THE DISTRIBUTION OF METAL IMPURITIES IN ELECTROLYTIC NICKEL DEPOSITS

By

Harlan Vance Ogle

A THESIS

Submitted to the School of Graduate Studies of Michigan State College of Agriculture and Applied Science in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

Department of Chemistry

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THESIS ABSTRACT

Iso-current density curves on an "inclined cathode" are illustrated for several current density regions. Spectrographic methods were used in the analyses for the metal impurities. The concentration distribution of aluminum, boron, cadmium, calcium, cobalt, copper, iron, lead, magnesium, manganese, silicon, and zinc in electrolytic nickel deposits as influenced by current density, pH, chloride content, some organic constituents, and the efficiency of nickel deposition is reported. General trends of the deposition rates for the impurities and of the relative energy efficiencies for impurity depositions are discussed.

ACKNOWLEDGMENTS

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INTRODUCTION

It is practically impossible to obtain and maintain an aqueous solution containing only one electro-depositable metal. Blum and Hogaboom (1) have concluded from studies of the effects of impurities in plating solutions that small concentrations may significantly affect the deposition of other metals, whether codeposited or not. DuMond and Cohen (2) have stated that differing results for the exact value of the Faraday might possibly be traced in certain instances to "inclusions" of electrolyte in the deposit coating. It is also known that trace and small amounts of impurities in an electrodeposit of nickel affect, sometimes to a marked degree, the chemical and physical properties of this deposit (1,3,4,5,6,7). Thus a study of the effect of various factors on the deposit concentration of metal impurities present in electroplating solutions is important to those who desire to know more concerning the fundamentals involved in electrodeposition as well as to those who wish to obtain electrodeposits with certain chemical and physical properties.

There are summarized in Table 1 some of the published results regarding the effect certain factors have on the concentration of an impurity in the electrodeposit. This table lists fourteen of the impurities found in electrolytic nickel deposits, and shows how the deposit concentration of some of these impurities varies with an increase

in the solution concentration of the impurity, or the current density, or the pH.

In general, studies of impurity depositions from nickel plating solutions have been confined to one impurity rather than a mixture of impurities as was done in this research.

Spectrochemical analysis is useful for quantitatively determining the concentration of several metals, simultaneously, under conditions of limited sample quantities and small concentrations. Electrodeposition on an inclined cathode (8) is accomplished over a range of current densities in one operation. Together they furnish a means of studying the effect of current density upon the deposit concentration of small amounts of metal impurities codeposited under identical conditions.

These techniques were utilized to study the depositions of twelve metal impurities from four types of nickel deposition solutions. The pH for each solution was held a constant during deposition. The temperature was a constant for all depositions. The volume of the solutions used was sufficient to maintain the solution concentrations relatively constant during the depositions.

TABLE 1

THE EFFECT OF AN INCREASE OF THE RESPECTIVE VARIABLES ON THE DEPOSIT CONCENTRATION OF THE IMPURITY

Impurity	Solution Concentration of Impurity	Current Density	pH
Boron (9)			
Cadmium	increase (10)	decrease (10)	
Carbon (7)			
Chlorine (7)			
Cobalt	linear increase (11,12)	maximum (13) 0.3 amp./dm.2	increase (14)
Copper	linear increase (12,15)	decrease (13)	maximum (15) near pH of 1
Hydrogen		minimum (7) 2-3 amp./dm.2	increase (7)
Iron	linear increase (16)	maximum (17) 0.5 - 1.3 amp./dm.^{2}	increase (18)
Lead (19)			
Manganese		increase (20)	increase (21)
Oxygen		minimum (7) 2 amp./dm.^{2}	increase (7)
Sodium (9)			
Sulfur (7)			
Zinc	linear increase (12)	decrease (5,22)	

EXPERIMENTAL

The compositions of the electrodeposition baths used were as follows: the Watts type-240 g./l. of nickelous sulfate heptahydrate, 45 g./l. of nickelous chloride hexahydrate, and 30 g./l. of boric acid; the organic type--263 g./l. of nickelous sulfate, 60 g./l. of nickelous chloride, 34 g./l. of boric acid, 7.5 g./l. of nickel benzene-disulfonate, and 0.14 ml./l. of triaminotolyldiphenyl-methane chloride; the chloride type--300 g./l. of nickelous chloride and 30 g./l. of boric acid. The pH* of the solutions was adjusted with sulfuric acid, hydrochloric acid, or nickelous carbonate as needed to 2.2 or 4.7 for the Watts type solution, to 3.2 for the organic type solution, and to 2.0 for the chloride type solution. Eleven metal impurities, ten milligrams of each per liter of solution, were added to the solutions as a chloride or sulfate, except for silicon which was added as sodium meta-silicate, as follows: bi-valent calcium, cadmium, cobalt, copper, iron, magnesium, manganese, lead, zinc, and tri-valent aluminum. Tri-valent chromium was added to one 4.7 pH Watts type solution.

Electrodepositions were carried out at three currents; namely, 4.3, 1.1, and 0.22 amp./dm.^{2} of cathode surface. During depositions the temperatures of the baths were maintained at 55° C. The solutions were stirred electromagnetically, the solution passing the cathode face toward the anode at a rate of sixty centimeters per minute when a current of 4.3 amp./dm.^{2} of cathode surface was passed.

* Determined electrometrically.

The two-liter volumes of plating solutions were placed in a cylindrical jar*, twenty centimeters in diameter, which had a hollow cylinder*, eight and one-half centimeters in diameter, that was centrally located to increase the efficiency of stirring. The five by nine centimeter steel cathode was so positioned that there was a forty-five degree angle between its face and the face of the eight by five centimeter, bagged, electrolytic nickel anode. The separation between the centers of the anode and the cathode was six and one-half centimeters.

Prior to the electrodeposition process the cathode surfaces were cleaned by (a) successive immersions in carbon tetrachloride, acetone, and water, (b) anodic electrocleaning at a temperature of 95° C. and a current density of 12 amp./dm.^{2} for two minutes in a liter solution containing 21 g. of sodium hydroxide, 15 g. of sodium meta-silicate, 18 g. of tri-sodium phosphate, 6 g. of sodium carbonate, and 7 1/2 g. of sodium acetate, and (c) immersion in a dilute hydrochloric acid solution and rinsing in water. Nickel was deposited from a 2.2 pH Watts type solution, which had been purified according to the procedure of Ewing, Rominski, and King (23), to form a nickel base for deposits numbered I-A, I-B, I-C, II-C, and III-C. The Roman numeral refers to the type of solution, the letter to a deposit obtained from that solution as denoted in Table 3.

To determine the deposit thickness distribution on an inclined cathode for the three currents used, we divided the deposits numbered 3, 4, and 5 as listed in Table 3 into five millimeter square sections. The thickness of the deposit at the center of each of these sections

* Made of glass.

was then determined with the aid of a calibrated Magne-Gage (24). The thicknesses of deposits numbered I-A, I-B, and I-C were calculated from the weight and measured surface dimensions of stripped, one centimeter square sections of the deposits.

The solution samples which were spectrochemically analysed were samples of the plating solutions before and after each deposition process and representative samples of stripped deposits numbered I-A, I-B, and I-C which were dissolved in hydrochloric and nitric acid.

Spectrochemical analyses were made of representative one centimeter square sections of deposits numbered I-A, I-B, I-C, II-A, II-B, II-C, III-A, III-B, III-C, IV-A, IV-B and IV-C.

Concerning spectrochemical analyses, specially purified graphite electrodes were used for the solution analyses and as counter electrodes for the analyses of the metal deposits.

A medium-sized spectrograph with quartz optics and a Cornu type of prism was used with an entrance slit which had dimensions of two by twenty-five thousandths millimeters. A quartz condensing lens was used to collimate the light from the spark source at the lowest wavelength used.

The spark source, which had a three-quarter K.V.A. input, consisted of a transformer that had a rating of 25,000 volts on the secondary when 110 volts was impressed on the primary, a 1.2 millihenry inductance unit, a 0.015 microfarad capacitor, and an electrode gap of three millimeters. The exposure time was five seconds.

The Spectrum Analysis No. 1 emulsions were developed in D 19 developer for five minutes at 18.5° C.

The Internal Standard Method (25) was used.

The calibration curve for the emulsion was originally determined with the aid of a logarithmic stepped sector. The curve was periodically checked with some of the nickel reference lines which are listed together with the analytical lines in Table 2.

The Be 3130.4 A. line (26) was used as an auxiliary internal standard line in the solution analyses. Beryllium had a concentration of 0.003 g./l. in the solution samples.

TABLE 2

THE ANALYTICAL LINE PAIRS

Element	Element Line	Nickel Reference Line
Aluminum	3092.7 A. 3961.5	3181.7 A. 3973.6
Boron	2497.7	2540.0
Calcium	3179.3 3968.5	3181.7 3973.6
Cadmium	2144.4	2161.2
Cobalt	2378.6	2362.1
Copper	2136.0 3274.0	2161.2 3286.9
Iron	2599.4	2540.0
Magnesium	2795.5 2852.1	2821.3 2821.3
Manganese	2576.1	2540.0
Lead	2833.1	2821.3
Silicon	2516.1	2540.0
Zinc	3345.6	3286.9

RESULTS

A general description of the deposits, the currents used, the cathode current efficiencies obtained, and observations made during the deposition process concerning the necessity of pH adjustments, visible gassing at the cathode, and whether or not a precipitate was formed are included in Table 3. In addition to the eleven impurities added to the other solutions, ten milligrams of tri-valent chromium was added to a 4.7 pH Watts type solution. During electrolysis at a current of 4.3 amp./dm.^{2} of cathode surface a large amount of gassing occurred at the cathode, a precipitate formed, and the solution required continuous pH adjustment. A black, pitted, crumbly deposit formed on the cathode. Initially this black deposit appeared at the high current density end of the inclined cathode; then it appeared at successively lower current density areas of the plate as more plates were run. The cathode current efficiency decreased from fifty to twenty-one per cent in the six plates made. No further work was attempted with solutions containing chromium.

It was noticed that whenever a precipitate formed, it appeared first at the cathode surface and then later it was distributed generally throughout the solution, depositing on the surface of the container and the outside of the anode bag. At no time did any of the precipitate appear on the inside of the anode bag. An analysis of the precipitate which appeared during the formation of deposit number II-C as well as an analysis of the electrolytic nickel anode is given in Table 4.

The conversion of deposit thicknesses into current densities for deposits numbered 3, 4, and 5, checked, generally within five per cent, the results obtained from the one centimeter square, stripped sections of deposits numbered I-A, I-B, and I-C. The largest differences occurred at the very high and the very low current densities. The more impure deposits had an apparent current density which was about ten per cent low at the highest current densities and about the same percentage high at the lowest current densities. From this information the data for the iso-current density curves of Figures 1, 2, and 3 were obtained.

