time of the reaction was 75 minutes. Under otherwise similar conditions, 90% of the EDTA decomposes in 0.5 M NaOH containing Ni(II) or Co(II) and 85% decomposes with Mn(II) or Fe(III) present. The tested d-elements have no apparent catalytic effect on EDTA decomposition by hypochlorite.

3.1.4 Decomposition by BrO^-

The formal oxidation potential for the reaction

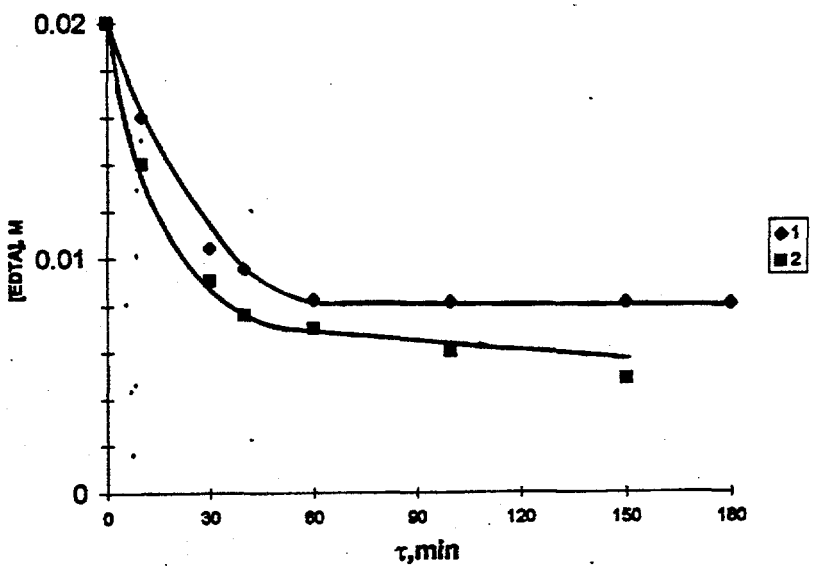
$$BrO^- + H_2O + 2\ e^- \rightarrow Br^- + 2\ OH^- \qquad (3.10)$$

is 0.76 V in 1 M NaOH (Bratsch 1989). Therefore, hypobromite, like hypochlorite, can oxidize and decompose EDTA in alkaline solution. However, the process will be complicated by decomposition of BrO^-.

The kinetics of EDTA decomposition by BrO^- were studied in 0.5 to 5.0 M NaOH. About 5% EDTA decomposition occurs after 5 hours' reaction in 0.5 M NaOH containing 0.02 M EDTA and 0.025 M KBrO at 25°C. Decomposition increases to 10% by increasing KBrO concentration to 0.1 M.

Increasing temperature increases EDTA decomposition. The reaction continued 20 to 30 minutes after the reactants were mixed. After 15 minutes at 40°C, EDTA decompositions are 15 and 10%, respectively, in 0.5 and 5.0 M NaOH containing 0.1 M KBrO. Rates of EDTA decomposition by BrO^- in alkaline media at 95°C are shown in Figure II.3.11. At 95°C, as well as at lower temperatures, the reaction continues with moderate rate for 30 to 40 minutes. Concurrent BrO^- decomposition reactions with EDTA and with other solution components apparently is occurring.

Addition of d-element salts increases the extent of EDTA decomposition by hypobromite. Thus, at 40°C in 0.5 M NaOH containing 0.02 M EDTA and 0.1 M KBrO, 15% of the EDTA decomposes in 15 minutes. In the presence of 5×10^{-4} M Mn(II), Fe(III), Co(II), Ni(II), or Cu(II), EDTA decomposition increases, respectively, to 25, 40, 60, 55, or 58%. At 40°C in 5 M NaOH containing 0.02 M EDTA, 0.1 M KBrO, and Ni(II), Co(II), or Cu(II), EDTA decomposition reaches 20 to 22% in 30 minutes.



0.02 M EDTA (initial); 95°C

[NaOH], M: 1 - 5.0
2 - 0.5

Figure II.3.11. EDTA Decomposition Kinetics by 0.2 M BrO^- as a Function of NaOH Concentration

3.2 HEDTA Decomposition

Studies of oxidative HEDTA decomposition were conducted in aqueous alkaline solutions by the same procedure as was used for EDTA studies. The unreacted oxidant was destroyed by a small excess of aqueous sodium sulfite. With $NaNO_2$ present, the unreacted oxidant and nitrite were removed by a small excess of hydrazinium nitrate solution. The HEDTA concentration was determined by complexometric titration with xylenol orange after the solutions' acidification to pH 1. Prior experiments showed that moderate amounts of sulfur dioxide or hydrazine do not appreciably affect HEDTA concentration determination by complexometric titration with xylenol orange.

3.2.1 Decomposition by H_2O_2

Hydrogen peroxide in alkaline solutions can react as an oxidant, especially in the presence of metal ions. As seen in Table II.3.4, only cobalt and copper demonstrated marked catalytic activity in HEDTA reaction with H_2O_2.

Light-brown and dark-brown precipitates, respectively, formed 5 to 10 minutes after mixing in solutions containing iron and manganese compounds. Homogeneous solutions of cobalt display a characteristic blue-violet color, probably because of formation of Co(III) HEDTA complexes.

Table II.3.4. HEDTA Decomposition in Alkaline Solutions Containing Metal Salts

0.037 M HEDTA; 0.15 M H_2O_2

[NaOH], M	Catalyst, 5 x 10^{-5} M	T,°C	t, hours	Decomposition, %
0.5	--	22	49	15
0.5	$Ni(NO_3)_2$	22	49	15
0.5	$FeCl_3$	22	49	15
0.5	$Cu(NO_3)_2$	22	49	62
0.5	$Co(NO_3)_2$	22	49	27
0.5	$MnCl_2$	22	49	6
0.28	--	80	2.5	9
0.28	$Co(NO_3)_2$	80	2.5	32
0.28	$FeCl_3$	80	2.5	8
0.28	$Ni(NO_3)_2$	80	2.5	15
0.28	$PbCl_2$	80	2.5	17

Further experiments were performed using stepwise addition of hydrogen peroxide. As shown in Table II.3.5, the most effective catalyst for HEDTA decomposition in strong alkali is cobalt(II). Again, cobalt in both valent states does not hydrolyze to form the corresponding hydroxides or hydrated oxides in NaOH solution.

