THE REDUCTION OF QUADRAVALENT CERIUM AT A NICKEL ANODE DURING ELECTROLYSIS

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THE [illegible] OF [illegible] WITH [illegible]
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ABSTRACT

The phenomenon of the reduction of cerium (IV) in a buffered nickel sulfate solution occurring at a nickel anode when current is flowing, as well as when it is not, was investigated. Samples of the solution were analyzed periodically for cerium (IV) during the course of the reduction. A method of analysis designed to detect and measure trace amounts of quadrivalent cerium in a nickel sulfate solution and distinguish it from trivalent cerium was developed. This method was based upon the colorimetric method of determination of hexavalent chromium which utilizes the color developed upon adding diphenyl-carbizide.

Cerium (IV) was found to be reduced in the presence of a nickel anode when a current was flowing as well as when it was not. The rate of reduction was increased by increasing the acidity of the solution and by using nickel containing graphite.

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Introduction

Previous investigations in this laboratory have shown that during electrolysis, i.e., the electrodeposition of nickel from a "Watt's Bath", the ferric and chromate salts were reduced to the lower valent forms in the anode compartment where oxidation normally occurs. The "Watt's Solution" used consisted of 300 g/l of $NiSO_4 \cdot 7H_2O$, 45 g/l of $NiCl_2 \cdot 6H_2O$ and 30 g/l of Boric Acid. Reduction of the iron (III) ions to the iron (II) ions was reported by L. Pyenson (1). Later, John T. Werner (2) reported the reduction of hexavalent chromium to the trivalent form. Prior to these investigations in this laboratory, Pierson (3) reported having used a diaphragm to separate the anolyte from the catholyte to show that electrolytic reduction took place at the anode. Brenner (4,5,6) maintained that a chemical process, rather than electrolytic reduction, occurred. This process was considered to be independent of the electrolysis, and did not necessarily occur at the anode surface. A number of examples of apparent anodic reduction referred to by Franklin (7) were explained as being due to secondary reactions. Stevenson (8) expressed the view that secondary reactions occurred as a result of normal oxidation products which were formed at the anode. This view was supported by Hinchley (9). In the observed case of the apparent reduction of chromium (VI) and manganese (VII) at a platinum anode, his explanation was that F_2O_2 was formed which

acted as a reducing agent in the acid solutions where the reduction occurred. Bancroft (10) then stated that there was no basis for explaining the anodic reactions by assuming the intermediate formation of H_2O_2. No general agreement for the cause of this apparent anomaly was shown. Therefore it was desirable to determine whether this effect was peculiar to iron, chromium and manganese, or if it also applied to other multivalent salts, and to define some of the factors governing the reaction.

To accomplish this, cerium was chosen where the reduction from cerium (IV) to cerium (III) could be followed. This was done both with and without current flowing. No method for the determination of cerium was found which would detect it in trace amounts and distinguish between the respective oxidation states. However, a method was developed based on the colorimetric method for determining hexavalent chromium which utilizes the color developed upon adding diphenylcarbizide (11).

EXPERIMENTAL

The electrolytic cell used consisted of a beaker containing the electrolyte, a porous cup to separate the anode compartment (inside) from the cathode compartment (outside), mineral anode, a cathode of low carbon steel and a motor driven stirrer. A cooling finger was used to maintain a constant temperature, both electrolytic and cast nickel containing graphite were used respectively for the anodes. A "Watt's Solution" was used for the electrolyte. A Beckman pH meter was used for acidity measurements. The Klett Summerson Colorimeter was utilized for the analytical work. Reagents used were diphenylcarbazide, chromic acid, ferrous sulfate, sulfuric acid, nitric acid, ethyl alcohol and ceric sulfate. All of the reagents were of C. P. grade.

EXPERIMENT I

A "Watt's Solution" was made in a fairly large quantity to serve as a stock solution throughout the experiment. Ceric sulfate was dissolved in a dilute sulfuric acid solution and then added to a portion of the stock ("watt's") nickel solution. This solution, hereinafter referred to with respect to ceric sulfate, was used as a source of cerium (IV) for each successive run.

The rate of reduction of cerium (IV) by electrolytic nickel was measured by dipping an electrode with a surface area of twelve square inches (77.4 sq. cm.) into 600 ml. of the nickel solution after adjusting the pH and the cerium (IV) concentration to the desired values. This was allowed to stand, with continuous stirring, until the reduction of cerium (IV) was complete or until the reaction ceased. Sulfuric acid was added periodically to counteract a slow rise in pH. At various intervals, small samples were removed and analyzed. The amount of cerium (IV) remaining was then plotted against the time, as shown in Figure 1. The rate of reduction was determined from the slope of the curve. This process was repeated with solutions at different pH levels. The rate of reduction was then plotted against the pH, as shown in Figure 5.

