

THE ELECTROCHEMICAL DEPOSITION OF MANGANESE FROM AN AQUEOUS SOLUTION

Thesis for the Degree of M. S. MICHIGAN STATE UNIVERSITY James Irvie Hoffman III 1965





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ABSTRACT

AN ELECTROCHEMICAL DEPOSITION OF MANGANESE FROM AN AQUEOUS SOLUTION

by James Irvie Hoffman III

Manganese nodules have been found extensively in large areas of many of the ocean basins. The majority of the nodules have been found in the deeper areas of the sea and in connection with basic volcanic materials.

There have been several theories put forth concerning both the source of the manganese and the method of its accumulation. The validity of many of these theories has not been proved and several theories have been disproved. The electrochemical theory of extraction has been tested in this work an proven to be a possible means of deposition for the ferromanganese parts of the nodules. This method is similar to the electroplating action of an electric cell; it is not to be taken as the only means of deposition for the manganese, but as a working principle, that with other processes, may yield the manganese nodule as the end product.

A linear relationship has been established and has been extrapolated to those conditions which could occur in nature. The rate of accumulation is on the order of 10^{-7} grams per hour per 80 square mm. The driving force for the electrical potential in nature would be onedirectional currents resulting from submarine vulcanism.

THE ELECTROCHEMICAL DEPOSITION OF MANGANESE FROM AN AQUEOUS SOLUTION

Вy

James Irvie Hoffman III

A THESIS

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TABLE OF SYMBOLS

(H)	•	•	•	٠	surface area factor (0.0200) grams
(G)	•	•	•	•	weight loss due to handling (0.00079) grams
(#)	•	•	•	•	electrode number
(W)	•	•	•	•	plated weight in grams
(V)	•	•	•	•	voltage
(A)	•	•	•	•	current in amps
(T)	•	•	•	•	time in hours
*(0/00)) 。	•	'n	o	salinitygram weight of solid material added to 1000 ml. of water
*(S)	•	•	•	٥	test solution
(P)	•	•	•	2	pole of the electrode (positive or negative)
(<u>x</u>)	•	a	•	o	low concentration
(\overline{X})	•	٥	٥	o	high concentration
(X)	•	•	•	•	average concentration
(X*)	•	ø	J	•	trace concentration
(X**)	•	•	•	•	identification questionable

*The exact chemical composition for each group of salinities appears at the top of each table, or preceding the data for the respective solution. The symbol (S) stands for test solution. EXAMPLE: $S = 23.00 \text{ NaCl} + 3.00 \text{ MnCl}_2 / 1000 \text{ H}_20$ This corresponds to a salinity of 26.00.

CHAPTER I

INTRODUCTION

Ferromanganese oxide minerals have been found concentrated in the pelagic sediments as either coatings or potato sized nodules in the ocean basins and on plateaus around the world. There has been a great deal of speculation as to the origins of these concentrations with particular interest in the formation of the manganese nodules.

The problems surrounding the manganese nodules must deal with the source of the manganese, the methods of accumulation, their structure and mineralogy, and their geographic distribution.

The composition of the nodules varies from place to place, but almost all of them contain iron (6.0 - 20.0%)manganese (11.0 - 25.0\%), with nickel, cobalt, and copper accounting for another 3%. The above elements are largely in the oxide form, with the remaining portion of the nodules being a light colored material consisting mainly of phillipsite. Reference to the mineralogy and chemistry of the nodules may be found in Mero (1962), Willis and Ahrens (1962), and Pachadzhanov (1963).

The source of the manganese has been theorized to be from submarine vulcanism or from continental erosion. Most of the high concentrations of the nodules have been found in areas of submarine vulcanism, and this would be a ready source of manganese. References concerning the source may be found in Bonatti and Nayudu (1965), Pettersson (1959), Rovou and Ermishkima (1959), and Rubin (1954).

The structure of the nodules is rather constant considering the wide geographical distribution and the different oceanic environments. Most are layered structures around some central core of a hard material, such as shark teeth, whale ear bones, and zeolites. Detailed analysis of individual manganese nodules may be found in Goldberg (1954), Willis and Ahrens (1962), and a more qualitive analysis in Bonatti and Nayudu (1965).