The influence of NaOH concentration (4 and 0.91 M) on HEDTA decomposition by H_2O_2 was studied for solutions containing manganese, copper, lead, and palladium (compare Tables II.3.5 and II.3.6). In solutions containing $MnCl_2$, a brown precipitate forms in the first few minutes after mixing.

Stepwise addition of hydrogen peroxide to alkaline HEDTA solutions containing cobalt compounds destroys most of the HEDTA. Copper loses its catalytic effect at NaOH concentrations above 1 M. However, hydrogen peroxide quickly decomposes in solutions containing copper, cobalt, or iron, even at room temperature. Therefore, in subsequent experiments, hydrogen peroxide also was added in small portions.

Table II.3.5. Decomposition of 0.01 M HEDTA in 4 M NaOH by Stepwise 0.03 M H_2O_2 Additions with Catalysts at 80°C

H_2O_2 additions at 0, 30, 60, 90, and 120 minutes; solution heating ended at 150 minutes.

Catalyst, 5 x 10^{-4} M	HEDTA Decomposition, %					
	30 Min.	60 Min.	90 Min.	120 Min.	150 Min.	1440 Min.
$Co(NO_3)_2$	47	60	72	83	87	87
$Cu(NO_3)_2$	13	20	20	23	27	27
$Pb(NO_3)_2$	13	20	25	37	42	42
$PdCl_2$	17	23	32	37	42	--

Table II.3.6. Decomposition of 0.02 M HEDTA in 0.91 M NaOH by Stepwise 0.02 M H_2O_2 Additions with Catalysts at 80°C

H_2O_2 additions at 0, 30, 60, 90, and 120 minutes

Catalyst, 5 x 10^{-4} M	HEDTA Decomposition, %					
	30 Min.	60 Min.	90 Min.	120 Min.	180 Min.	240 Min.
$MnCl_2$	16	19	21	26	32	-
$Cu(NO_3)_2$	26	31	35	35	55	63
$Pb(NO_3)_2$	15	18	21	37	33	35
$PdCl_2$	18	23	24	39	32	35

Increasing temperature increases HEDTA decomposition but hydrogen peroxide is also decomposed more vigorously. With stepwise addition of hydrogen peroxide to alkaline HEDTA solution, approximately 85% of the starting compound was destroyed at 80°C. These results are given in Table II.3.7.

Hydrogen peroxide was added at 0, 30, 60, 90, and 120 minutes, after which heating was ended. As shown in Table II.3.7, in 0.55 to 2.7 M NaOH, cobalt compounds demonstrate catalytic activity at concentrations over 1×10^{-4} M.

The catalytic activity of copper(II) is comparable to that of cobalt at NaOH concentrations up to 1 M. Data illustrating this are shown in Table II.3.8.

Tests showed 1 M sodium nitrite hindered HEDTA decomposition. Reaction of HEDTA with Co(III) introduced as $Co(NH_3)_6Cl_3$ and $Co(NH_3)_6Co(CO_3)_3$ were studied in the same manner as was done for EDTA. First, a solution containing 1 M NaOH and 0.02 M HEDTA was prepared. To one portion of this solution, $Co(NH_3)_6Cl_3$ was added to 0.02 M. At the same time, $Co(NH_3)_6Co(CO_3)_3$ was added to a second portion of the NaOH/HEDTA solution to a 0.02 M concentration in $Co(NH_3)_6^{3+}$. Both samples were heated in a thermostatted bath for two hours. After heating, HEDTA concentrations in both solutions were determined. It was found that 65% of the HEDTA decomposed in both samples. Thus, cobalt(III) destroys HEDTA more extensively than EDTA under comparable conditions. Again, $Co(NH_3)_6^{3+}$ hydrolysis product is the active catalyst.

Table II.3.7. Decomposition of 0.02 M HEDTA in NaOH Solutions by Stepwise 0.03 M H_2O_2 Additions with Co(II) at 80°C

H_2O_2 additions at 0, 30, 60, 90, and 120 minutes

[NaOH], M	[Co(II)], M	HEDTA Decomposition, %				
		30 Min.	60 Min.	90 Min.	120 Min.	1440 Min.
0.9	0	13	--	23	28	--
0.9	5×10^{-5}	16	--	23	28	--
0.9	1.0×10^{-4}	15	19	27	33	33
0.9	2.0×10^{-4}	16	22	30	36	48
0.9	4.0×10^{-4}	23	31	37	47	50
0.7	2.0×10^{-3}	59	79	87	87	87
0.55	4.0×10^{-3}	70	82	87	87	87
2.7	0	11	15	19	22	--
2.7	5.0×10^{-4}	35	19	63	78	--
2.7	1.0×10^{-3}	51	19	77	89	--

Table II.3.8. Decomposition of 0.02 M HEDTA in NaOH Solutions by Stepwise 0.02 M H_2O_2 Additions with Co(II) or Cu(II) at 60°C

H_2O_2 additions at 0, 30, 60, 90, and 120 minutes

[NaOH],M	[Co(II)], M	[Cu(II)], M	HEDTA Decomposition, %				
			30 Min.	60 Min.	90 Min.	120 Min.	150 Min.
0.05	1.0×10^{-3}	--	62	72	76	89	89
0.05	--	1.0×10^{-3}	62	68	66	83	92
0.14	5.0×10^{-4}	--	14	28	31	45	59
0.14	1.0×10^{-3}	--	17	28	31	45	48
0.14	--	1.0×10^{-3}	14	28	34	45	59
0.73	2.0×10^{-3}	--	31	37	46	44	51
0.73	--	2.0×10^{-3}	31	39	59	64	74