To determine the effect of ions in polarization, such as that encountered in electrolytic nickel operations, on the rate of reduction

of cerium (IV), a special cell was used. A 500 ml. porous cup containing 350 ml. of anolyte was used to separate the latter from the catholyte. The anode was placed in the center, while a cylindrical cathode made from sheet iron was placed around it (outside the porous cup) to insure uniform current density at the anode. A motor stirrer provided continuous agitation of the anolyte and a cooling finger was used to maintain a temperature approximately that of the room. A current of 6.6 amperes was passed giving a current density at the anode of 8.6 amp./dm.^{2} (80 amp./ft.^{2}), corresponding to that used in normal plating conditions. As before, various pH levels were used and the rate of reduction of the cerium (IV) determined accordingly.

Anodes of cast nickel were used in another series, both with and without current, to determine the effect on the reduction of the cerium (IV) caused by the presence of the added carbon or graphite which is used to promote anode corrosion in commercial plating. A very slow rise in pH tended to occur in the absence of current, while a definite drop occurred when current was passed. Again sulfuric acid was used to depress the rise in pH, while the drop, though not prevented was recorded, as shown in Table IV.

The determination of cerium (IV) was accomplished by adding a measured amount of ferrous sulfate solution (in excess) to the sample being analyzed. After acidifying with sulfuric acid and mixing to complete the reaction, a measured amount of solution containing hexavalent chromium was added in excess. Finally, the characteristic color for

[illegible] chromium was developed by the addition of diphenylcarbazide. The density was then measured on a Klett Summerson colorimeter. A blank was run in which no carbon was present. The difference in readings represented the carbon (C) present in the sample. Preliminary work showed a linear relationship to exist over the range of concentrations used.

TABLE I

ADSORPTION OF CARBON (IV) ON ACTIVATED CHARCOAL

Time (hours)	Carbon (IV) in Solution, (mg.)					
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
0.00	55	49	50	52	47	48
0.25		49	48	49	43	47
0.50	39	32	41	40	40	47
0.75	31	26				
1.00	28	21	36	40	37	47
1.50	14	11	24	31		
1.75					22	
2.00	11	6	20	33		
2.25					33	
2.50	9	3	25	30		
2.75					28	
3.00	6	1	23			

TABLE II

EXTRACTION OF CHROMIUM (IV) BY [illegible] FROM
[illegible] (Conc. of D2EHPA 0.6 mol/l)

Time (hours)	Chromium (IV) in Solution, (mg.)				
	pH 1.5	pH 2.0	pH 2.3	pH 3.0	pH 4.1
0.00	125	73	119	96	118
0.25	108	72	106		
0.50	69	63	102	68	115
0.75		53		78	
1.00	60	45	83		110
1.50	42	33	74	79	
2.00	19		60	65	
2.25		14			
2.50	0		51	57	
3.00			31		
3.25		3			
3.50			20		
4.00			11		

TABLE III

[illegible]

Time (hours)	Cerium (IV) in Solution, (mg.)							
	pH 1.0	pH 2.4	pH 2.7	pH 4.9	pH 5.0	pH 5.5	pH 5.7	pH 5.8
0.00	114	73	75	[illegible]	[illegible]	63	[illegible]	27
0.25	[illegible]	[illegible]	[illegible]					
0.50	91	[illegible]	[illegible]	[illegible]	67		[illegible]	17
1.00	72	[illegible]	[illegible]	[illegible]		62	[illegible]	27
1.50					69			
2.00	[illegible]	32	[illegible]	[illegible]		[illegible]		17
2.50	[illegible]				77			
3.00	[illegible]	22	24	[illegible]		[illegible]		
4.00	16	14	15			[illegible]		
5.00	8	8	10					
5.50					[illegible]			
6.00		5						
8.00	4	1	2					27

TABLE IV

[illegible] OF CARBON (II) BY [illegible]
[illegible]

Time (hours)	I		II		III	
	MG.	pH	MG.	pH	MG.	pH
[illegible]	[illegible]2	3.0	[illegible]	1.8	[illegible]	5.9
0.25			9[illegible]			
0.50	31	2.8	[illegible]	2.5	99	
0.75	19	2.7	[illegible]			
1.00	0	2.6	19	2.[illegible]	51	5.[illegible]
1.25			29			
1.50			12			
1.75			0			
2.00					60	
2.50						5.3
3.00					32	
3.25					20	5.0
3.50					13	4.9
3.75					0	