The rates of accumulation have been and are still disputed, as is most of the manganese problem; and no good overall explanation has yet been obtained. The most frequently given data on accumulation rates is lmm/1000 years, Goldberg (1954). This seems too low in most cases, for the nodules would be buried before they could form.

CHAPTER II

THE EXTRACTION OF MANGANESE FROM SEA WATER

The theories dealing with the accumulation of ions and compounds into the structural materials that make up the nodules are many and varied. These theories may be classified under three different headings: biologic, inorganic, and electrochemical.

The biologic theory was one of the first proposed when the nodules were discovered by the Challenger expedition in 1891. The first good biologic theory stated that manganese might be extracted from sea water by certain types of foraminifera and then be depostied after their death. This theory does not explain the formation of nodules and the rate of accumulation could not account for the observed concentrations. Graham (1959) built the best case for a biologic deposition by pointing out the organic remains in some of the nodules. This theory was disproved by close examination of the organic matter; a lack of peptide bonds between the amine acids was discovered. Ecnatti and Nayudu (1965) are convinced that the organic material had been absorbed, not grown in place.

The inorganic theory as proposed by Kuenen (1950) advocated straight precipitation from sea water.

In areas of the sea where rates of accumulation of bottom sediment were low the manganese concentration would be greatly enriched. The trouble here is that again the formation of individual nodules was not explained, nor was a mechanism described for the precipitation of manganese which has concentration of 1 - 10 ugr./liter in sea water.

The author agrees that there is a lack of evidence to support these other theories and, therefore has turned his attention to the electrochemical theory first postulated by Goldbery (1954). This original theory assumed the manganese and iron to be in a colloidal suspension in the sea water. These charged colloidal particles could then be attracted to any hard object projecting above the ocean floor. Currents such as tidal currents, moving parallel to the ocean floor and the horizontal component of the earth's magnetic field, would establish a potential on these natural electrodes and plating would take place.

Four years later Goldberg and Arrhenius (1953) revised this original theory for two reasons. The manganese was found to exist mainly in solution, not in the colloidal form and tidal currents were thought to provide the necessary potential for accumulation. The new version of the electrochemical theory concerned the catalytic action of the iron colloid at the oxygen rich

boundary of the sediment and water. The iron hydroxide gel would act as a catalyst to oxidize divalent manganese in solution to the tetravalent state which would combine with the available oxygen to form manganese dioxide. The resulting composition of the two layered structure concurs with the analysis of most of the nodules.

Keeping with the above discussed theory a onedirectional current would be a relatively powerful natural extraction device. The presence of some of the other scarce elements, such as copper, nickel, and cobalt, in relatively high concentrations (1% compared to their sea water concentrations (1 ugr./liter) has been attributed to the ability of both manganese and iron to scavenge these ions from solution. This scavenging effect was a part of the original electrochemical theory, and the revised theory held that scavenging could play a significant part in the accumulation of the less abundant elements.

CHAPTER III

ELECTROCHEMICAL DEPOSITION OF MANGANESE

The electrochemical theory as revised by Goldberg and Arrhenius (1958) was used as the basis for this experiment. Working with high concentrations of manganese chloride dissolved in deionized water showed no colloidal tendencies for manganese in the preliminary analysis. Experimental solutions of iron sulfate did indicate that some of the iron would exist in the colloidal state. No quantitative relationship was established for the relative percentages of iron hydroxide gel vs. ionic iron in solution, since this would be a function of the other ions in solution.

Both iron hydroxide gel and manganese ions have a positive oxidation potential, and thus would be expected to collect on the cathode in an electrolitic cell. Experimentation was designed to yeild an excess number of negative electrodes with enough positive electrodes to act as a check.

The scavenging effect as predicted in the original electrochemical theory was also tested for several ions, such as copper, cobalt, and nickel. By adding minor amounts of the trace elements often found in the manganese nodules to the test solutions, this selective absorbtion

effect was checked. The scavenging effect involves the attraction of a positive or negative charged particle for one of the opposite charge. Two particles of opposing charge would act like the north - south poles of two magnets. Since the manganese and iron hydroxide are both positively charged, they would be expected to attract the negative ions. Nickel, cobalt, and copper are also positively charged, so the scavenging effect should not take place. This repulsion effect that two positively charged particles would show was recognized in the revised electrochemical theory and the scavenging effect was questioned, but not disallowed.