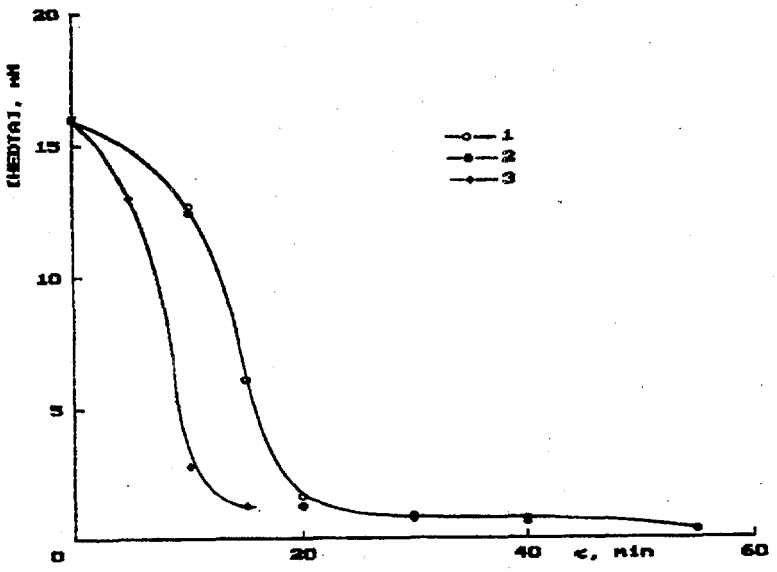
3.2.2 Decomposition by $S_2O_8^{2-}$

The most powerful and rapid oxidant tested was sodium persulfate. Almost complete decomposition of HEDTA was achieved in alkaline solution in the presence of a 20-fold molar excess of sodium persulfate. Even at room temperature, the oxidation was rapid and complete in less than 60 minutes. The decreases in HEDTA concentration with time for various concentrations of sodium persulfate and HEDTA are shown in Figures II.3.12 and II.3.13 for room temperature tests, and in Figure II.3.14 for tests at 60°C.

The data show that NaOH concentration in the range 0.91 to 1.83 M has no significant influence on the reaction rate. Decomposition sharply accelerates in more concentrated NaOH solutions. The effect of NaOH concentration on the process rate may be attributed to decreasing persulfate stability and increased dissociation of the HEDTA alcoholic hydroxyl group in more concentrated alkali. Complete loss of the complexing ability of 0.02 M HEDTA solutions is not achieved at $S_2O_8^{2-}$:HEDTA molar ratios of 5:1 even at 60°C (Figure II.3.14).

The complexing ability does not change in some cases during the initial 5 to 10 minutes. This phenomenon, and the incomplete loss of complexing ability even at five-fold molar excess of oxidant, probably occur because the primary oxidation product is also an aminocarboxylate with properties similar to those of the initial HEDTA. The complexometric titration analytical technique cannot distinguish related chelating agents. With further destruction of the primary product, the complexing abilities decrease, resulting in the observed concentration decrease.

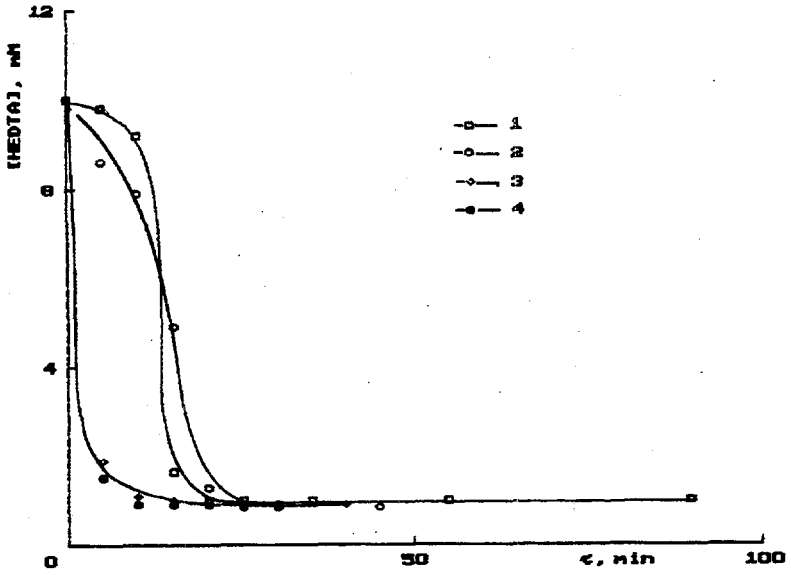
Sodium nitrite might be expected to consume oxidant. However, sodium nitrite in the reaction mixture does not markedly affect either the kinetics or the extent of HEDTA decomposition over the tested concentration range (Figure II.3.15). Evidently, sodium persulfate is a suitable reagent for oxidative decomposition of HEDTA in alkaline aqueous solution.



0.016 M HEDTA (initial)

[NaOH], M: 1 - 0.91, 2 - 1.83, 3 - 3.7

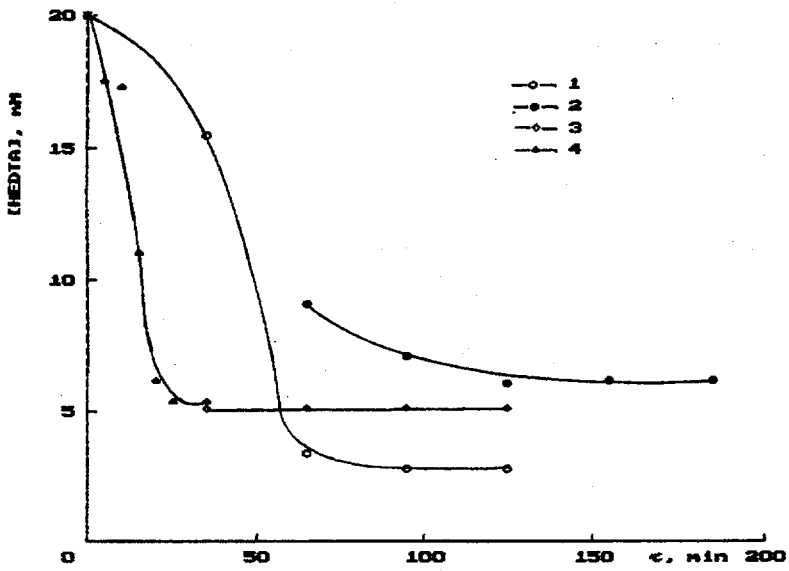
Figure II.3.12. HEDTA Decomposition Kinetics by 0.2 M $S_2O_8^{2-}$ as a Function of NaOH Concentration at 20°C