TABLE V

EFFECT OF pH AND ANIONIC SURFACTANT CONCENTRATION ON THE RATE OF OXIDATION OF CHROMIUM (III) BY POTASSIUM PERMANGANATE
Concentration (1.0 x 10⁻³ mol/dm³)

pH	Rate of Oxidation of Cr(III), (mol/dm³/hr)	
	Myristyltrimethyl	Tetradecyl
1.8	33	40
2.0		31
2.3	25	22
2.6	15	
3.0		13
3.4	9	
4.1	5	6
5.2	0	

TABLE VI

EFFECT OF pH AND [illegible] UPON THE RATE OF
REDUCTION OF CERIUM (IV) [illegible]
[illegible]

pH	Rate of Reduction of Cerium (IV), (mg./hr.)	
	Nonpolarized	Polarized
1.9	30	
2.4	21	
2.5		47
2.7	10	
2.9		42
4.9	6	
5.0	5	40
5.3		35
5.5	2	
5.7	0.75	29
5.8	0	
5.9		6

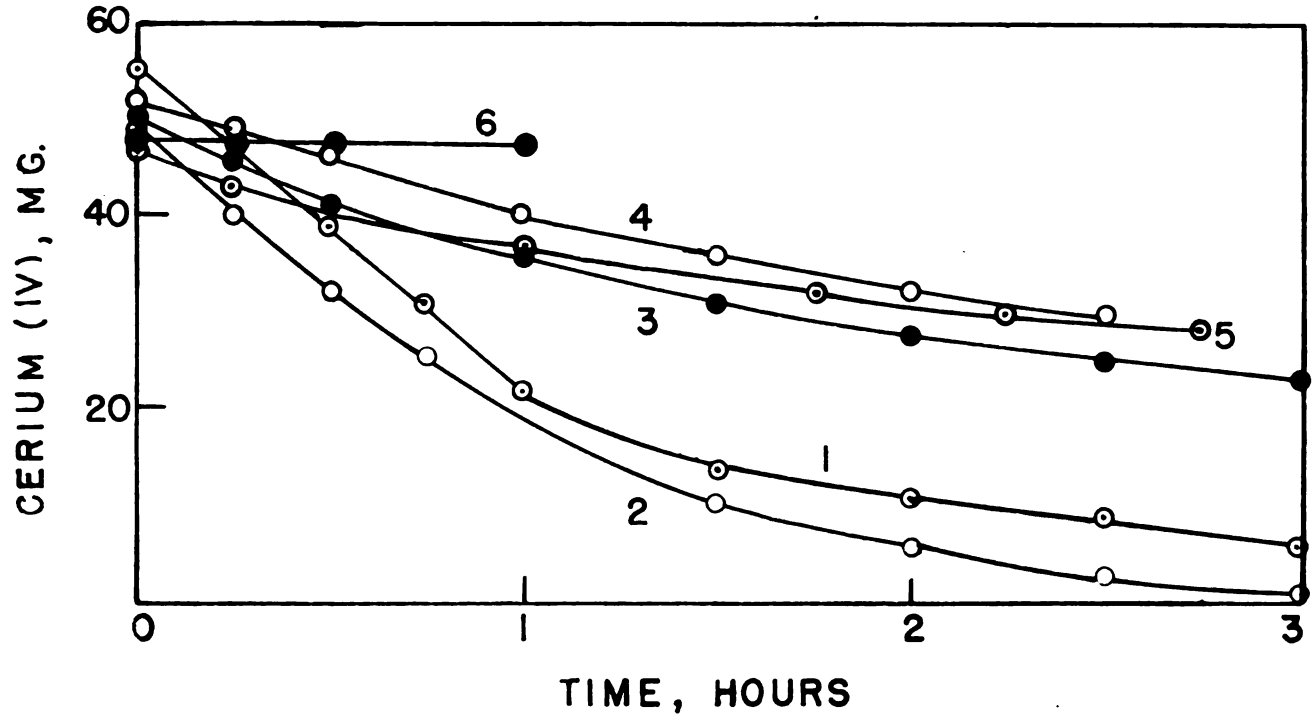

FIG. 1. EFFECT OF pH ON THE REDUCTION OF CERIUM (IV) BY ELECTROLYTIC NICKEL

1. pH 1.5	2. pH 2.3	3. pH 2.8
4. pH 3.4	5. pH 4.1	6. pH 5.1

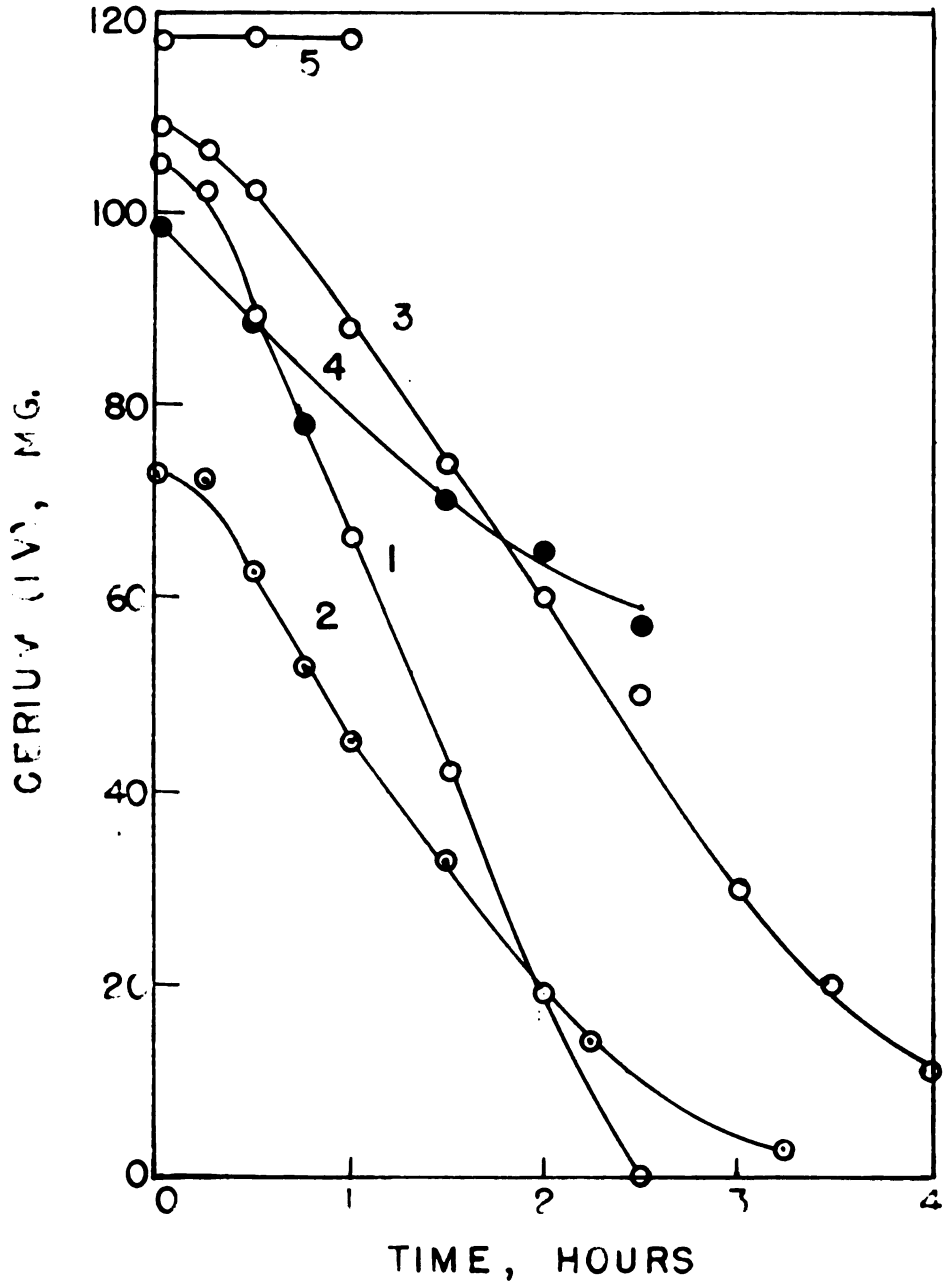

FIG. 2. EFFECT OF pH ON THE REDUCTION OF CERIUM (IV) BY ANODICALLY POLARIZED (C.D. 8.6 AMP./DM.^{2}) ELECTROLYTIC NICKEL.