The analyses of the electrodeposition solutions are given in Tables 5, 6, 7, and 8. Included in these tables are the calculated concentrations of nickel and boron as calculated from the quantities of the respective substances used in making the solutions. The analysis listed under each sample number is the composition of the solution at the start of the deposition which yielded a plate with this same number. The last sample number for each solution represents the solution composition after the last deposit was made. Thus the analysis given for solution sample I-A was the composition of the deposition solution at the start of the deposition process which produced deposit I-A.

The compositions of the deposits obtained at high, moderate, and low currents from the low pH Watts, the high pH Watts, the organic, and the chloride type solutions are listed in Tables 9 through 20.

A deposit-solution concentration ratio for a certain current density in a particular solution is obtained when the per cent concentration value of the impurity in the resultant deposit is divided by the average concentration in the bath in grams of impurity per one-hundred grams of nickel.

TABLE 3

GENERAL CHARACTERISTICS OF THE ELECTRODEPOSITIONS AND THE DEPOSITS

Solution Type	Deposit No.	Current amp./dm.^{2} of Cathode	Cathode Current Efficiency Per Cent	During Deposition Process: pH Adjustment Necessary	During Deposition Process: Visible Cathodic Gassing	During Deposition Process: Precipitate Formed	Deposit Description (Includes color; light, gray, black; finish; matte, semi-bright; other items; stressed, reddish-brown or velvety brown tinge, etc.)
Watts (purified) pH 2.2	3	4.3	100	no	no	no	gray, matte, semi-bright at high c.d.
	4	1.1	100	no	no	no	gray, matte
	5	0.22	91	no	no	no	gray, matte
Watts pH 2.2	I-A*	4.3	100	no	no	no	gray, matte, semi-bright at high c.d.
	I-B*	1.1	100	no	no	no	gray, matte, mottled below 0.9 amp./dm.^{2}
	I-C*	0.22	96	no	no	no	gray, matte, reddish tinge increasing toward high c.d. edge.
Watts pH 4.7	II-A	4.3	66	continuously	above 7 amp./dm.^{2}	yes	light, semi-bright, stressed
	II-B	1.1	53	continuously	high c. d. edge	yes	light, semi-bright above 1 amp./dm.^{2} increasingly dark below; r.-b. tinge below 0.5 amp./dm.^{2}
	II-C*	0.22	5.6	continuously	no	yes	black
Organic pH 3.2	III-A	4.3	91	continuously	above 9 amp./dm.^{2}	yes	light with reddish-brown tinge, semi-bright 1.8 to 3.0 amp./dm.^{2}
	III-B	1.1	91	continuously	no	yes	light, matte, r.-b.tinge, semi-bright above 1 amp./dm.^{2}
	III-C*	0.22	63	continuously	no	yes	light, matte, and r.-b. tinge above 0.14 amp./dm.^{2}, rest large black spots
Chloride pH 2.0	IV-A	4.3	102	no	no	no	gray, matte, v.b. tinge
	IV-B	1.1	108	no	no	no	gray, matte, v.b. tinge
	IV-C	0.22	106	no	no	no	gray, matte, v.b. tinge down to 0.22 amp./dm.^{2}, increasing r.-b. tinge up to 0.22 amp./dm.^{2}

* Signifies that this deposit was made on an electrolytic nickel deposit which had been previously obtained by deposition on a steel plate from a purified, low pH Watts type solution.

TABLE 4

THE IMPURITY COMPOSITIONS OF THE ELECTROLYTIC NICKEL ANODE AND A PRECIPITATE FORMED DURING DEPOSITION

Element	Per Cent by Weight	
	Electrolytic Nickel Anode	Precipitate Formed During II-C Deposition
Aluminum	0.014	0.054
Boron	0.004	0.16
Cadmium	0.006	0.018
Calcium	0.0046	0.028
Cobalt	0.31	trace
Copper	0.063	0.12
Iron	0.041	plus Nickel, over 50
Lead	0.034	0.039
Magnesium	0.002	0.0055
Manganese	0.003	0.0071
Silicon	0.026	0.35
Zinc	0.012	0.016

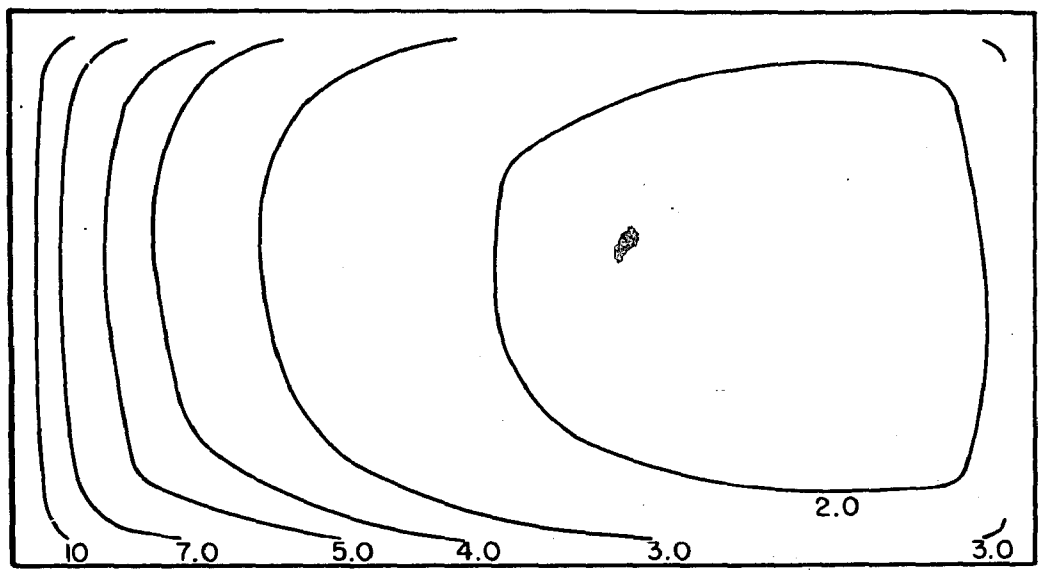


FIG. 1. ISO-CURRENT DENSITY CURVES FOR AN INCLINED CATHODE.
(AMPERES PER SQUARE DECIMETER)
(CATHODE CURRENT 4.3 AMP./DM. ^{2})

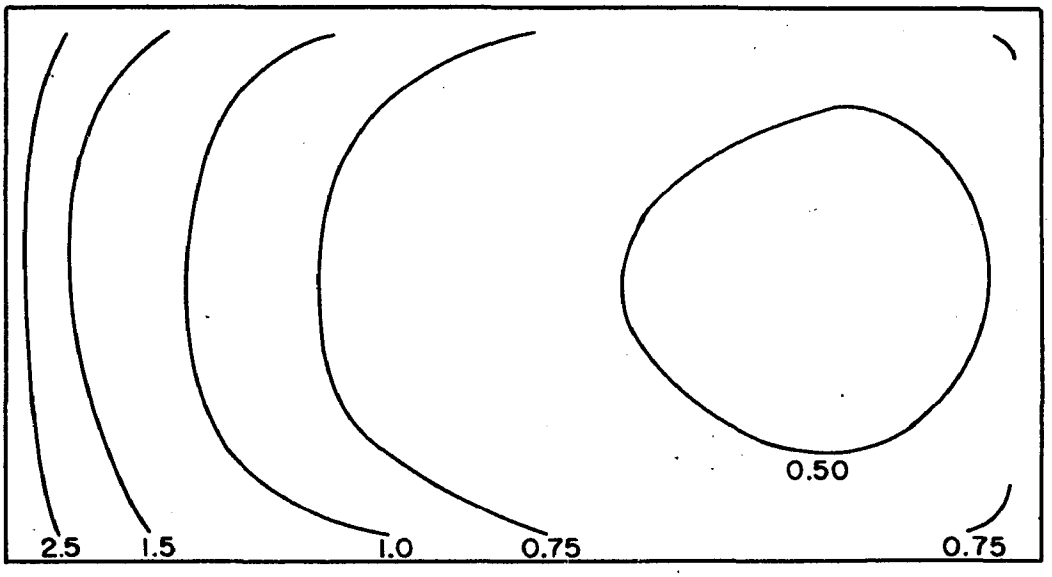


FIG. 2. ISO-CURRENT DENSITY CURVES FOR AN INCLINED CATHODE.
(AMPERES PER SQUARE DECIMETER)
(CATHODE CURRENT 1.1 AMP./DM. ^{2})

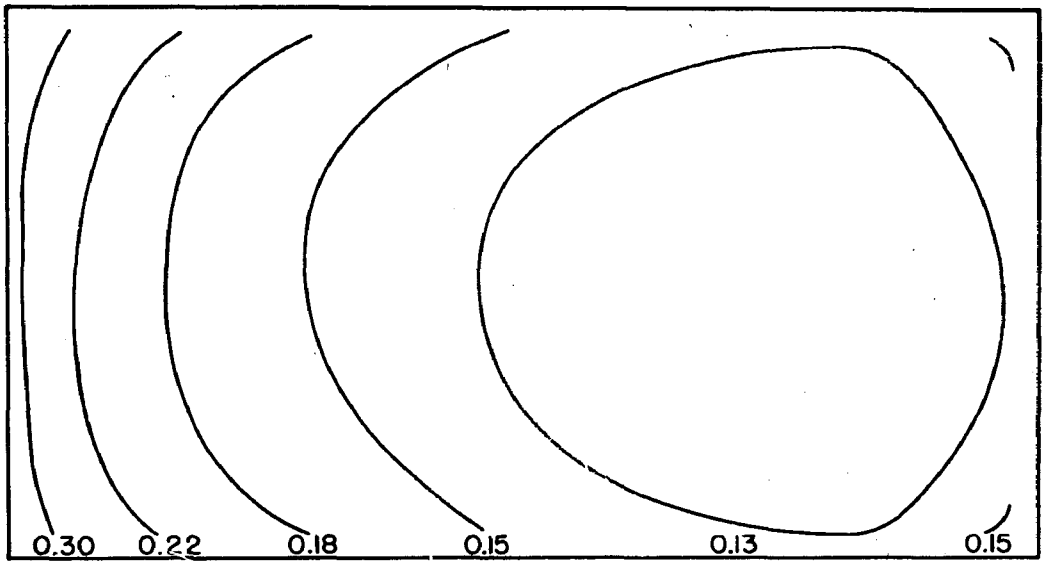


FIG. 3. ISO-CURRENT DENSITY CURVES FOR AN INCLINED CATHODE.
(AMPERES PER SQUARE DECIMETER)
(CATHODE CURRENT 0.22 AMP./DM. ^{2})

TABLE 5

THE METAL IMPURITY COMPOSITION OF THE 2.2 pH WATTS TYPE SOLUTION
(Nickel concentration, 62 grams/liter)

Element	Grams of Impurity/100 Grams of Nickel			
	*Sample I-A	I-B	I-C	I-D
Aluminum	0.036	0.040	0.039	0.037
Boron	8.5			
Cadmium	0.016	0.014	0.013	0.0057
Calcium	0.039	0.036	0.034	0.034
Cobalt	0.19	0.18	0.17	0.16
Copper	0.13	0.11	0.061	0.026
Iron	0.067	0.060	0.063	0.065
Lead	0.035	0.032	0.023	0.018
Magnesium	0.16	0.18	0.14	0.15
Manganese	0.073	0.071	0.069	0.073
Silicon	0.039	0.034	0.047	0.039
Zinc	0.026	0.024	0.024	0.018

* The analysis listed under each sample is the composition of the solution at the start of the deposition which yielded a deposit with the same number.