0.01 M HEDTA (initial)

[NaOH], M: 1 - 0.4, 2 - 0.4, 3 - 4.0, 4 - 5.1

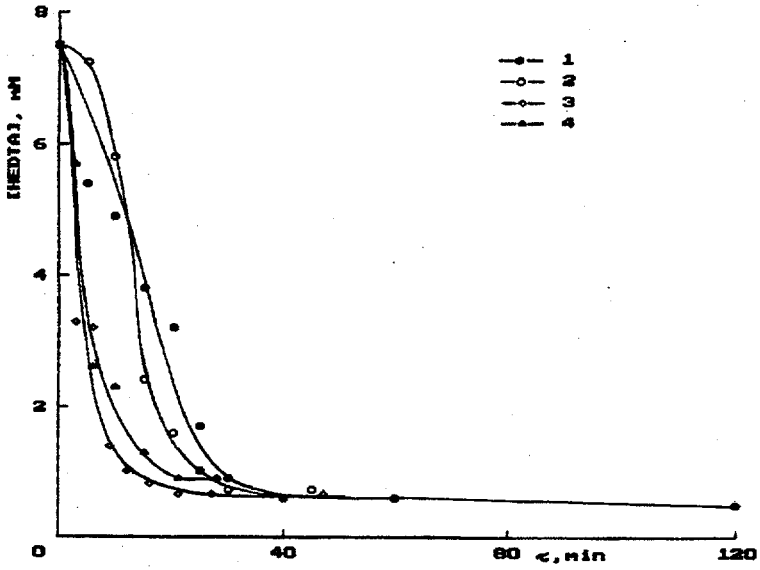
Figure II.3.13. HEDTA Decomposition Kinetics by 0.24 M $S_2O_8^{2-}$ as a Function of NaOH Concentration at 20°C



0.02 M HEDTA (initial)

[NaOH], M: 1 - 0.5, 2 - 0.91, 3 - 2.0, 4 - 5.0

Figure II.3.14. HEDTA Decomposition Kinetics by 0.1 M $S_2O_8^{2-}$ as a Function of NaOH Concentration at 60°C



0.0075 M HEDTA (initial)

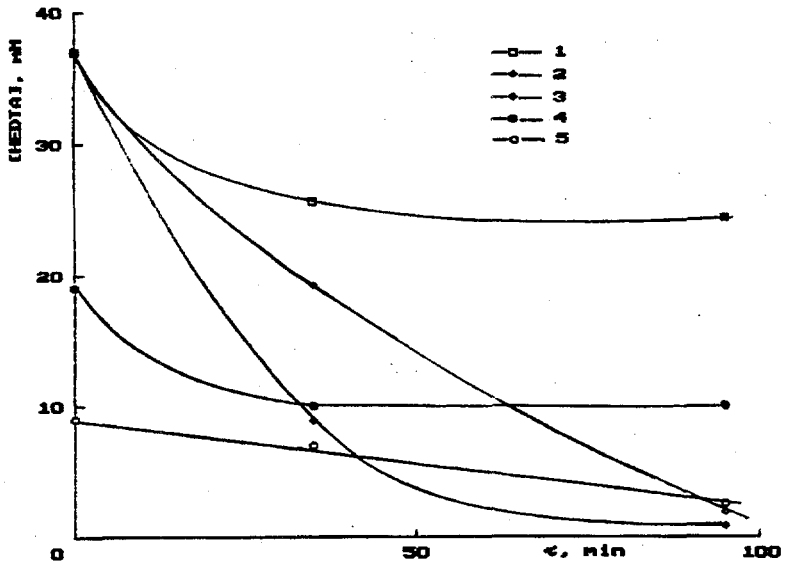
[NaOH]/[$NaNO_2$], M: 1 - 0.5/0, 2 - 0.5/1.0, 3 - 4.0/0, 4 - 4.0/1.0

Figure II.3.15. HEDTA Decomposition Kinetics by 0.25 M $S_2O_8^{2-}$ as a Function of NaOH and $NaNO_2$ Concentrations at 20°C

3.2.3 Decomposition by ClO^-

Another candidate oxidant for aminopolycarboxylate (e.g., EDTA, HEDTA) destruction in alkaline solution is hypochlorite. The dependencies of HEDTA concentration on time in 0.68 M NaOH solutions with various hypochlorite concentrations are shown in Figure II.3.16. The oxidative process is relatively slow at room temperature. Furthermore, more than 4-fold excess of oxidant is necessary to achieve full decomposition of the HEDTA.

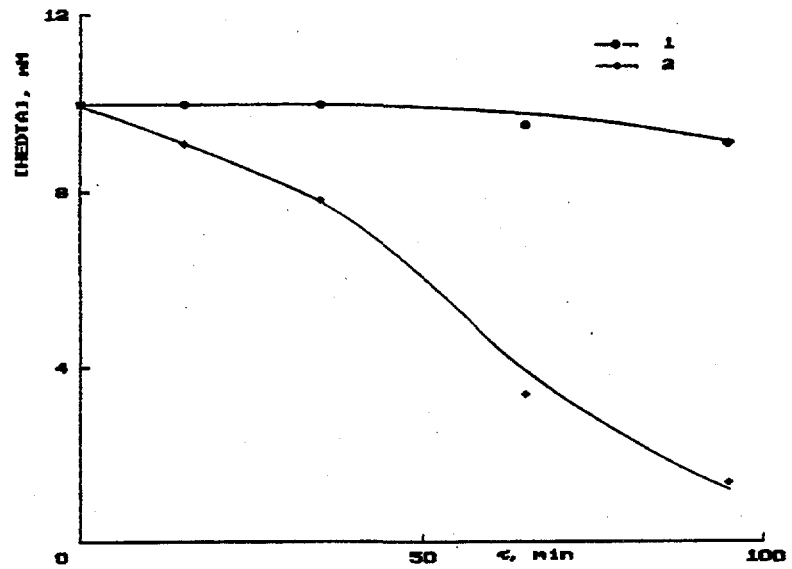
The reaction rate increased with increasing hypochlorite concentration (Figure II.3.16, curves 1, 2, and 3). The latter experiments had sufficient oxidant to achieve full HEDTA decomposition. Addition of sodium nitrite accelerates HEDTA decomposition in 0.5 to 1.0 M NaOH solutions (Figures II.3.17 and II.3.18) but decreases the rate in more concentrated NaOH solutions (Table II.3.9). In contrast, increasing NaOH concentration achieves more rapid and complete HEDTA decomposition in the absence of $NaNO_2$.