The overall problem dealing with the formation of the manganese nodules has been shown to be very broad; therefore, only one aspect was undertaken in this research: that concerned with the process of accumulation or growth of the nodules. Through the use of electrolytic cells, an attempt was made to grow manganese oxides from solutions similar to those found in nature. Curves have been plotted which allow extrapolation to those realms of electrical energy compatible with those that might be found in nature.

CHAPTER IV

EXPERIMENTAL PROCEDURE

The experimental apparatus was designed to yield sustained low voltages and amperages over a long period of time, operating on direct current. Consideration was initially given to the use of batteries as a power source. The large storage batteries of low voltage were found to produce a very high amperage (140+ amps), and this would have required the extensive use of resistors. Smaller batteries would yield the necessary amperage, but their life was limited to a short period of time. A 120 volt built in power source was finally elected because it was of low energy and showed no deterioration with time; however, the power source was not steady.

The basic electroplating apparatus is diagramed in Plate I. Two capacitors were wired in parallel to stabilize the current, reducing the current variation from 0.5 amps to 0.05 amps over a 24 hour period. Voltage fluctuations were held to 0.1 volts.

The cores of the nodules found in nature would all have a high resistance; therefore, carbon electrodes were chosen for this experiment because of their high resistance. The purity of the carbon electrodes insured

that a minimum of unknown or undesirable ions would be introduced into the analysis, they were easy to handle, the surface area variation could be kept to a minimum, and direct spectrochemical analysis was possible. Each electrode was pointed and immersed into the test solution to a depth of 8mm. This part of the experiment contained the most error, for no accurate way of determining the rate of evaporation of the solutions or the exact surface area of each electrode could be calculated.

In preparation, each carbon rod was washed with deionized water several times, dryed thoroughly in an oven, and then weighed. Following plating, the electrodes were again washed and soaked in deionized water to remove any of the test solution from the interior of the rods. They were dried and their weights recorded. Accuracy in this part of the experiment was again affected by the handling of the soft carbon rods.

The initial experimentation was carried out with solutions of manganese chloride in distilled, deionized water to determine if manganese would plate out from solution. From this data an attempt would be made to determine some rate of accumulation based on various voltages and amperages. The amperage and the voltage were found to vary directly, i.e. a voltage drop would be effected by a drop in amperage. This was anticipated from the work equation: power = voltage times amperage.

Once the ability to extract manganese from a concentrated solution was established, the concentrations were reduced to one part of manganese chloride per thousand parts of water. After it was known that manganese could be extracted from dilute solutions, the experimental solutions were graded into a basic sea water mixture. The final stages of testing were undertaken with solutions approaching that of natural sea water.

Several drawbacks were encountered which should be corrected before further work of this type is done. The water used was not completely deionized: it was found to contain a relatively large percentage of calcium. The calcium ion, which is highly electropositive, was probably plated preferentially to the manganese, or at least along with the manganese. The presence of an unknown amount of calcium affected the weights used in calculating the rate of manganese deposition. The instruments used were not sufficently accurate at the low currents, and thus extrapolations from higher current measurements had to be made. The abnormal behavior of electrolytic solutions increases with increased currents so that extrapolation may not be exact.

CHAPTER V

EVALUATION OF EXPERIMENTAL RESULTS

The first experiments were carried out using aluminum and copper electrodes. The action of the chlorine liberated during the reaction at the anode created an acid solution which consumed the electrodes before any plating could take place. To counteract the action of the hydrochloric acid created during the reaction, a thin coating of petroleum jelly was placed over the electrodes. This allowed enough protection for some plating to take place. Plate II is a picture of the electrodes following plating.

The dark brown plated material was washed, dried, removed from the electrodes and subjected to x-ray analysis. Table 1. shows the composition of the solutions used for testing, and the electrical conditions under which plating took place. The resulting pictures were entirely unsatisfactory. The lines that were visible on the film were both too dark and too few in number for any evaluation. It was concluded that the sample would need to be collected over a period of at least a week, and the best available electrode (copper) with the protective measures would not last more than 15 hours.