TABLE 6

THE METAL IMPURITY COMPOSITION OF THE 4.7 pH WATTS TYPE SOLUTION
(Nickel concentration, 62 grams/liter)

Element	Grams of Impurity/100 Grams of Nickel			
	*Sample II-A	II-B	II-C	II-D
Aluminum	0.016	0.019	0.027	0.018
Boron	8.5			
Cadmium	0.018	0.018	0.018	0.018
Calcium	0.016	0.014	0.019	0.013
Cobalt	0.053	0.055	0.053	0.047
Copper	0.055	0.063	0.042	0.024
Iron	0.017	0.030	0.040	0.028
Lead	0.024	0.027	0.024	0.014
Magnesium	0.018	0.018	0.016	0.014
Manganese	0.021	0.018	0.014	0.014
Silicon	0.023	0.029	0.024	0.024
Zinc	0.016	0.016	0.017	0.012

* The analysis listed under each sample is the composition of the solution at the start of the deposition which yielded a deposit with the same number.

TABLE 7

THE METAL IMPURITY COMPOSITION OF THE ORGANIC TYPE SOLUTION, pH 3.2
(Nickel concentration, 70 grams/liter)

Element	Grams of Impurity/100 Grams of Nickel			
	*Sample III-A	III-B	III-C	III-D
Aluminum	0.037	0.034	0.039	0.033
Boron	8.5			
Cadmium	0.016	0.013	0.012	0.0093
Calcium	0.030	0.037	0.036	0.039
Cobalt	0.051	0.056	0.056	0.054
Copper	0.057	0.056	0.041	0.033
Iron	0.031	0.030	0.035	0.035
Lead	0.032	0.030	0.024	0.020
Magnesium	0.064	0.071	0.076	0.076
Manganese	0.014	0.014	0.014	0.014
Silicon	0.017	0.017	0.017	0.017
Zinc	0.024	0.020	0.020	0.019

* The analysis listed under each sample number is the composition of the solution at the start of the deposition which yielded a deposit with the same number.

TABLE 8

THE METAL IMPURITY COMPOSITION OF THE CHLORIDE TYPE SOLUTION, pH 2.0
(Nickel concentration, 74 grams/liter)

Element	Grams of Impurity/100 Grams of Nickel			
	*Sample IV-A	IV-B	IV-C	IV-D
Aluminum	0.027	0.027	0.026	0.027
Boron	7.1			
Cadmium	0.012	0.012	0.011	0.0093
Calcium	0.014	0.015	0.015	0.015
Cobalt	0.42	0.37	0.41	0.43
Copper	0.063	0.069	0.061	0.053
Iron	0.050	0.062	0.070	0.088
Lead	0.034	0.029	0.030	0.029
Magnesium	0.032	0.027	0.031	0.034
Manganese	0.020	0.019	0.020	0.023
Silicon	0.018	0.018	0.018	0.019
Zinc	0.018	0.019	0.018	0.018

* The analysis listed under each sample number is the composition of the solution at the start of the deposition which yielded a deposit with the same number.

TABLE 9

THE IMPURITY COMPOSITION OF DEPOSIT I-A OBTAINED FROM THE 2.2 pH WATTS TYPE SOLUTION AT A CURRENT OF 4.3 AMP./DM.^{2} OF CATHODE SURFACE

Element	Concentration, Per Cent by Weight					
	Current Density of Deposit Section in amp./dm.^{2}					
	9.6	8.0	4.0	2.4	1.9	1.6
Aluminum	0.010	0.0095	0.0098	0.0095	0.0093	0.0090
Boron	0.0031	0.0031	0.0028	0.0030	0.0030	0.0030
Cadmium	0.013	0.013	0.020	0.022	0.027	0.032
Calcium	0.0079	0.0035	0.0040	0.0031	0.0028	0.0029
Cobalt	0.64	0.65	0.78	1.1	1.3	1.5
Copper	0.056	0.064	0.072	0.097	0.11	0.14
Iron	0.17	0.16	0.15	0.28	0.26	0.37
Lead	0.033	0.027	0.041	0.040	0.045	0.043
Magnesium	0.0025	0.0017	0.0015	0.0016	0.0011	0.0011
Manganese		0.0028	0.0020		0.0018	
Silicon		0.017	0.011		0.010	
Zinc	0.019	0.019	0.021	0.027	0.025	0.026

TABLE 10

THE IMPURITY COMPOSITION OF DEPOSIT I-B OBTAINED FROM THE 2.2 pH WATTS TYPE SOLUTION AT A CURRENT OF 1.1 AMP./DM.^{2} OF CATHODE SURFACE

Element	Concentration, Per Cent by Weight				
	Current Density of Deposit Section, amp./dm.^{2}				
	1.4	1.1	0.81	0.56	0.43
Aluminum	0.010	0.0095	0.010	0.0090	0.0093
Boron	0.0031	0.0031	0.0031	0.0033	0.0033
Cadmium	0.027	0.033	0.038	0.045	0.049
Calcium	0.0036	0.0028	0.0039	0.0038	0.0046
Cobalt	1.5	1.6	1.8	2.2	2.3
Copper	0.13	0.17	0.19	0.27	0.36
Iron	0.44	0.39	0.54	0.61	0.62
Lead	0.044	0.045	0.045	0.050	0.060
Magnesium	0.0030	0.0012	0.0017	0.0014	0.0017
Manganese		0.0022			0.0020
Silicon		0.013			0.010
Zinc	0.026	0.024	0.025	0.030	0.026

TABLE 11

THE IMPURITY COMPOSITION OF DEPOSIT I-C OBTAINED FROM THE 2.2 pH WATTS TYPE SOLUTION AT A CURRENT OF 0.22 AMP./DM.^{2} OF CATHODE SURFACE

Element	Concentration, Per Cent by Weight			
	Current Density of Deposit Section, amp./dm.^{2}			
	0.26	0.21	0.14	0.11
Aluminum	0.0098	0.0098	0.0098	0.0095
Boron	0.0030	0.0028	0.0031	0.0030
Cadmium	0.046	0.051	0.052	0.052
Calcium	0.0036	0.0029	0.0040	0.0033
Cobalt	2.2	2.2	1.7	1.3
Copper	0.15	0.14	0.18	0.20
Iron	0.61	0.50	0.34	0.22
Lead	0.046	0.046	0.060	0.055
Magnesium	0.0014	0.0013	0.0018	0.0014
Manganese	0.0022	0.0021	0.0022	0.0022
Silicon	0.0087	0.0064	0.0098	0.0070
Zinc	0.025	0.023	0.025	0.029

TABLE 12

THE IMPURITY COMPOSITION OF DEPOSIT II-A OBTAINED FROM THE 4.7 pH WATTS TYPE SOLUTION AT A CURRENT OF 4.3 AMP./DM.^{2} OF CATHODE SURFACE

Element	Concentration, Per Cent by Weight		
	Current Density of Deposit Section, amp./dm.^{2}		
	8.3	4.1	1.9
Aluminum	0.0098	0.0095	0.0090
Boron	0.088	0.030	0.018
Cadmium	0.026	0.030	0.038
Calcium	0.016	0.0035	0.0034
Cobalt	0.17	0.28	0.33
Copper	0.069	0.061	0.081
Iron	8.6	1.0	0.34
Lead	0.038	0.046	0.047
Magnesium	0.0026	0.0014	0.0014
Manganese	0.012	0.0047	0.0025
Silicon	0.015	0.010	0.011
Zinc	0.018	0.022	0.027

TABLE 13

THE IMPURITY COMPOSITION OF DEPOSIT II-B OBTAINED FROM THE 4.7 pH WATTS TYPE SOLUTION AT A CURRENT OF 1.1 AMP./DM.^{2} OF CATHODE SURFACE

Element	Concentration, Per Cent by Weight			
	Current Density of Deposit Section, amp./dm.^{2}			
	1.4	0.81	0.56	0.45
Aluminum	0.0090	0.0086	0.0088	0.0090
Boron	0.014	0.017	0.023	0.016
Cadmium	0.048	0.053	0.057	0.058
Calcium	0.0026	0.0035	0.0034	0.0028
Cobalt	0.44	0.49	0.41	0.44
Copper	0.12	0.21	0.34	0.48
Iron	0.29	0.20	0.26	0.29
Lead	0.053	0.063	0.065	0.071
Magnesium	0.0010	0.0010	0.0011	0.00088
Manganese	0.0025	0.0021	0.0020	0.0021
Silicon	0.012	0.010	0.010	0.011
Zinc	0.023	0.036	0.029	0.034

TABLE 14

THE IMPURITY COMPOSITION OF DEPOSIT II-C OBTAINED FROM THE 4.7 pH WATTS TYPE SOLUTION AT A CURRENT OF 0.22 AMP./DM.^{2} OF CATHODE SURFACE

Element	Concentration, Per Cent By Weight			
	Current Density of Deposit Section, amp./dm.^{2}			
	0.30*	0.22*	0.14*	0.11*
Aluminum	0.00062	0.00072	0.00071	0.00081
Boron	0.028	0.024	0.023	0.0071
Cadmium	0.080	0.074	0.065	0.060
Calcium	0.00011	0.00013	0.000076	0.000095
Cobalt	0.0090	0.0080	0.0090	0.0070
Copper	3.3	3.5	3.3	3.8
Iron	0.044	0.066	0.11	0.15
Lead	0.60	0.64	0.63	0.64
Magnesium	0.00034	0.00033	0.00035	0.00033
Manganese	0.00051	0.00057	0.00058	0.00059
Silicon	0.0022	0.0025	0.0026	0.0027
Zinc	0.020	0.019	0.020	0.023

* Black Deposit

TABLE 15

THE IMPURITY COMPOSITION OF DEPOSIT III-A OBTAINED FROM THE ORGANIC TYPE SOLUTION (pH 3.2) AT A CURRENT OF 4.3 AMP./DM.^{2} OF CATHODE SURFACE

Element	Concentration, Per Cent by Weight		
	Current Density of Deposit Section, amp./dm.^{2}		
	8.3	3.9	1.9
Aluminum	0.013	0.010	0.010
Boron	0.0078	0.0042	0.0046
Cadmium	0.016	0.018	0.028
Calcium	0.0050	0.0032	0.0030
Cobalt	0.20	0.25	0.38
Copper	0.031	0.049	0.081
Iron	0.40	0.11	0.090
Lead	0.034	0.046	0.058
Magnesium	0.0017	0.0016	0.0013
Manganese	0.0029	0.0022	0.0020
Silicon	0.014	0.011	0.011
Zinc	0.023	0.023	0.029