0.68 M NaOH

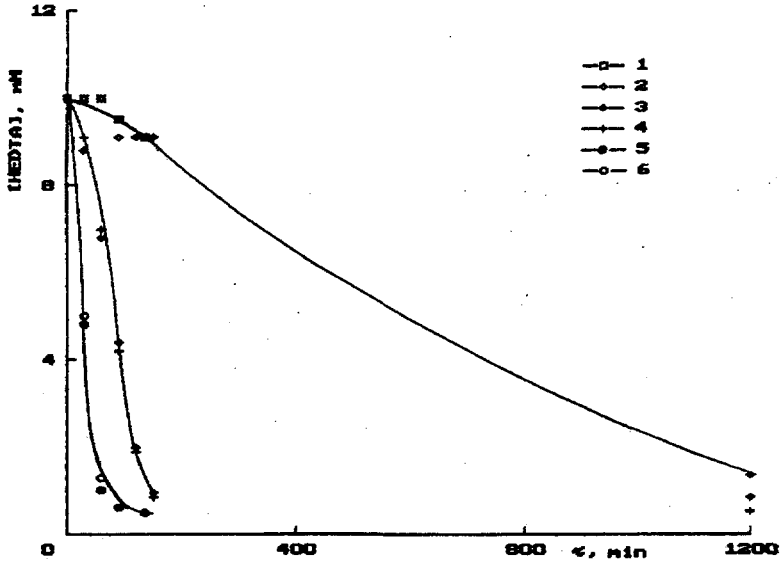
$[HEDTA]_0/[KClO]_0$, M: 1 - 0.037/0.089
2 - 0.037/0.178
3 - 0.037/0.356
4 - 0.019/0.089
5 - 0.009/0.089

Figure II.3.16. HEDTA Decomposition Kinetics by ClO^- as a Function of HEDTA and ClO^- Concentrations at 20°C



0.01 M HEDTA (initially); 0.36 M KClO; 0.5 M NaOH
$[NaNO_2]$, M: 1 - 0, 2 - 1.0

Figure II.3.17. HEDTA Decomposition Kinetics by ClO^- as a Function of $NaNO_2$ Concentration at 14°C



0.01 M HEDTA (initially); 0.36 M KClO; 0.5 M NaOH
$[NaNO_2]$, M: 1 - 0, 2 - 0, 3 - 0.5, 4 - 0.5, 5 - 1.0, 6 - 1.0

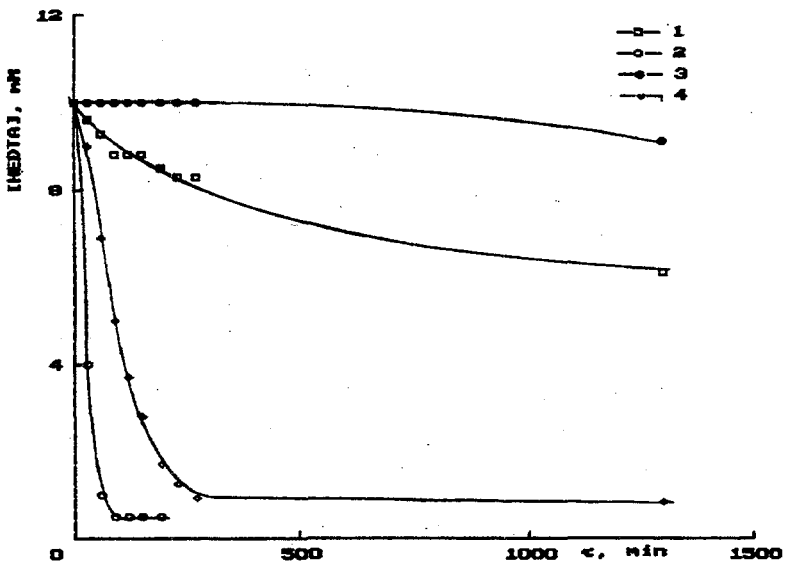
Figure II.3.18. HEDTA Decomposition Kinetics by ClO^- as a Function of $NaNO_2$ Concentration at 20°C

Table II.3.9. Decomposition of 0.01 M HEDTA by 0.36 M KClO as Functions of NaOH and $NaNO_2$ Concentrations at 14°C[(a)]

[NaOH], M	[$NaNO_2$], M	HEDTA Decomposition, %						
		30 Min.	60 Min.	90 Min.	130 Min.	170 Min.	200 Min.	1280 Min.
1	0	0	0	2	2	9	36	90
1	1.0	18	60	73	85	92.6	93.2	95.0
2	0	0	0	3	29	53	66	91.5
2	1.0	2	16	27	37	49	56	95.0
4	0	0	0	26	63	76	81	97
4	1.0	0	0	0	2	14	30	86

(a) Unreacted KClO and $NaNO_2$ were neutralized by N_2H_4.

Compounds of cobalt, iron, copper, lead, and palladium did not significantly affect the HEDTA and ClO^- reaction. Tests of HEDTA and EDTA oxidation under comparable conditions demonstrate HEDTA to be more easily decomposed (Figure II.3.19).



0.36 M KClO; 0.5 M NaOH; 20°C

[HEDTA]/[$NaNO_2$], M: 1 - 0.01/0, 2 - 0.01/1.0
[EDTA] / [$NaNO_2$], M: 3 - 0.01/0, 4 - 0.01/1.0

Figure II.3.19. EDTA and HEDTA Decomposition Kinetics by ClO^- as a Function of $NaNO_2$ Concentration

Excess unreacted hypochlorite was neutralized with aqueous solutions of hydrogen peroxide, sodium sulfite, or hydrazinium nitrate. Adding a slight excess of hydrogen peroxide (compared with KClO) causes intense gas evolution in tests with large residual amounts of unreacted KClO. The corresponding HEDTA decomposition rates found for solutions treated with hydrogen peroxide solutions are higher than those found for solutions treated with sodium sulfite (Table II.3.10). Solutions treated with hydrazinium nitrate gave results comparable to those found for sodium sulfite.