1. pH 1.5 2. pH 2.0 3. pH 2.3
4. pH 3.4 5. pH 4.1

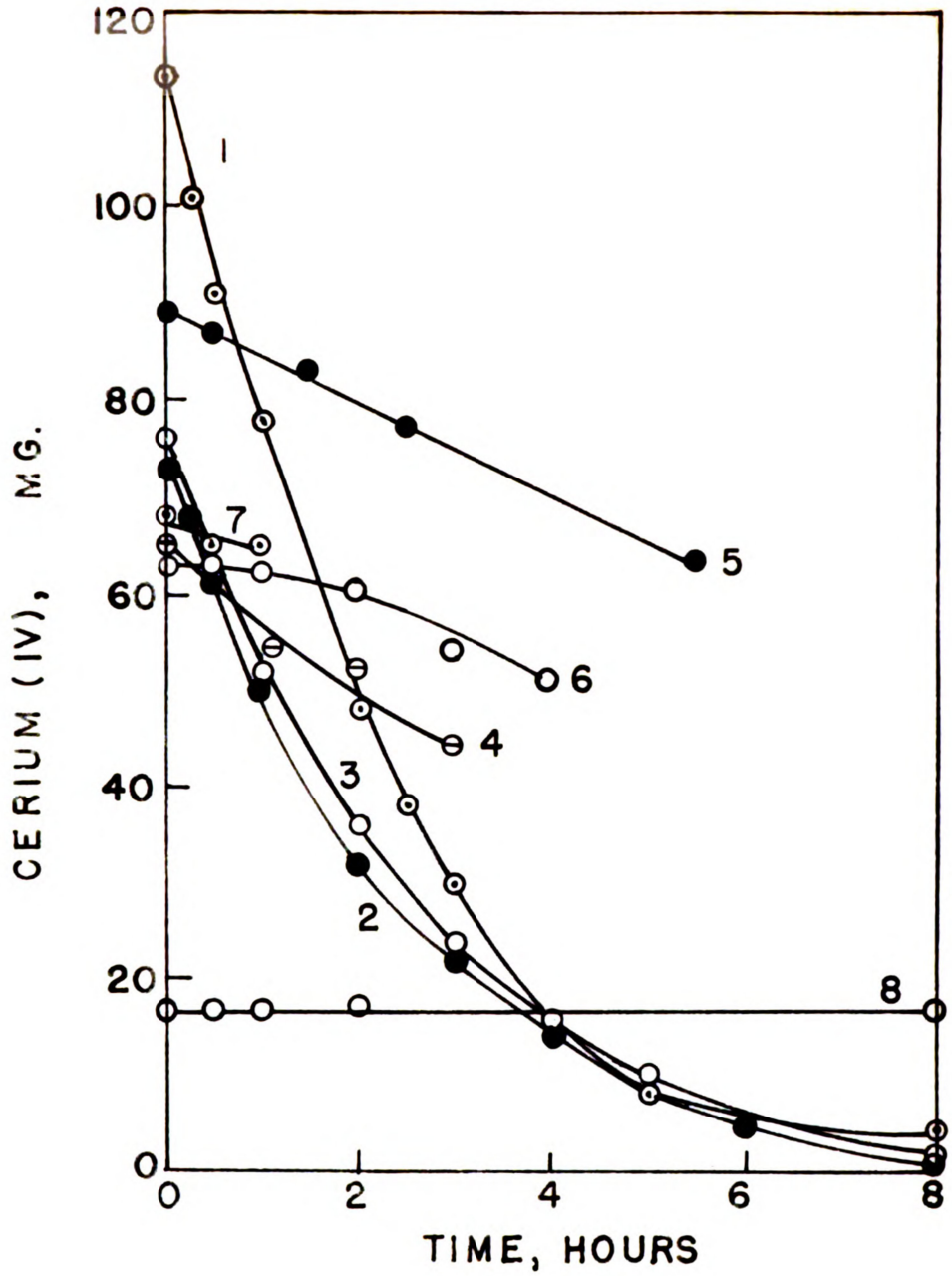

FIG. 3. EFFECT OF pH ON THE REDUC — TION OF CERIUM (IV) BY CAST NICKEL.