TABLE 16

THE IMPURITY COMPOSITION OF DEPOSIT III-B OBTAINED FROM THE ORGANIC TYPE SOLUTION (pH 3.2) AT A CURRENT OF 1.1 AMP./DM.^{2} OF CATHODE SURFACE

Element	Concentration, Per Cent by Weight			
	Current Density of Deposit Section, amp./dm.^{2}			
	1.4	1.1	0.56	0.45
Aluminum	0.011	0.010	0.011	0.011
Boron	0.0048	0.0051	0.0079	0.0084
Cadmium	0.032	0.037	0.045	0.049
Calcium	0.0038	0.0025	0.0030	0.0027
Cobalt	0.48	0.56	0.63	0.58
Copper	0.067	0.087	0.22	0.24
Iron	0.13	0.12	0.31	0.40
Lead	0.058	0.066	0.072	0.071
Magnesium	0.0012	0.0011	0.0011	0.0010
Manganese	0.0019	0.0019	0.0019	0.0022
Silicon	0.0094	0.010	0.010	0.012
Zinc	0.028	0.031	0.036	0.036

TABLE 17

THE IMPURITY COMPOSITION OF DEPOSIT III-C OBTAINED FROM THE ORGANIC TYPE SOLUTION (pH 3.2) AT A CURRENT OF 0.22 AMP./DM.^{2} OF CATHODE SURFACE

Element	Concentration, Per Cent by Weight			
	Current Density of Deposit Section, amp./dm.^{2}			
	0.30	0.19	0.16	0.12*
Aluminum	0.036	0.043	0.062	0.033
Boron	0.039	0.034	0.048	0.27
Cadmium	0.050	0.046	0.048	0.066
Calcium	0.0031	0.0030	0.0033	0.00005
Cobalt	0.32	0.30	0.24	0.11
Copper	0.18	0.26	0.29	1.9
Iron--	1.2	1.0	2.1	0.22
Lead	0.065	0.059	0.060	0.32
Magnesium	0.0012	0.0011	0.0011	0.00035
Manganese	0.0021	0.0018	0.0019	0.00034
Silicon	0.017	0.010	0.016	0.014
Zinc	0.031	0.029	0.027	0.059

* Black Deposit

TABLE 18

THE IMPURITY COMPOSITION OF DEPOSIT IV-A OBTAINED FROM THE CHLORIDE TYPE SOLUTION (pH 2.0) AT A CURRENT OF 4.3 AMP./DM.^{2} OF CATHODE SURFACE

Element	Concentration, Per Cent by Weight				
	Current Density of Deposit Section, amp./dm.^{2}				
	9.6	5.2	3.9	2.9	1.9
Aluminum	0.011	0.0093	0.0090	0.0090	0.010
Boron	0.0041	0.0033	0.0033	0.0034	0.0038
Cadmium	0.015	0.019	0.026	0.030	0.039
Calcium	0.0077	0.0025	0.0022	0.0035	0.0024
Cobalt	0.59	0.78	0.97	1.0	1.3
Copper	0.024	0.032	0.046	0.056	0.098
Iron	0.064	0.064	0.070	0.099	0.15
Lead	0.044	0.048	0.055	0.054	0.059
Magnesium	0.0012	0.0010	0.00084	0.0011	0.00096
Manganese	0.0021	0.0021	0.0020	0.0021	0.0024
Silicon	0.010	0.0094	0.0085	0.010	0.011
Zinc	0.024	0.019	0.026	0.022	0.025

TABLE 19

THE IMPURITY COMPOSITION OF DEPOSIT IV-B OBTAINED FROM THE CHLORIDE TYPE SOLUTION (pH 2.0) AT A CURRENT OF 1.1 AMP./DM.^{2} OF CATHODE SURFACE

Element	Concentration, Per Cent by Weight		
	Current Density of Deposit Section, amp./dm.^{2}		
	1.4	0.66	0.43
Aluminum	0.0086	0.0086	0.012
Boron	0.0031	0.0032	0.0044
Cadmium	0.042	0.048	0.053
Calcium	0.0026	0.0055	0.0027
Cobalt	1.3	1.1	1.0
Copper	0.12	0.27	0.35
Iron	0.19	0.32	0.34
Lead	0.055	0.071	0.068
Magnesium	0.00088	0.0013	0.0011
Manganese	0.0022	0.0023	0.0025
Silicon	0.011	0.011	0.012
Zinc	0.022	0.025	0.030

TABLE 20

THE IMPURITY COMPOSITION OF DEPOSIT IV-C OBTAINED FROM THE CHLORIDE TYPE SOLUTION (pH 2.0) AT A CURRENT OF 0.22 AMP./DM.^{2} OF CATHODE SURFACE

Element	Concentration, Per Cent by Weight		
	Current Density of Deposit Section, amp./dm.^{2}		
	0.26	0.13	0.11
Aluminum	0.010	0.010	0.010
Boron	0.0030	0.0032	0.0032
Cadmium	0.054	0.054	0.061
Calcium	0.0029	0.0025	0.0027
Cobalt	0.29	0.15	0.13
Copper	0.39	0.49	0.58
Iron	0.050	0.043	0.034
Lead	0.074	0.077	0.084
Magnesium	0.0010	0.0011	0.0011
Manganese	0.0021	0.0023	0.0023
Silicon	0.011	0.034	0.042
Zinc	0.022	0.020	0.020

In Figures 4 through 15 this concentration ratio versus current density is plotted logarithmically for the twelve metal impurities and the four baths. Black deposits are represented in these figures by solid black points whose curves are not connected to the regular deposit curves.

The trends found from calculations of impurity deposition rates and relative energy efficiencies for impurity depositions are presented in the discussion section.

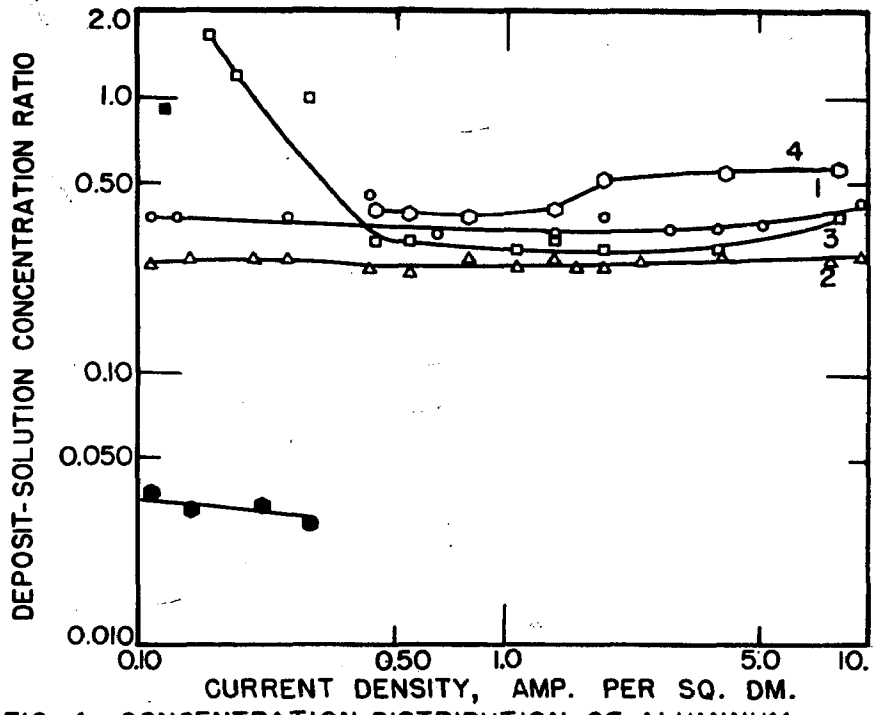


FIG. 4. CONCENTRATION DISTRIBUTION OF ALUMINUM. (1), CHLORIDE; (2), WATTS LOW PH; (3), ORGANIC; AND (4), WATTS HIGH PH TYPE BATH.

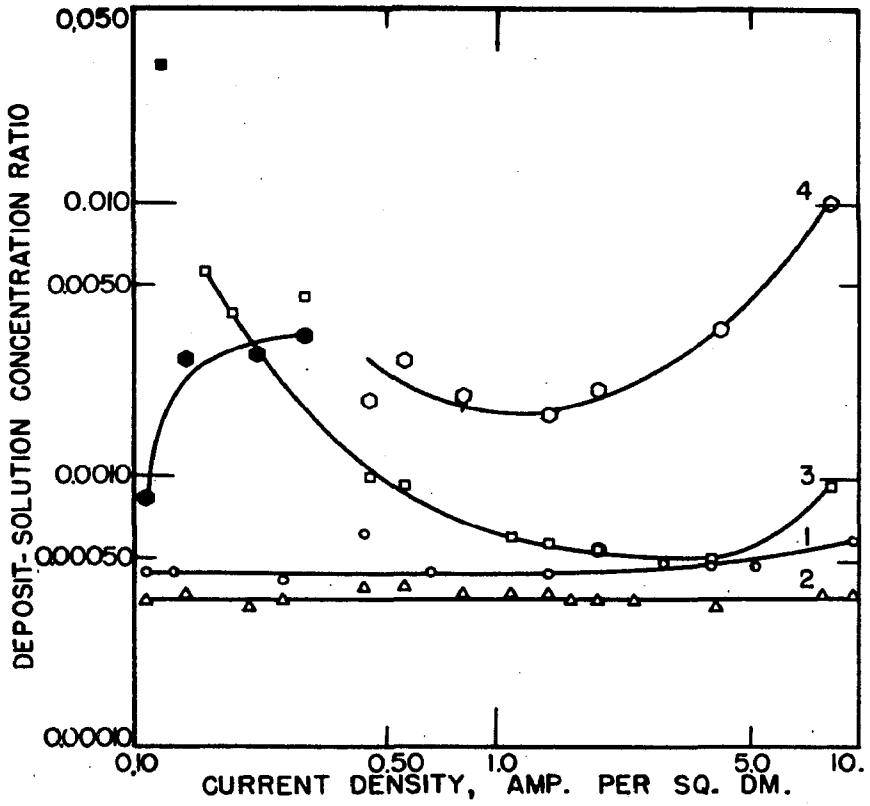


FIG. 5. CONCENTRATION DISTRIBUTION OF BORON. (1), CHLORIDE; (2), WATTS LOW PH; (3), ORGANIC; AND (4), WATTS HIGH PH TYPE BATH.