Table II.3.10. Effect of Reductive Neutralizers of Excess Hypochlorite on HEDTA Decomposition

0.01 M HEDTA and 0.19 M KClO initially; 0.5 M NaOH

$[NaNO_2]$, M	Neutralizer	HEDTA Decomposition, %			
		10 Min.	40 Min.	80 Min.	1200 Min.
0	Na_2SO_3	5	10	10	92
1	Na_2SO_3	20	81	92	98
0	H_2O_2	12	26	21	95
1	H_2O_2	93	96	98	99

The reaction between hydrogen peroxide and hypochlorite in alkaline media is known to generate singlet oxygen, an effective and powerful oxidant. This may account for the somewhat increased observed decomposition.

3.3 Citrate Decomposition

Citrate is stable in alkaline solution. It is not decomposed by reaction with oxygen or hydrolyzed by reaction with hydroxide. Persulfate and hydrogen peroxide were tested as possible oxidants to decompose citrate.

3.3.1 Decomposition by H_2O_2

It was found that 0.1 M H_2O_2 does not decompose 0.1 M citrate in 0.5 to 5.0 M NaOH at 20 and 95°C in 24 and 1.5 hours, respectively. Further tests on the decomposition of citrate in 2 M NaOH have been performed with 5 x 10^{-5} to 2 x 10^{-4} M Cr(III), Mn(II), Fe(III), Co(II), Ni(II), and Cu(II) and stepwise addition of H_2O_2. No decomposition of citrate was observed after 1.5 hours of treatment at 80°C for any tested conditions.

3.3.2 Decomposition by $S_2O_8^{2-}$

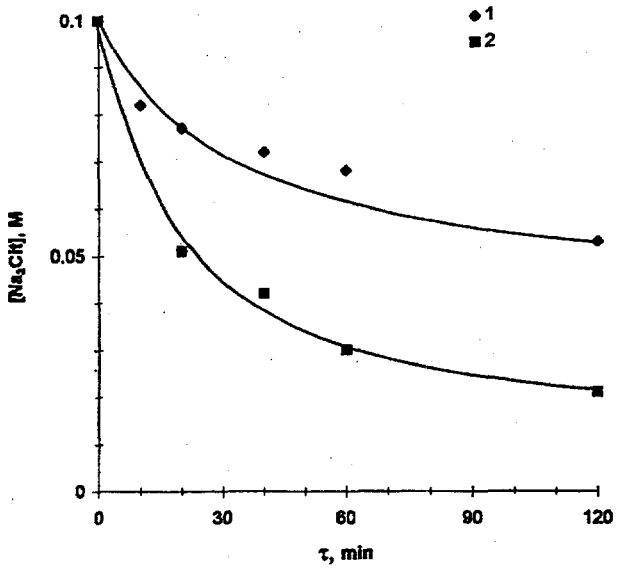
Citrate is decomposed by persulfate. At 25°C and 4 hours, 0.1 M citrate treated with 0.35 M sodium persulfate decreased 31 and 43% in 1 and 4 M NaOH, respectively. After 72 hours, citrate concentrations decreased to 43 and 74%, respectively. Increasing alkali concentration increases citrate decomposition by persulfate.

Increasing temperature to 40 and 80°C accelerates citrate decomposition, as shown by comparing Figures II.3.20 and II.3.21. At 80°C, complete decomposition occurs in less than 1 hour. At 40°C, the addition of 5 x 10^{-4} M $AgNO_3$, or especially $Co(NO_3)_2$, accelerates decomposition, allowing the process to occur at moderate temperature (Figure II.3.22, compared with Figure II.3.20).

Nitrite hinders citrate decomposition. About 80% decomposition of 0.1 M citrate in 1 to 4 M NaOH containing 0.1 M $NaNO_2$ occurs at 80°C one hour after addition of 0.4 M persulfate. Increasing $NaNO_2$ concentration decreases the extent of citrate decomposition.

3.4 Glycolate Decomposition

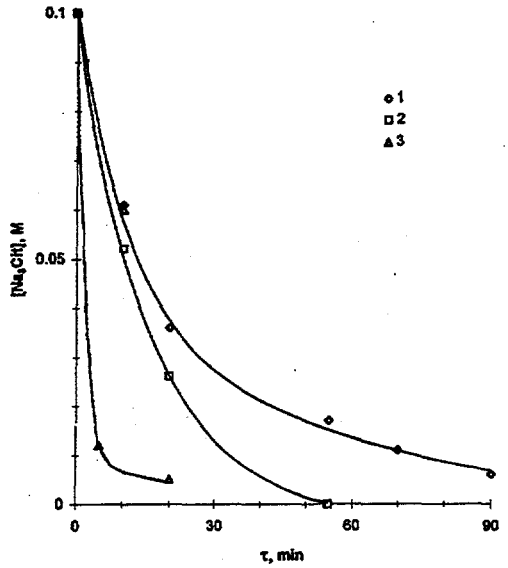
Glycolate decomposition studies were complicated because oxidant or reductant residues in the tests interfere with the reaction of glycolic and chromotropic acids in concentrated sulfuric acid and distort analytical optical absorbance measurements. As described previously, interferences were minimized by using sulfite, measuring standard solutions, and by thermal (cold) quenching of the development of the colorimetric reaction. Despite quenching, optical absorbance continued to increase in sulfuric acid for at least 1.5 hours at the glycolic acid concentrations used. It was found, however, that absorbance values were proportional to the initial glycolic acid concentrations at various color development times (Table II.3.11). Reliable measurements were obtained by carefully controlling color development times and measuring appropriate standard solutions.



0.1 M citrate (initially)

[NaOH], M: 1 - 1.0, 2 - 4.0

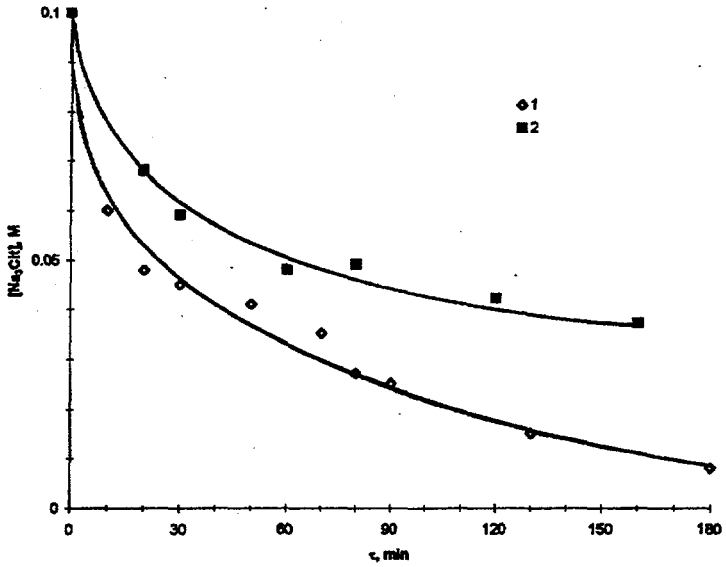
Figure II.3.20. Citrate Decomposition Kinetics by 0.4 M $S_2O_8^{2-}$ as a Function of NaOH Concentration at 40°C