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1.	100.0	27.50	0.26-0.36	9.00-9.70	0.00715	(+)	Brown coating
.4	100.0	27.50	0.26-0.36	9.00-9.70	-0.00113	-)	consumed by acid
1.0	53.30	24.00	0.06-0.12	6.92-6.88	0.00207	(-+)	Brown coating
	53.30	24.00	0.06-0.12	6.92-6.88	-0.00041	-+)	consumed by acid
1.7	134.8	66666	0.10	8.38	22222222	(+)	consumed by acid
1.8	134.8	66666	0.10	.38	22222222	+)	consumed by acid
1.9	134.8	15.00	0.10	3.10	0.00013	(+	dark brown coating
1.10	134.8	15.00	0.10	3.10	-0.00080	-)	consumed in part
1.11	134.8	30.00	0.00-1.20	9.00	-0.00506	(+	consumed in part
1.12	134.8	30.00	0.00-1.20	9.00	-0.00506	-)	consumed in part

TABLE 1.--S = X grams MnCl₂/1000 H₂0

The plated material has not been identified precisely, but the color, lack of solubility, and specific gravity (3.8 - 4.1) would indicate that it is the desired manganese oxide, probably in a hydrated, partially amorphous form. The following are specific gravities that the residue could have, depending on what it was:

manganese chloride MnCL₂ ---- 2.997 manganese oxide MnO₂ ---- 4.75 MnO --- 5.44 MnO(OH) -- 4.2 - 4.4

iron oxide Fe) \cdot (OH) - 3.6 - 4.1 The test solutions used in this part of the experiment did not contain any iron; therefore, the plated material must have been manganese, probably in the hydrated form.

The fact that the manganese found in the analysis was not due to the adsorption by the electrode from the solution was shown by electrode (1.2) (Table 1). This carbon electrode was placed in a high concentration of manganese chloride solution for twenty hours with no applied electrical current. No deposition was measured, and only calcium was detected in the spectrochemical analysis. Electrode (1.1) was placed in the deionized water and then analyzed. The calcium was again discovered, which showed that the deionized water contained calcium.

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1000
Mncl ₂ /
grams
×
H
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!
N
TABLE

Remarks	Ma, Ca, Al, Sr	6 6>> 6>	Mn, Ca, Al, Sr Mr Cr Al Sr	Mn, Ca, Al, Sr Mn, Ca, Al, Sr Mn, Ca, Al, Sr Mn, Ca, Al, Sr Wn, Ca, Al, Sr	Mn, Ca, Al, Sr Mn, Ca, Al, Sr	Mn, Ca, Al, Sr Mn, Ca, Al, Sr	Mn, Ca, Al, Sr Mn, Ca, Al, Sr	Mn, Ca, Al, Sr Mn, Sr Mn, Sr	Mn, Ca, Al, Sr Mn, Sr Mn, Sr Mn, Sr Mn, Sr
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14.00 14.00 23.50 23.50 23.50 23.50	23.50 23.50 25.50 25.50	25.50 25.50		21.25 21.25 13.50	25175 25.75	45.00 15.00	15.00	15.00 15.00 15.00	17.00 887.00 880.00 880.00 80.000 80.000 80.000 80.000 80.0000 80.0000 80.0000 80.00000000
84.80 84.80 94.35 94.32	94.35 94.32		94.35 94.35	,	33.35 33.35 33.35	????? 13.63 08.97	10.02	08.14 08.14 08.14	08.14 08.14 08.14 05.12 02.54 02.55
	55 55	0 m-t				111 111	2.16	2.16 2.17 2.18	2.16 2.19 2.19 2.20 2.21 2.21 2.21 2.21 2.21 2.21 2.21

The use of electrical current would increase its adsorption for the oxidation potential of the calcium ion is higher than that of the manganese ion, and thus the former would be expected to be depostied more easily than the manganese. The results show that more calcium is often deposited than manganese. The extraction of strontium and aluminum was expected because of their high oxidation potential, and their presence in the manganese chloride used in making the test solutions.