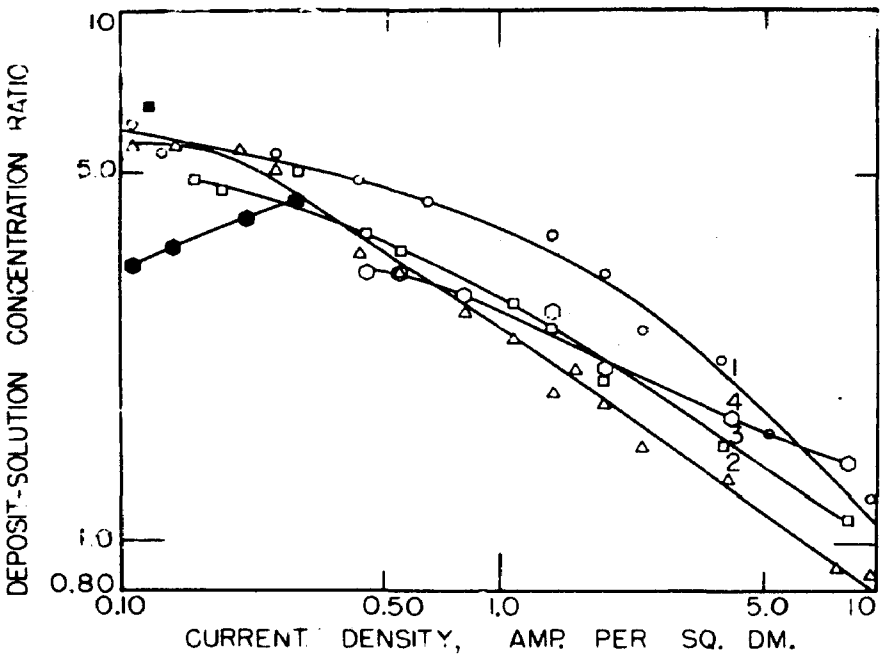


FIG. 6. CONCENTRATION DISTRIBUTION OF CADMIUM. (1), CHLORIDE; (2), WATTS LOW PH; (3), ORGANIC; AND (4), WATTS HIGH PH TYPE BATH.

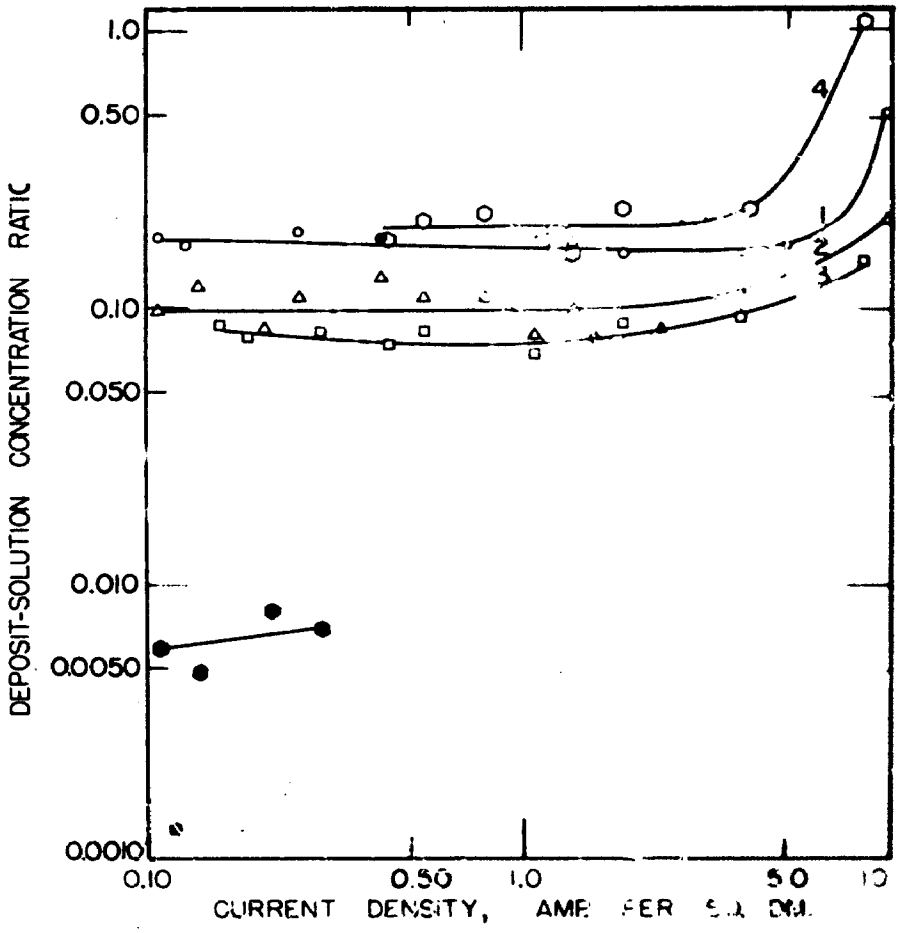


FIG. 7. CONCENTRATION DISTRIBUTION OF CALCIUM. (1), CHLORIDE; (2), WATTS LOW PH; (3), ORGANIC; AND (4), WATTS HIGH PH TYPE BATH.

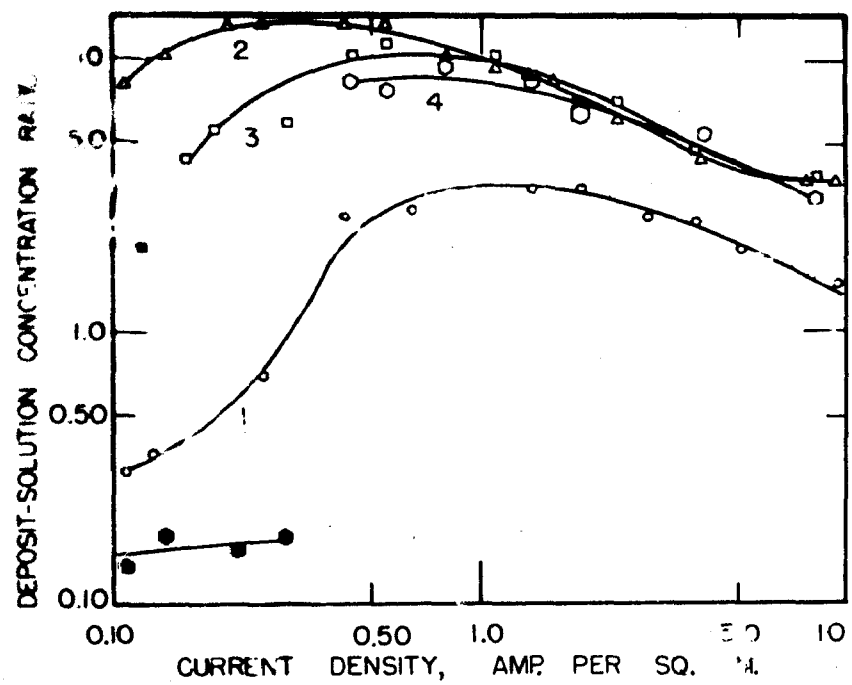
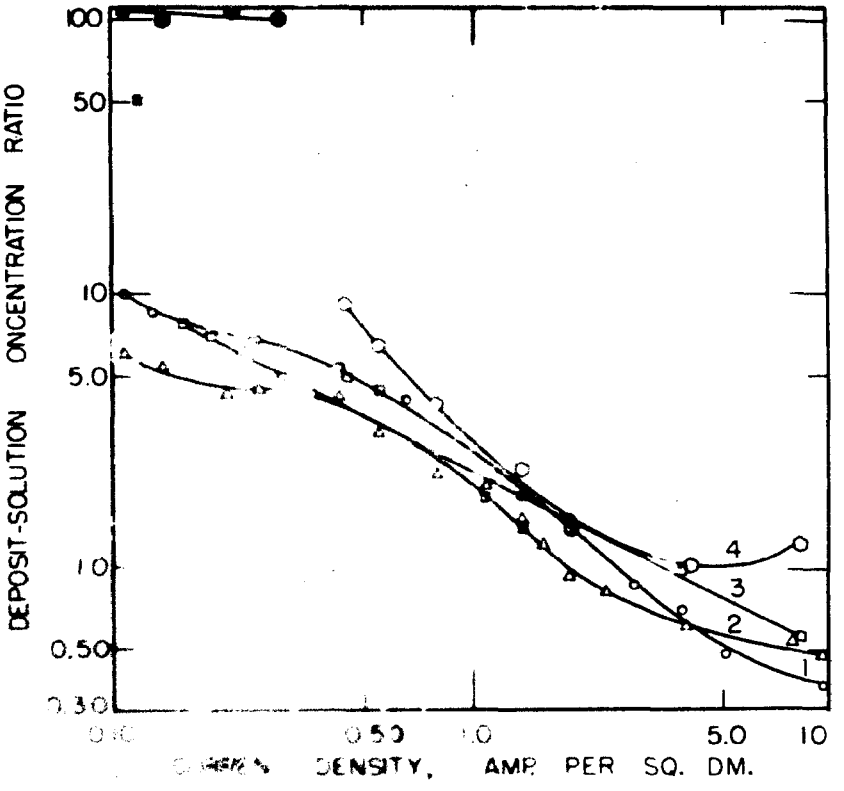


FIG. 8. CONCENTRATION DISTRIBUTION OF COBALT. (1), CHLORIDE; (2), WATTS LOW PH; (3), ORGANIC; AND (4), WATTS HIGH PH TYPE BATH.



DISTRIBUTION OF COPPER.
WATTS LOW PH; (3), ORGANIC;
PH TYPE BATH.

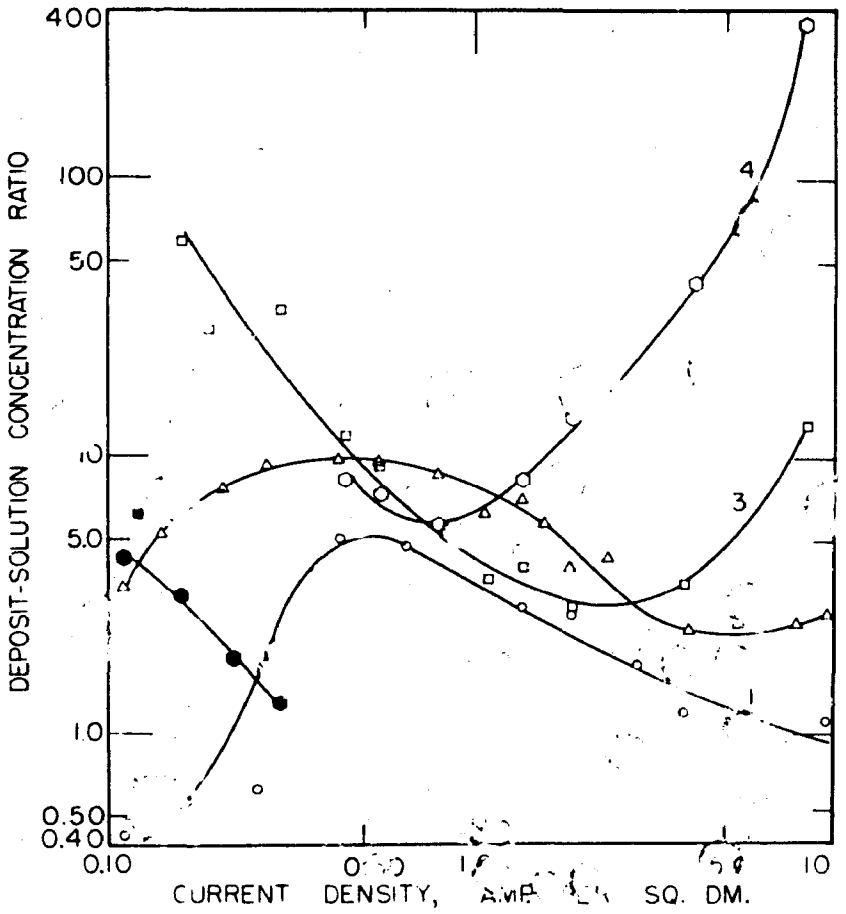


FIG. 10. CONCENTRATION DISTRIBUTION OF IRON.
(1), CHLORIDE; (2), WATTS LOW PH; (3), ORGANIC; AND (4), WATTS HIGH PH TYPE BATH.