0.1 M citrate (initially)

[NaOH], M: 1 - 0.5, 2 - 1.0, 3 - 4.0

Figure II.3.21. Citrate Decomposition Kinetics by 0.4 M $S_2O_8^{2-}$ as a Function of NaOH Concentration at 80°C



0.1 M citrate (initially); 1.0 M NaOH; 40°C

1 - 5 x 10^{-4} M Ag(I), 2 - 5 x 10^{-4} M Co(II)

Figure II.3.22. Citrate Decomposition Kinetics by 0.4 M $S_2O_8^{2-}$ as a Function of Catalysts

Table II.3.11. Optical Absorbance of Standard Samples after Glycolic Acid Reaction with Chromotropic Acid

[Glycolate], M	Absorbance		
	30 Min.	60 Min.	90 Min.
1.0×10^{-2}	0.44	0.77	1.10
5.0×10^{-3}	0.24	0.33	0.49
2.5×10^{-3}	0.10	0.15	0.23
1.25×10^{-3}	0.053	--	--

3.4.1 Decomposition by H_2O_2

Data obtained in tests of alkaline solutions containing various concentrations of glycolate and hydrogen peroxide are shown in Table II.3.12.

Brown precipitates formed in a few minutes in alkaline solutions containing glycolate, hydrogen peroxide, and cobalt compounds. The corresponding supernatant solutions were colorless.

As shown in Table II.3.12, glycolate decomposition by peroxide occurs in alkaline solution at higher temperatures. However, self-decomposition of peroxide occurs more rapidly under the experimental conditions.

Table II.3.12. Decomposition of 0.01 M Glycolate in 0.91 M NaOH by H_2O_2

$[H_2O_2]$, M	$[Co(NO_3)_2]$, M	T,°C	Time, Hours	Decomposition, %
1.83	0	87	1.5	52[a]
1.83	0	90	1.5	29
0.9	0	90	1.5	18
1.83	0	90	3.0	29[b]
0.9	0	90	3.0	18[b]
0.9	5×10^{-4}	90	1.0	21
0.9	5×10^{-4}	90	1.0	30[c]
After heating, solutions were kept. (a) 96, (b) 16, and (c) 30 hours at room temperature.				

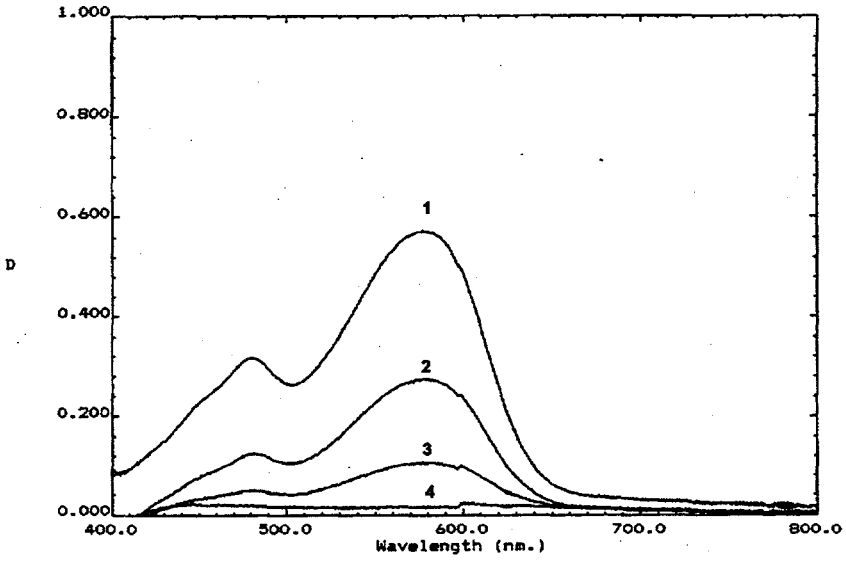
3.4.2 Decomposition by $S_2O_8^{2-}$

Reaction of glycolate with persulfate occurs at an appreciable rate at room temperature in alkaline solution. In Figure II.3.23 are given spectra obtained for tests containing various initial concentrations of sodium persulfate. The dependence of glycolate concentration on time in 1.83 M NaOH and various $Na_2S_2O_8$ concentrations is shown in Figure II.3.24. The rate clearly increases with increasing $Na_2S_2O_8$ concentration.

Complete decomposition of 0.01 M glycolate ultimately was reached in 0.1 to 0.4 M $Na_2S_2O_8$. However, the reaction required more than 50 hours at room temperature even when 40-fold molar excess of oxidant was used. In 3.6 M NaOH containing 0.01 M glycolate and 0.4 M sodium persulfate, 50% of the glycolate remained through 24 hours, similar to the results found in 1.83 M NaOH solutions (Figure II.3.24). In 90°C solution containing 0.01 M glycolate, 0.2 M persulfate, and 0.91 or 1.83 M NaOH, 95 and 92 % of the glycolate decomposed, respectively. These results show that persulfate may be used for oxidative destruction of glycolate in alkaline solutions.