Table 2 is a group of experiments carried out using only MnCl₂ and water. The aim of this series of tests was to determine the currents and potential conditions under which manganese could be plated. The tests were designed to grade from high potentials and high concentrations of manganese chloride ot low concentrations and low potentials. An excess number of negative electrodes were also used. Since a positive electrode might be used several times, the exsposure time for several electrodes is high (2.13, 2.22).

The manganese found on some of the positive electrodes may be due to colloidal manganese produced by the high concentrations of manganese in solution. The manganese sol would be attracted to the positive electrode, but weight of plated material and the semiquantitative s spectrochemical data shows in most cases a smaller concentration of manganese on the positive electrode then

TABLE	3 . S = 5.	.0066MnCl2	o + 9.9368 Nac	11 + 0.4852 KC	1 / 1000 li ₂ 0	0	
#	0/00	EH	Λ	A	м	<u>с</u> ,	Remarks
⊣ « m mmm	15.43 15.43	24.00 34.00	0.05-0.06 0.05-0.06 0.05-0.06	9.77-9.85 9.80-9.90 9.77-9.90	0.00185 0.00185 0.00126	$\left(\begin{array}{c} \\ - \\ \end{array}\right)$	Mn, Ca, Al, <u>Sr</u> Mn, Ca, Al, Sr Mn, Ca, Al, Sr
	1685 50. 12.10 12.10 12.10	12.50 07.50 12.50 20.00	1. 50 Macci 2 + 0.06 0.06		0.60 KG1 / 1 0.00010 -0.00004	(+) (+)	Mn, Ca, Al,* Sr Mn, Ca, Sl,* Sr Ca,
	Test Sol	lution = (0.50 MnCl2 + 1	0.00 NaCl + 0	.50 KC1 /100	ο ² Η ο	
	11.00 11.00 11.00	6.00 3.00 9.00	0.02 0.04 0.02	9.65-9.70 9.70 9.65-9.70	0.00008 0.00038 -0.00053	$\overbrace{-}^{+}$	Mn, Ca, <u>Sr</u> Mn, Ca, <u>Sr</u> Mn, Ca, <u>Sr</u> *
	Test Sol	lution = 0	0.10 MnCl ₂ + 1	3.00 NaCl + 1	.00 KCl / IC	00 H ₂ 0	
3.10 3.11	14.10 14.10	6.00 6.00	0.04	9.80 08.0	0.00074 0.00039	(+) -)	Mn, Ca, Sr Mn, Ca
3.12 3.12	14.10 14.10	3.00 3.00 3.00	0.05 0.05 0.05	9.9 • 8 8 8 8	0.00065 0.00055	(+) -)	Mn, Ca, Al, Sr Mn, Ca, Al, Sr

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on the negative electrode. This effect was not noticed until other ions had been introduced into the test solutions. Sodium and potassium ions may have caused an interaction with the manganese, reducing the colloidal effect the occured when these other ions were not present. Table 3 shows the effect of the added ions when compared with Table 2. (remarks).

If the manganese was partially collodial, then the negative charge of the manganese sol would attract the highly electropositive calcium, aluminum, and strontium ions and would cause these ions to be deposited along with the manganese on the positive electrode. This action which is called scavenging is an example of the scavenging effect that was thought to be a part of the electrochemical theory.

Table 3 represents the beginning of the series of tests that graded into test solutions similar in composition to natural sea water. The tests were made at moderate electrical potential,s with salinities less than those but found in sea water with a higher concentration of manganese. The effect of the added ions on the plating of manganese is indicated in the remarks. The manganese extracted on the positive electrode was greatly reduced or missing, while the manganese plated on the negative electrode was increased.



In order to arrive at some idea of the size of the potentials and currents which might operate in a marine environment, a series of plots were made, and curves were extrapolated to a zero value (current in amps or potential in volts) below which the energy would not be great enough to allow extraction to take place.

Figure I shows a plot of the weight/time vs. the voltage for the negative electrodes from Tables 2 and 3. Since the voltage could not be accurately obtained by the available instruments, the plot was erratic.