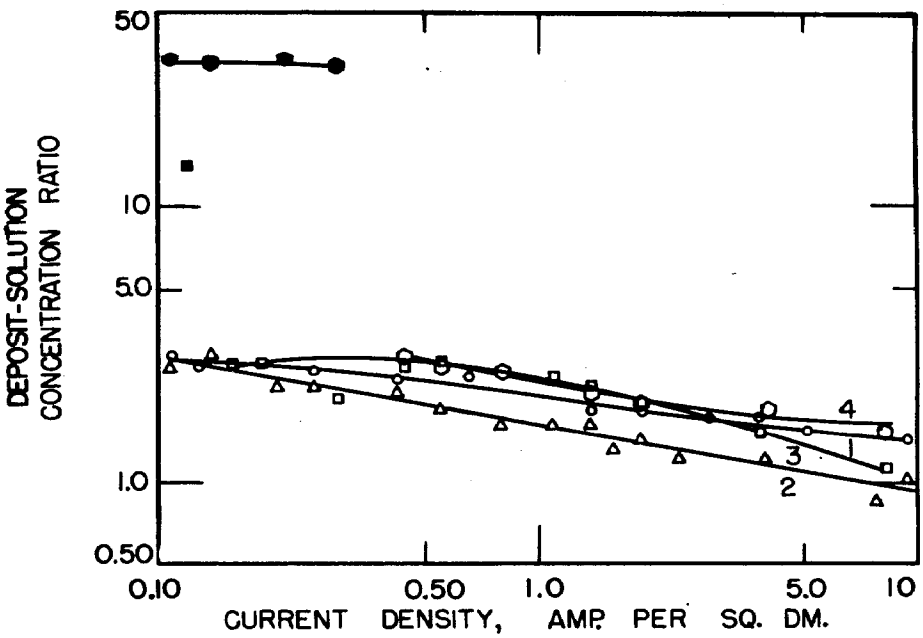


FIG. 11. CONCENTRATION DISTRIBUTION OF LEAD. (1), CHLORIDE; (2), WATTS LOW PH; (3), ORGANIC; AND (4), WATTS HIGH PH TYPE BATH.

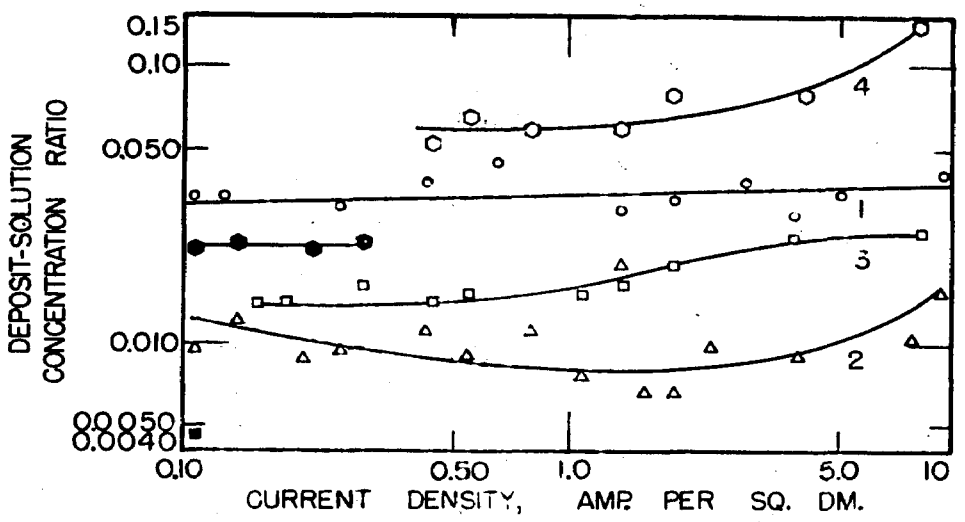


FIG. 12. CONCENTRATION DISTRIBUTION OF MAGNESIUM. (1), CHLORIDE; (2), WATTS LOW PH; (3), ORGANIC; AND (4), WATTS HIGH PH TYPE BATH.

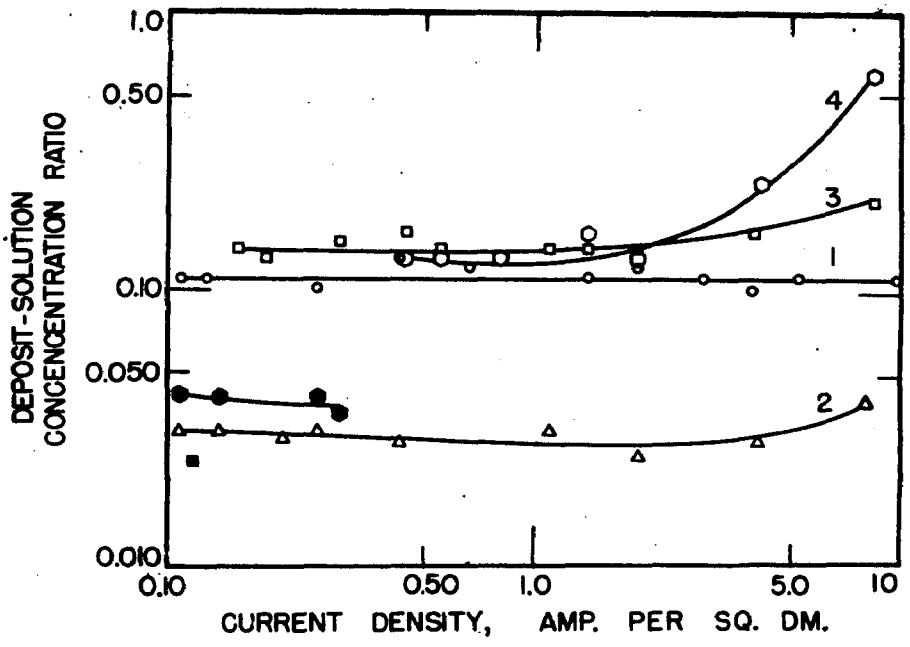


FIG. 13. CONCENTRATION DISTRIBUTION OF MANGANESE. (1), CHLORIDE; (2), WATTS LOW PH; (3), ORGANIC; AND (4), WATTS HIGH PH TYPE BATH.

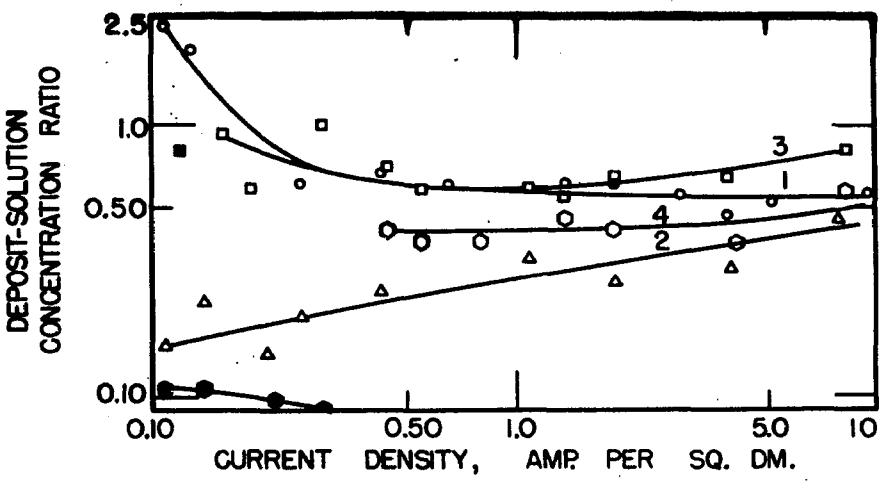


FIG. 14. CONCENTRATION DISTRIBUTION OF SILICON. (1), CHLORIDE; (2), WATTS LOW PH; (3), ORGANIC; AND (4), WATTS HIGH PH TYPE BATH.

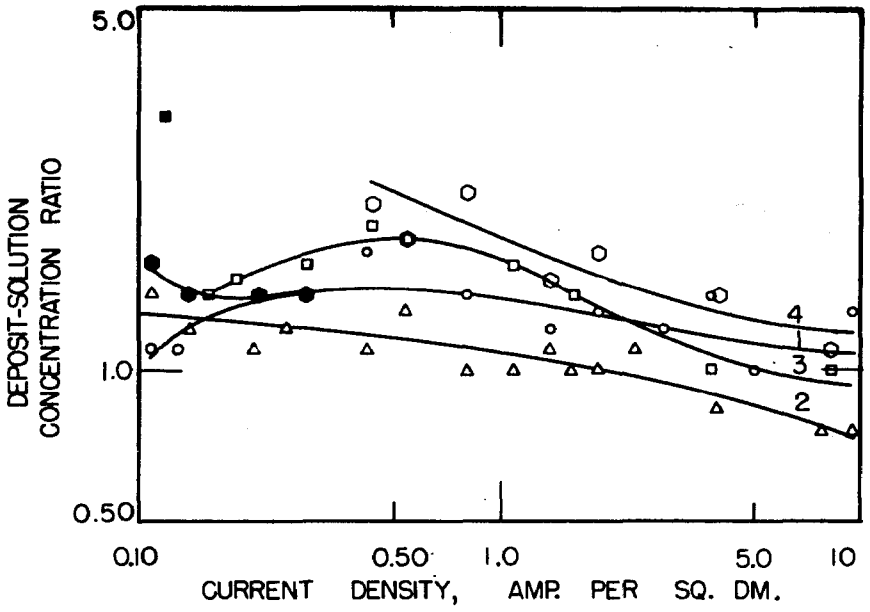


FIG. 15. CONCENTRATION DISTRIBUTION OF ZINC. (1), CHLORIDE; (2), WATTS LOW PH; (3), ORGANIC; AND (4), WATTS HIGH PH TYPE BATH.

DISCUSSION

The impurities present in the solution affected the cathodic current efficiencies to such an extent that there was a reversal of the general trend, which is that an increase in efficiency occurs when the pH is increased (1,7). The presence of the ten milligrams of trivalent chromium per liter of solution in combination with the other impurities present in the high pH Watts type solution decreased the efficiency even more.

Associated with the low current efficiencies obtained in the high pH solutions, there was visible gassing during deposition at the higher current densities; gassing started at a lower current density in the higher pH bath.