1. pH 1.0 2. pH 2.4 3. pH 2.7
4. pH 4.9 5. pH 5.0 6. pH 5.5
7. pH 5.7 8. pH 5.8

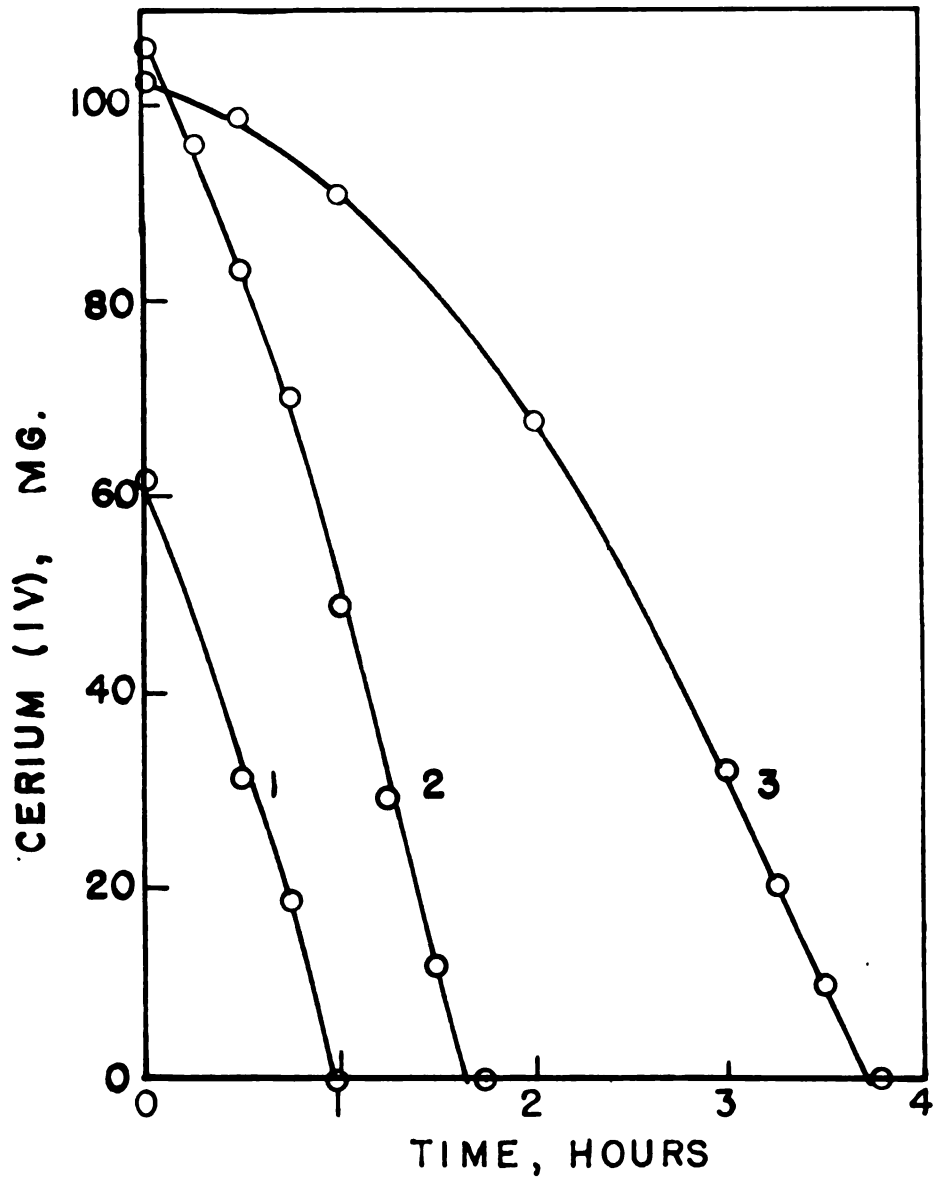

FIG. 4. EFFECT OF pH ON THE REDUCTION OF CERIUM(IV) BY ANODICALLY POLARIZED (C.D. 8.6 AMP./DM.^{2}) CAST NICKEL

1. pH RANGE GIVEN IN TABLE IV, SERIES I
2. pH RANGE GIVEN IN TABLE IV, SERIES II
3. pH RANGE GIVEN IN TABLE IV, SERIES III