Later more accurate low electric current data was not included in this plot. The number beside the points in Figure I indicate the respective electrodes for those points. Since there is no grouping from the effect of the solutions, then it may be assumed that there was no group of plots for an experimental group. The points were labled so that the reader may follow their plotting from the Tables. The future graphs will not be so labeled. Reference to the voltage or current will allow the reader to see which point corresponds to which negative electrode.

The voltages used in Figure I were all less than 0.08 volts. The first samples were run at high potential values, greater than <u>0.10 volts</u>, and the results obtained were not considered to be accurate due to the large

TABLE 5.--

		Sr	Н2О	Sr	H20	Sr	Sr	
	arks	A1 A1 <u>A1</u> ,	000	<u>A1</u> ,	000	A1, A1,	A1* A1*	
	Rem	Ca, Ca,	12/10	ပ် က က က က က	12/1	Ca, Ca,	Ca, Ca,	
		Mn, Mn	MnCJ	Mn, Mn	MnCl	Mn,	Mn,	
			.50		.10			
	പ	(+)	+	- +	+	(+ -	(+)	
			KCI		KCI			
	М	0630 4333 0159	0.72	1686 0280 0158	0.72	0430 0011	0178 0010	
			+ ~	000	+ N	00	00	
		0 0	cacı	LU ا	CaCl			
	А	0.0 0.0 0.0	.15	-9.6	15	60	0 0 0 0	
		9.50 9.50	г-1 +	9.80 9.00 9.00	1 +	<u>00</u>	თთ	
			g S04		g S04			
Н20		0.08 00.08 0.08	ъ5 М	13 10 0.10	25 М	880	04 04	
000		.10- .10-	+	•13-	т т	00	00	
Т 		0 0	Сlг	0	Cl ₂			
ncla	E		0 Mg		0 Mg		000	
ы С С		てら で て	2°	8 8 8 8 8 8 8 8 8 8 8 8 8 8 8 8 8 8 8	5° 8	цц	mm	
o		000	C1 =	000	C1 +	N N	20 0	
	00/0	555 555 555	0 Na	000 ••••	0 Na		м М С С С С С С	
			26.0		26.0			
	#	005 744	20 II	500 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5	וו וו	4.7 4.8	4.9 4.10	

TABLE 4.--S = 15.00 NaCl + 2.00 MgCl2 + 2.00MgSO4 + 1.00 KCl + 1.00 CaCl2 +

polarization effect that occurs at the higher voltages. This polarization effect will be considered near the end of this section.

The effect of added ions other than manganese was shown to have a noticable result in the manner in which the ions were removed from the solution. Table 4 is a continuation of this line of testing adding those ions which are principle constituants of sea water. The salinity of the test solutions were increased to that of natural sea water (33.00-34.00). These tests were carried out at moderately high electrical currents. The results show that again the manganese was concentrated on the negative electrode when compared to the positive electrode. No plots were made from this table because of the high current used in plating.

Table 5 represents the tests made with the artifical sea water solution, and low amounts of MnCl₂. The experiments were conducted at moderate currents to insure the extraction of manganese. The results show that manganese was plated when introduced in small quantities, and was concentrated on the negative electrode. The absence of manganese of the positive electrodes (5.4, and 5.8) determined the course for the rest of the experiments and justified the deleting of the higher current values from the figures. The lower the current, the greater would be the approach to natural conditions.