In agreement with the results of others (1,7) a decrease in current density resulted in a decrease in the cathodic current efficiency.

The formation of the precipitate occurred only during electrolysis in the two highest pH solutions and always appeared first at the cathode surface, none of the precipitate was ever found inside the anode bag. In the electrolyses of these two solutions it was necessary to add acid continuously in order to maintain the pH constant, and the cathodic current efficiency was lower than that of the other solutions. It has been noted (1,27) that a higher pH exists in the cathode layer than in the solution proper, especially when the cathodic current efficiency is

less than one hundred per cent. After calculating the ratio of the precipitate concentration to the solution concentration for the various metal impurities, the impurities were arranged according to their order of decreasing ratio value; namely, iron, copper, silicon, aluminum, calcium, lead, zinc, cadmium, manganese, magnesium, boron, and cobalt. Wiesner (28) has found that the order of increasing solubility at higher pH values in a boric acid-buffered, concentrated solution of nickel sulfate is as follows: tri-valent iron, and aluminum; bi-valent copper, zinc, iron, cadmium, and nickel. A comparison of the two orders shows that except for the reversal of the order of copper and aluminum, the elements common to both appear in the same order. A correlation of this information would indicate that the pH of the layer of solution adjacent to the cathode is sufficiently higher than the body of the solution to cause the formation of the precipitate.

The iso-current density curves for inclined cathodes as shown in Figures 1, 2, and 3 were obtained from calculations based on the value of the Faraday (29), the density of electrodeposited nickel (7), deposition time, and deposit thickness. The curves illustrate how, in general, the current density is less in those portions of the cathode which are more distant from the anode. The curves also illustrate how the current density increases towards the edges and especially toward the corners, the adjacent central portion of the plate, which may be closer to the anode, having a lower value.

Several investigators (12,15,16) have found that a linear relationship exists between the deposit and solution concentrations for cobalt,

copper, iron, and zinc. Thus a ratio of the deposit and the solution concentration for an impurity is a constant under a given set of conditions, at least for those impurities just mentioned. Although a linear relationship may not exist between the deposit and solution concentrations for some of the other impurities, the deposit-solution concentration ratio furnishes a convenient means of correlating and comparing the differences in impurity depositions found in the various current density regions and solutions. The concentration ratios were plotted logarithmically to better illustrate the differences found in different solutions and current density regions over the wide range of ratio values involved. The current densities were plotted logarithmically because it has been established (30) that there is linear relationship between cathode potential and the logarithm of the current density over a range of current densities.

Some of the results denoted by Figures 4 through 15 will be presented in a definite order to facilitate comparisons and reduce unnecessary repetition, as follows:

Element

a. The general concentration range found in the nickel deposits as compared to the solution concentration of an impurity.

b. The effect of pH on the deposit-solution concentration ratio of an impurity at low, moderate, and high current densities. The apparent pH order assumed by the organic or chloride type solutions as related to the two Watts type solutions due to the presence of the organic constituents or the high chloride concentration.

c. The effect on the concentration ratio due to the high chloride concentration, or presence of organic constituents, as differentiated from pH and current density effects as evidenced by the Watts type solutions.

d. The existence of a maximum or minimum ratio, and whether or not there is an inter-relationship among (1) the current density location of the maxima or minima, (2) pH, and (3) the magnitude of the maxima or minima ratio values.

e. The numerical location of the impurity according to the increasing order of deposit-solution concentration ratio values of the impurities at various current densities in the four solutions.

1. Aluminum.

a. The deposit concentration varied from about one-fourth to nearly twice the solution concentration; the lowest ratio was obtained from the low pH Watts type solution, the highest from the low current density region of the organic type solution. In general the ratios were nearly constant for the respective solutions, increasing slightly at high current densities.

b. The concentration ratios increased with an increase in pH at all current densities. The chloride type solution ratios behaved as though the pH were between that of the low pH Watts and the organic type solutions at low current densities, and between the organic and the high pH Watts type solutions at higher current densities.

c. The ratios of the organic type solution increased markedly with a decrease in current density at low current densities as compared to the nearly constant ratios found with the other solutions.

d. A minimum ratio occurred for the organic and the high pH Watts type solutions. The higher minimum ratio occurred at the higher pH and at a lower current density.

e. According to the increasing order of deposit-solution concentration ratios of the impurities at various current densities in the four solutions, aluminum rated a fifth position except at low current densities and the higher current density region of the high pH Watts type solution. At low current densities it was in sixth position except in the black deposit of the high pH Watts type solution where it ranked fourth. In the high pH Watts type solution it occupied the sixth position at current densities of two and four amp./dm.^{2}, the third position at a current density of eight amp./dm.^{2}

2. Boron.

a. The concentration of boron in the deposits varied from four ten-thousandths to one one-hundredth of the solution concentration. The concentration ratio which was nearly constant with increased current density for the low pH Watts type solution, increased with an increase in current density at the higher current densities, and increased with decreased current density for the organic and the high pH Watts type solutions at lower current densities.

b. With the chloride type bath occupying an apparent pH position between the low pH Watts and the organic type solutions, the concentration

ratios increased with an increase in pH, the differences between the values being more noticeable at high and low current densities. At low current densities the organic constituents tended to increase the ratio.

d. A minimum ratio was observed in the organic and high pH Watts type solutions; the higher minimum ratio occurred at the higher pH and at a lower current density.

e. Boron had the lowest ratio of all of the impurities except in the black deposit from the organic type solution where it had a rank of four.

3. Cadmium.

a. The concentration ratios of cadmium decreased from a value of about six to a value of about one with an increase in current density.

b. At low current densities the concentration ratio increased with a decrease in pH; at moderate current densities, the chloride type solution ratios were still the highest, with the organic, the high pH Watts, and the low pH Watts type solutions having, respectively, smaller ratios; at high current densities the ratio increased with an increase in pH, the chloride type solution occupying an apparent pH location between the organic and the high pH Watts type solutions.

c. The increased concentration of chloride in the solution favored a higher rate of deposition of cadmium.

d. Cadmium had a rank which varied from nine to eleven, the rank being generally higher with a higher pH.

4. Calcium.

a. The deposit concentrations of calcium varied from about one-tenth to slightly more than the solution concentrations. The general trend showed a constant ratio for most of the current density range with a decided increase in ratio with an increase in current density at high current densities.

b. Considering only the Watts type solutions the concentration ratio was higher in the higher pH solution. The apparent pH position of the chloride type solution was between the two Watts type solutions, and the apparent pH location of the organic type solution was below that of the low pH Watts type solution.

c. The higher concentration of chloride increased the calcium ratio, whereas the presence of the organic constituents decreased it.

e. Calcium had a rank of one and two in the organic and the high pH Watts type baths when low current density, black deposits were obtained. It had a rank of three for the rest of the current densities for the organic solution, a rank of six at very high current densities for the chloride and the high pH Watts type solutions, and a rank of four at the other current densities and for the other solutions.

5. Cobalt.

a. The concentration of cobalt in the deposits varied from one-third to thirteen times it's concentration in the solutions, with a maximum occurring for all the solutions.

b. At low and moderate current densities the concentration ratio decreased with an increase in pH; at higher current densities the ratios

for the chloride solution were lower than those for the other solutions whose ratios had practically the same value.

c. A higher chloride concentration tended to decrease the concentration ratio for cobalt.

d. For the solutions other than the chloride type, as the pH decreased the maximum concentration ratio value increased and the current density location of the maximum decreased. The maximum for the chloride type solution had a lower value and was located at a higher current density than the maximum for any of the other solutions.

e. Cobalt had a rank of five at very low current densities for the chloride solution; the rank increased with an increase of current density up to twelve at two amp./dm.^{2} It had the highest concentration ratio (rank of twelve) of any of the impurities at all current densities in the low pH Watts type solution. For the organic type solution the rank increased rapidly from seven in the low current density, black deposit to twelve at two amp./dm.^{2} and then decreased to eleven at very high current densities. In the high pH Watts type solution the rank of cobalt increased rapidly with increasing current density from seven in the low current density black deposit to eleven.

6. Copper.

a. The copper concentrations in the deposits varied from about one-half to over six times the solution concentrations. In general, the concentration ratio decreased as the current density increased.

b. The concentration ratios were higher the higher the pH of the solution. The apparent pH of the chloride type solution was higher

than that of the organic type solution at low and moderate current densities; at high current densities the chloride type solution had the lowest ratios in accordance with the general trend with respect to pH.

c. The higher chloride concentration increased the rate of copper deposition at low and moderate current densities.

d. A minimum occurred in the high pH Watts type solution ratios in the high current density region.

e. The rank of copper decreased with increasing current density and, at very high current densities, its rank increased with an increase in pH. The rank decreased from twelve at very low current densities, from eleven in the low pH Watts type solution, to seven at a current density of about four amp./dm.^{2} At a current density of about eight amp./dm.^{2} its rank increased with an increase in pH from a value of four in the chloride type solution to eight in the high pH Watts type solution.

7. Iron.

a. The deposit concentrations of iron varied from about one-half to over three hundred times the solution concentrations. The three highest pH solutions had a minimum, the two lowest a maximum concentration ratio.

b. At low and at high current densities the ratio increased with an increase in pH; at a current density of approximately three-fourths of an amp./dm.^{2} this relationship was reversed with the exception that the ratios for the chloride type solution were lower at all current densities.

c. The high chloride concentration tended to decrease the rate of iron deposition. At low current densities the organic constituents seemed to enhance the deposition rate.

d. The maximum concentration ratio was at a higher current density and had a lower ratio value for the lower pH solution, the chloride type solution, than that of the low pH Watts type solution. The minimum ratio values increased with the pH of the solution and decreased with an increased current density location.

e. In general, iron's rank, which varied from seven at a very low current density in the chloride type solution to twelve at high current densities in the high pH Watts type solution, increased with an increase in pH. The current density location of the highest rank for a particular solution was higher the higher the pH of the solution. Iron's rank for the chloride type solution increased rapidly from seven to eleven with a small increase in current density, and then decreased with continued increase in current density until a rank of eight was reached. In the low pH Watts type solution iron's rank increased rapidly from nine to eleven with an increase in current density. As the current density increased in the organic type solution the rank increased rapidly from a black deposit rank of nine to a rank of twelve, then decreased to eleven until very high current densities were reached when its rank changed back to twelve again. With increased current density in the high pH Watts type solution the rank of iron increased from ten in the low current density, black deposit region to twelve at higher current densities.

8. Lead.

a. The concentration ratios for lead decreased as the current density increased; the deposit's concentration varied from one to three times the solution concentration.

b. In general, the concentration ratio was higher the higher the pH of the solution; the chloride type solution had an apparent pH value between the values of the low pH Watts and the organic type solutions in the low and medium current density regions, and between those of the organic and the high pH Watts type solutions at high current densities.

c. The higher chloride concentration and the presence of the organic constituents tended to increase the rate of deposition of lead.

d. In general lead's rank had a minimum value of eight at moderately low current densities, the rating increased from this value with either an increase or a decrease in current density, except in the low pH Watts type solution where it remained constant with a decrease in current density. Lead had a maximum rank of eleven at a very high current density in the chloride type solution and at a very low current density in the two highest pH solutions.