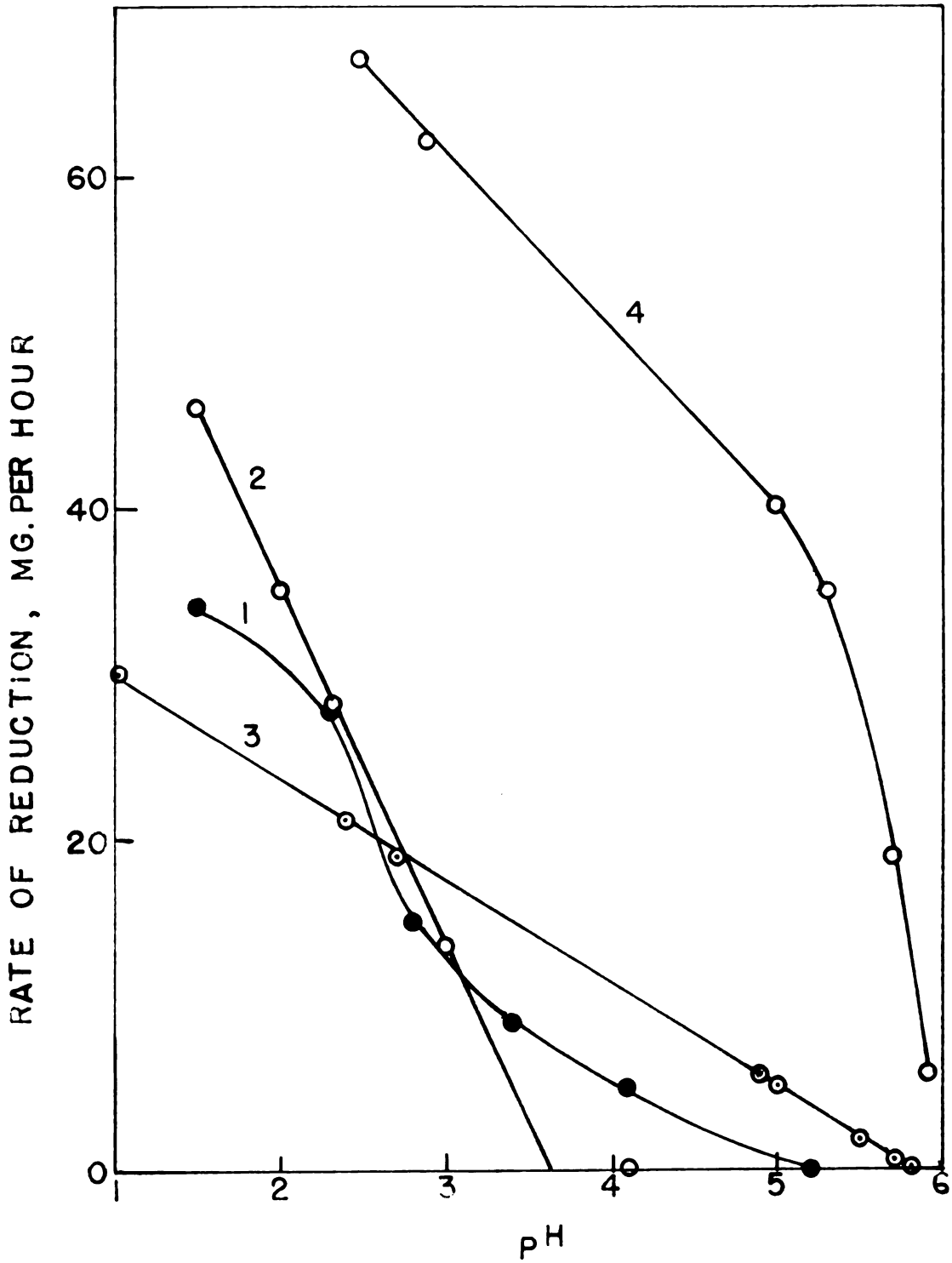

FIG. 5. EFFECT OF pH AND ANODIC POLARIZATION (C.D. 8.6 AMP./DM.^{2}) UPON THE RATE OF REDUCTION OF CERIUM (IV) BY ELECTROLYTIC AND CAST NICKEL.

1. ELECTROLYTIC NICKEL 2. POLARIZED ELECTROLYTIC NICKEL 3. CAST NICKEL 4. POLARIZED CAST NICKEL

DISCUSSION

The reduction of oxygen (O) was definitely shown to occur at a nickel anode when current was flowing as well as when it was not. In all cases, the rate of reduction was found to increase when the solution became more acid. As the acidity was lowered, the rate of reduction decreased until a point was reached where it ceased, except in the case of the cast nickel containing graphite where a maximum pH of 5.9 was obtained. It can be seen from the plot of the rate of reduction against the pH in Figure 5, that at a slightly higher pH, the reduction would be expected to cease in this case as well.