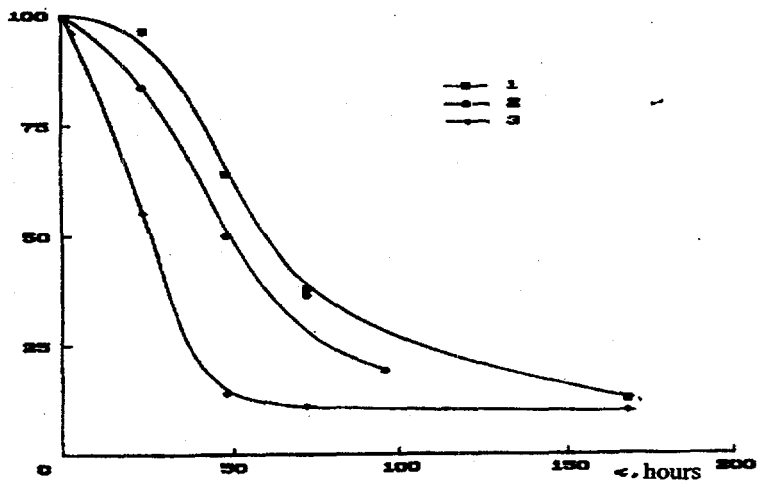
3.5 Oxalate Decomposition

Oxalate is stable in alkaline media and is not oxidized by atmospheric oxygen or decomposed by alkaline hydrolysis. Strong oxidants are required to destroy oxalate.



0.01 M glycolate (initially); 1.83 M NaOH; 20°C
$[S_2O_8^{2-}]$, M: 1 - 0, 2 - 0.1, 3 - 0.2, 4 - 0.4

Figure II.3.23. Chromotropic Acid Absorption Spectra Monitoring Glycolate Decomposition by $S_2O_8^{2-}$ as a Function of $S_2O_8^{2-}$ Concentration



0.01 M glycolate (initially); 1.83 M NaOH; 20°C
$[S_2O_8^{2-}]$, M: 1 - 0.1, 2 - 0.2, 3 - 0.4

Figure II.3.24. Glycolate Decomposition Kinetics by $S_2O_8^{2-}$ as a Function of $S_2O_8^{2-}$ Concentration

In experiments at 80 to 95°C, stepwise hydrogen peroxide additions were made to 0.5 to 5.0 M NaOH containing 0.05 M $K_2C_2O_4$ and 5 x 10^{-4} M $Co(NO_3)_2$. Oxalate was found not to decompose under such conditions.

In other experiments at 80°C, similar stepwise additions of KClO solution were made to 0.5 to 5.0 M NaOH solution containing 0.05 M $K_2C_2O_4$ and 5 x 10^{-4} M $Co(NO_3)_2$, $Ni(NO_3)_2$, or $Cu(NO_3)_2$. Again, no oxalate decomposition occurred.

The reaction of oxalate with persulfate,

$$C_2O_4^{2-} + S_2O_8^{2-} + 4\ OH^- \rightarrow 2\ SO_4^{2-} + 2\ CO_3^{2-} + 2\ H_2O \qquad (3.11)$$

requires heating, as shown in Table II.3.13. Salts of d-elements have only a small effect on oxalate decomposition. The data are given in Table II.3.14.

Increasing initial persulfate concentration to 0.2 M increases the extent of oxalate oxidation. Following 2 hours of reaction at 90°C, the initial 0.05 M oxalate concentration decreased 65 and 32%, respectively, in 0.5 and 5.0 NaOH. Again, concurrent decomposition reactions of persulfate seem to be occurring. Therefore, stepwise addition of $Na_2S_2O_8$ solution to test solutions was investigated for 0.05 M oxalate in 0.5 M NaOH at 90°C. The $Na_2S_2O_8$ was added in three portions over a one-hour interval to give a total added $Na_2S_2O_8$ concentration of 0.3 M. Complete decomposition of oxalate occurred in four hours.

Table II.3.13. Decomposition of 0.05 M Oxalate by 0.1 M $S_2O_8^{2-}$ at 90°C

[NaOH], M	Oxalate Decomposition, %		
	30 Min.	120 Min.	200 Min.
0.5	12	33	38
1.0	10	18	25
2.0	10	12	20
3.0	2 - 3	8	18
5.0	3 - 4	13	15

Table II.3.14. Effect of d-Element Salts at 5 x 10^{-4} M on 0.05 M Oxalate Decomposition by 0.1 M $S_2O_8^{2-}$ in 0.5 M NaOH at 90°C

Additive	Oxalate Decomposition, %		
	30 Min.	105 Min.	215 Min.
Co(II)	13	38	40
Ni(II)	15	40	45
Cu(II)	14	36	42
Ag(II)	16	30	38

Part III. Conclusions

Summary of the Results

This report presents results of an experimental research program conducted as part of a special agreement between the U.S. Department of Energy (DOE) and the Institute of Physical Chemistry of the Russian Academy of Sciences. The agreement is concerned with the problem of processing high-level radioactive waste at DOE defense material production facilities. Radioactive wastes include alkaline solutions and sludges of complex composition that have accumulated at the Hanford Site from processing irradiated nuclear materials. The wastes contain high concentrations of NaOH, $NaNO_3$, $NaNO_2$, organic complexants, uranium fission products, and the long-lived isotopes of neptunium, plutonium, and americium (Delegard et al. 1994).

Coprecipitation of transuranium elements with carriers generated homogeneously in alkaline solution by the Method of Appearing Reagents is a possible approach to decontaminate radioactive alkaline waste solutions. However, it was shown that neptunium(V) coprecipitation is poor in alkaline solution through coprecipitation by this technique. Recently, further experiments on neptunium removal by coprecipitation showed that reduction of neptunium to its tetravalent oxidation state substantially increases the efficiency of removal of neptunium (Bessonov et al. 1997).

A number of reductants have been tested, and it was shown that hydrazine nitrate and sodium formate in the presence palladium with heating reduce neptunium to the tetravalent state. The extent of reduction of 2×10^{-4} M Np(V) by 0.02 M vanadyl sulfate at 80°C is 98% in 1 M NaOH and 15 to 20% in 5 M NaOH. In all cases, however, nearly 98% of the initial neptunium was found in the precipitate. Thus, V(IV) acts as reductant and carrier simultaneously.

The organic complexants EDTA, HEDTA, citrate, and glycolate hinder the decontamination of alkaline solutions of neptunium and plutonium by coprecipitation with d-element hydroxides (Bessonov et al. 1997). Decomposition of the complexants before TRU removal from waste solutions would enhance decontamination. It was found that EDTA and HEDTA may be decomposed in alkaline solution by H_2O_2 in the presence of cobalt salts with heating and also by KClO and $Na_2S_2O_8$ under moderate temperatures. Citrate, glycolate, and oxalate are decomposed by $Na_2S_2O_8$ with heating. The amount of oxidant required is increased if $NaNO_2$ is also present in solution.

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