9. Magnesium.

a. The concentration of magnesium in the deposits varied from one- to fourteen-hundredths of its concentration in solution. The ratios were nearly constant at low and moderate current densities, but tended to increase with an increase in current density, the rate of increase being greater, the higher the pH.

b. The concentration ratios increased with an increase in pH; the chloride type solution had an apparent pH located between those of the organic and the high pH Watts type solutions.

c. The high chloride concentration favored a more rapid deposition rate for magnesium.

d. Magnesium had a rank of two at all current densities and for all solutions except for a rank of three in the high pH Watts type solution at very low current densities where a black deposit was obtained.

10. Manganese.

a. The concentration of manganese in the deposit varied from three- to sixty-hundredths of its solution concentration. The ratios were practically constant in the low and moderate current density regions; in the high current density region the ratio increased with an increase in current density, the rate of increase was greater the higher the pH of the solution.

b. The high pH Watts type solution had higher concentration ratios than the low pH Watts type solution.

c. At low and moderate current densities the organic constituents increased the rate of deposition of manganese sufficiently to give the solution an apparent pH higher than that of the high pH Watts type solution. The high chloride concentration improved the deposition rate of manganese sufficiently to yield higher ratios than those found for the low pH Watts type solution.

e. The rank of manganese which varied from three to five was three in the two lowest pH solutions. In the organic type solution the rank

increased from three at very low current densities to four at higher current densities. Its rank was three except at very high and very low current densities in the high pH Watts type solution where its rank was five. Thus, at very low and very high current densities, manganese's rank increased with an increase in pH; at current densities in the region between, its rank was three except for the organic type solution where its rank was four.

11. Silicon.

a. The concentration of silicon in the deposits varied from two-tenths to twice its solution concentration. The ratios increased with an increase in current density for the Watts type solutions. The chloride and the organic type solution ratios decreased with an increase in current density up to one amp./dm.^{2}; above this current density the chloride type solution's ratios continued to decrease slightly, while the organic type solution's ratios increased with increased current density.

b. An increase in pH yielded a higher concentration ratio for the Watts type solutions. The apparent pH order placed the organic type solution the highest, the chloride type solution next followed by the high pH and then the low pH Watts type solutions.

c. The high chloride concentration and the organic constituents increased the relative amounts of silicon in the deposits, especially at lower current densities.

d. The organic type solution had a minimum concentration ratio at moderate current densities.

e. Silicon's rank was six in the medium current density regions except in the high pH Watts type solution where it had a rank of five in the moderate and high current density regions. It had a low rank of four at very high current densities in the high pH Watts type solution and it had a high rank of nine at a very low current density in the chloride type solution.

12. Zinc.

a. The concentration of zinc in the deposit varied from three-fourths to twice its solution concentration. The concentration ratios were constant or tended toward a maximum in the low current density regions; however the ratios decreased with increased current density in moderate and high current density regions.

b. Excluding the chloride type solution, the ratios increased with an increase in pH. The apparent pH location of the chloride type solution ratios varied from the lowest pH location at very low current densities to a location between the low pH Watts type solution and the organic type solution at low and moderate current densities. At high current densities its ratios were between those of the organic and the high pH Watts type solutions.

c. The high chloride content increased the rate of deposition of zinc as the current density increased.

d. The zinc ratio had a maximum value in the organic and in the chloride type solution; the maximum value was higher and the current density location of the maximum was lower in the higher pH solution.

e. Zinc had ranks of seven or eight at all current densities and for all solutions except in the high current density region of the chloride type solution where its rank was nine.

In the high pH Watts type solution the relative amount of an impurity found in the black deposit decreased with increased current density for aluminum, iron, lead, manganese, and silicon; remained constant for copper, magnesium, and zinc; and increased for boron, cadmium, calcium, and cobalt.

Copper, lead, boron, cadmium, and zinc were found in larger relative amounts in the black deposits than in the adjacent non-black or regular deposits; aluminum, cobalt, magnesium, manganese, iron, and calcium were found in smaller amounts.

The order of impurities arranged according to their increasing deposit-solution concentration ratio values in the black deposit obtained at a current density of 0.11 amp./dm.^{2} from the high pH Watts type solution was boron, calcium, magnesium, aluminum, manganese, silicon, cobalt, zinc, cadmium, iron, lead, and copper; for the black deposit obtained at a current density of 0.12 amp./dm.^{2} from the organic type solution the order was changed so that boron followed manganese, aluminum followed silicon, and cadmium followed iron.

The per cent concentration values listed in Tables 14 and 17 for the black deposits refer to the amount of impurity deposited per coulombic equivalent of one hundred grams of nickel deposit. Since the amount of nickel present in the deposit was considerably lower than that

in the adjacent regular deposits, a comparison of the orders of the impurities, arranged according to the increasing deposit-solution concentration ratio values, between a regular deposit and an adjacent black deposit should show how the various impurity depositions were affected by the codeposition of nickel, assuming that the deposition potential of the impurities was exceeded in the adjacent deposits and that the change in potential existing at the time of deposition between the two areas was not sufficient to cause a change in their order. On this basis, we can say that the relative amount of aluminum, calcium, cobalt, iron, and manganese (in the organic type solution) depositing was increased by the co-deposition of nickel.

As has been mentioned previously, there is a linear relationship between the deposit and solution concentrations for several impurities. From this it would seem that the time rate of change of concentration of an impurity in solution due to electrodeposition should be directly proportional to the concentration. Although no electrodeposition rates were carried out as such in this research project, data published by Rominski (4), Clark (5), Ewing, Brouwer, Clark, Owen, Rominski, and Werner (32) were found to conform to this concept when the impurities had a solution concentration of more than ten milligrams per liter. As a deposition rate constant could be expected to be a definite value only for a certain set of electrodeposition conditions, we will discuss only the general trends established by our work rather than state specific values.

In general the time rates of deposition for the impurities increased as the current density increased. Several exceptions to this general trend occurred in that there was a maximum or a nearly constant rate at low or moderate current densities with the rate increasing again at higher current densities, thus obtaining a type of inverted S-shaped curve, if the rates were plotted with respect to current density. A minimum deposition rate also occurred.

Copper had a maximum rate of deposition in the lower current density regions; the maximum was located at a higher current density with a lower pH of the solution. It was also observed that the copper deposition rate was the highest at the current density where no nickel, comparatively speaking, deposited from the two highest pH solutions. This follows an observation by Fink and Rohrman (15) that the maximum removal of copper occurs between the point where nickel deposition stops and the point where the concentration effect of hydrogen ions comes into play.

The same general type of deposition rate curve is found for iron as for copper, except that the rates are higher than those for copper in the high current density regions. As in the case of copper, the location of the maximum with respect to current density decreased with an increase in pH; however, the maxima for the two lowest pH solutions were at somewhat higher current densities than those for copper, while the maxima for the two highest pH solutions were at somewhat lower current densities. Iron, as compared with copper, deposited at a lower, rather than higher rate when nickel deposition effectively stopped.

There was a noticeable increase in the rate of deposition of lead, similar to the case of copper, when nickel effectively stopped depositing. However, no maximum was present in the rate-current density curve when regular nickel deposits were obtained.

Boron and aluminum had a minimum deposition rate for the organic solution only at a current density of about four-tenths amp./dm.^{2}

Cobalt had no maximum rate but there was a leveling off in the deposition rates at a current density somewhat higher than where the maxima occurred in the iron deposition rates.

Relative energy efficiency calculations, assuming the resistance of the cell to be constant over the current density range concerned, indicated that, in general, there was a decrease in energy efficiency of impurity deposition with an increase in current density.

Cobalt and iron had maximum energy efficiencies in the low current density region of the two lowest pH solutions, and iron had a minimum efficiency at a moderate to a high current density in the two highest pH solutions. The maxima of cobalt and iron, and the minima of iron decreased in their current density location with an increase in the pH of the solution.

It is known that the effective resistance to the passage of current through the bath increases with increased durrent density (1,33). This would alter the relative energy efficiency values so that the rate of decrease in the energy efficiency for impurity deposition with increased current density would be increased, or in other words, higher relative energy efficiencies would be obtained at lower current densities than the previous discussion might indicate.

SUMMARY

The cathodic current efficiency decreased as the pH of the solution increased due to the presence of the impurities in the solutions. This trend is the reverse of what is generally found with less contaminated solutions.

In the lower current density region the nickel deposition efficiency decreased as the current density decreased.

The composition of the precipitate formed in the higher pH cathode layer is about what one might expect from solubility measurements made in similar solutions at various pH values.

The iso-current density curves on an inclined cathode showed that the regions of the cathode which were more distantly located from the anode had lower current densities, except when proximity to an edge or corner partially counteracted the distance relationship.

It was found that with increasing current density the deposit-solution concentration ratio values were generally nearly constant or increasing for aluminum, calcium, magnesium, and manganese; for cadmium, copper, and lead the ratio values either were nearly constant or decreasing. A maximum concentration ratio was found for cobalt, iron, and zinc; a minimum ratio for aluminum, boron, and iron. In general the larger value for the maximum or minimum was obtained from the higher pH solution and was at a lower current density, cobalt being an exception.

For the Watts type solutions an increase in pH resulted in an increased concentration ratio for aluminum, boron, cadmium (high current densities), calcium, copper, iron (low and high current densities), lead, magnesium, manganese, silicon, and zinc; a decreased ratio for cadmium (low current densities), cobalt, and iron (around 0.75 amp./dm.^{2}).

The high chloride concentration resulted in an increase in the concentration ratio for aluminum, boron, cadmium, calcium, copper (low current densities), lead, magnesium, manganese, silicon, and zinc; a decrease in the ratios for cobalt and iron.

The presence of the organic constituents resulted in an increased ratio for aluminum, boron, iron (low current densities), lead, manganese, and silicon; a decreased ratio for calcium.

The codeposition of nickel increased the concentration ratio for aluminum, cobalt, magnesium, manganese, iron, and calcium; it had no effect or decreased the ratio for copper, lead, boron, cadmium, and zinc.

In general there was a continuous increase in the deposition rates of the impurities with increasing current density. Copper and iron had maximum rates in the low or moderate current density region, and then in the high current density region the rate increased with increasing current density. Cobalt's rates were similar except that a nearly constant rate rather than a maximum was obtained at slightly higher current densities than the maxima in the iron curves. A minimum deposition rate occurred for aluminum and boron from the organic type solution.

The current density location for the maximum in the rate curves for copper and iron decreased with an increase in the pH of the solution.

In general it was found that the energy efficiency of impurity deposition decreased with an increase in current density. Cobalt and iron had a maximum energy efficiency in the low current density region of the two lowest pH solutions, iron had a minimum efficiency in the two highest pH solutions. The current density location of the maxima and minima decreased with an increase in the pH of the solution.

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