Although the increase in the rate of reduction with increase in acidity was common to all cases tested, other differences were noted. Over the acidity range from a pH of about 2.2 to 3.2, the rate of reduction in the presence of electrolytic nickel was the same both with and without current. At higher pH values, however, the effect of anode polarization reduced the rate, as expected, when the current was flowing. Reduction ceased at a much lower pH level (pH of 3.7 obtained by extrapolation) than it did when the electrode was not polarized (pH of 5.2). The fact that the rate of reduction in the presence of the unpolarized electrode increased less rapidly with increased acidity until finally it fell below that which occurred in the presence of the polarized electrode may be explained by the fact that in the former

case a steady rise in pH occurred during the course of the reaction. Although this was slow, and was repressed by the periodic addition of sulfuric acid, the local effect at its origin, i.e., the surface of the electrode, would be of sufficient magnitude to have an appreciable deleterious effect on the reduction.

When an inert impurity, such as graphite, is added to the nickel, the activity would be expected to be lowered, perhaps by a dilution effect or decrease in active surface area. This was actually found to occur in the case of the cast nickel electrode up to a pH of 2.7. At this point the rate of reduction was equal to that of the electrolytic nickel, both with and without current. At higher values of pH, the rate was greater than those for electrolytic nickel. This appeared to be due to the decreased retardation effect caused by the slow rise in pH during the course of the reaction, which was much less than that previously described. The activity range is thus extended up to a pH of 5.7.

The anodic polarization of the cast nickel electrode containing graphite produced a striking contrast to that of the electrolytic nickel electrode. A very marked increase in the rate of reduction of the cerium (IV) was noted. An active surface, maintained by the efficient anode corrosion enhanced by the graphite, undoubtedly contributed to this increased activity. A more startling effect was that of the rapid drop in pH during the course of the reaction. This was reflected in the progressively increasing rates of descent of the curves

in Figure 4. Whereas the previously mentioned alkaline condition generated at the surface of the electrode may have had a retarding effect on the reduction, this acid condition here described was shown to have a profound accelerating effect. Although at the highest pH studied (5.2) there was still an appreciable amount of reduction, the plot of the curve of the rate of reduction versus the pH indicates that reduction would cease at a slightly higher value. This is probably limited by the nature of the reaction. As would be expected, this phenomenally rising rate of reduction with increasing acidity begins off at the lower pH values where the pH gradient in the electrolyte between the electrode surface and the interior of the electrolyte decreases.

The principle involved in the analytical method used for the determination of cerium (IV) are quite straight forward. In the colorimetric determination of bivalent cerium, which distinguishes it from the lower valent form as well as from other ions which might be present, the specific color developed in the presence of diphenylcarbazide was utilized. To adapt this method to the determination of quadrivalent cerium in the presence of trivalent cerium, an equivalent amount of lower valent cerium was used to develop the color. This was done in the following manner. A measured amount of ferrous sulfate was added to the sample containing cerium (IV). This was reduced to cerium (III) while the ferrous ions were in turn oxidized to the ferric state. A measured amount of hexavalent chromium was then added. The resulting ferric ions, which were also in excess, then removed a portion of the

hexavalent chromium. A blank was run in which no cerium (IV) was present. As none of the ferrous ions were oxidized by cerium (IV), a corresponding equivalent of hexavalent chromium was retained. Taking into consideration the difference in valence change in going from the hexavalent to the trivalent state of chromium and the quadrivalent to the trivalent state of cerium, the difference in the chromium determination of the sample containing cerium and that containing the blank solution then represents the equivalent amount of cerium (IV). These reactions are represented by the following equations:

(1) $3[yCe\ (IV) + (y-xm)Fe\ (II) \rightarrow yCe\ (III) + yFe(III) + (xm)Fe\ (II)]$

(2) $3(xm)Fe\ (II) + (y-xm)Cr\ (VI) \rightarrow 3(xm)Fe\ (III) + (xm)Cr\ (III) + (y-xm)Cr\ (VI)$

(3) (Blank) $3(y-xm)Fe\ (II) + (y-xm)Cr\ (VI) \rightarrow 3(y-xm)Fe\ (III) + (y-xm)Cr\ (III) + (y-xm)Cr\ (VI)$

From this, it follows that:

(4) $yCe\ (IV)$ = $Cr\ (VI)_{[Ce\ (IV)\ sample]} - Cr\ (VI)_{[blank]}$

(1) Cerium (IV) was found to be reduced in the presence of pure electrolytic nickel electrodes even when anodically polarized.

(2) The presence of graphite in cast nickel, which had only a negligible effect on the unpolarized electrode, greatly increased the reducing activity of the anodically polarized electrode.

(3) Reduction of cerium (IV) in the presence of nickel electrodes, both polarized and unpolarized, and with or without graphite, was favored by acidic conditions.

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