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#	00/0	Ы	Λ	А	M	Ч	Results
S: = Y	+ 0.02 Zn	so4 + 0.02	MnCl2 / 100	0 Н20			
50 00	34.55 34.55	6.00 6.00	0.02 0.02	8.7-8.80 8.7-8.80	0.00373 -0.00128	(+) -)	Mn, Ca Mn; Ca
S: = Y	+ 0.023601	1.504 + 0.0	276 MnCl2 /	1000 H ₂ 0			
	34.55 34.55	6.00	0.02	8.70 8.70	0.00220 0.00029	(+))	Mn, <u>Ca</u> Mn ; Ca
S = Y	+ 0.02 Na ₂ (3r207 + 0.	0233 MnCl2 /:	1000 H ₂ 0			
<u>ол</u>	34.55 34.55	5.00	0.024 0.04	<i>b</i> [⊤] c 8.70 8.70	0.00390 -0.00084	$\begin{pmatrix} + \\ - \end{pmatrix}$	Mn, Ca <u>Mn</u> , Ca
S = Y	+ 0.026 Ba(31 ₂ + 0.02	06 MnCl ₂ /100	о ^с н ₂ о			
N-00	34.55 34.55 e	5.00	0.02 0.02	8.60 8.60	0.00198 -0.00083	$\begin{pmatrix} + \\ - \end{pmatrix}$	Mn, Ca Mn, Ca
S = Y	+ 0.01 FeS(04 + 0.018	MnC12 /1000	Н20			
	34.55 34.55	5.00	0.02	8°00 8°00	0.00333	(+) -)	Mn, Ca, Al, Sr Mn, Ca
2 1 2 1 2 1 2	+ 0.05 MnC: 026 FeSO4 ,	l2 + 0.018 / 1000 H ₂ 0	ZnSo4 + 0.0	2 cuso4 + 0.(003 Na2Cr207	+ 0.015	BaCl2 +
	3333 44. 555 555 555 555 555 555 555 555 555	6.00 20.00 20.00	0.01 0.01 0.01-0.00 0.01-0.00	00000 00000 00000	0.00091 -0.00130 0.02235 -0.00077	$\overbrace{}^{+}$	Mn, Ca, Sr* Mn , Ca, Sr* Mn, Ca, Al, Sr* Ca, Al, Sr*

Tables 6 through 9 contain the data for the most accurate and the most important phases of the experiment. Low currents of less than nine amps were used in all of the tests, and many different elements were added to the aftifical sea water to test for the scavenging effect and for possible interactions with the manganese ion.

Table 6 shows the first of the major changes in the results. Aluminum and strontium were not detected in the spectrochemical analysis. Since aluminum and strontium is an impurity in the MnCl₂ and the concentration of the added $MnCl_2$ was reduced to 0.02 grams, the number of aluminum and strontium ions present in the solutions were not high enough to be plated in detectable amounts. When ${\rm FeSO}_4$ was added (6.9 - 6.14) the aluminum and strontium which were present in the FeSO4, and many of the other added salts, were again present in high enough concentration to be detected. The amount of MnClo salt added in the experiments recorded in Tables (7-9) was high enough to insure the presence of aluminum and strontium in the results. The calcium contamination of the washing solution insured the presence of this ion in all the results. The concentration of manganese was always greated on the negative electrode when compared to the positive electrode.

Tables (6-8) show an increasing number of trace elements added to the test solutions and Tables (8-9)

TABLE	<u>/</u>							
#	0/00	E	Λ	A	Ņ	<u>с</u> ,	Remarl	KS X
Let Z : 1S =	= 3.26 MgSC 0.104 NaN = 27.00 NaC	14 + 2.30 03 1 + 0.124	MgCl2 + 1.16 MnCl ₂ + 0.6	6 cacl2 + 0.7 013 Sncl2/100	2 KCl + 0.198 0 H ₂ 0	3 caco3	+ 0.092 Na2B	+ Lot
7.1 7.2	33.90 33.90	6.00 6.00	0.005 0.005	ກ.ກ • . ຍ ຍ ຍ ຍ	0.00000 -0.00030	(+) -)	Mn, Ca, Al Mn, Ca, Al	k Sr¥Fe* Sr`s
2S :	= Z + 26.00	NaC1 + 0	.10 MnCl ₂ +	0.013 SnC1 ₂	+ 0.013 Co(NC	3)2 + C	.02 HgCl ₂ /100	00 H ₂ 0
7.57	33.98 33.98 33.98 33.98	16.00 16.00 6.00	0.000 0.000 0.015 0.015	66 JJ 66 JJ 700 77 700	0.01065 -0.00231 0.00135 -0.00028	$\overbrace{}^{1}+\overbrace{}^{1}+$	Mn, Ca, Mn, Ca, Mn, Ca, Mn, Ca,	555 552 555 55
 ນ	= Z + 26.00 • 0.02 • K2(S	NaCl + 0 2 FeSO4 + 04)•24H ₂ 0	.101 MnCl2 0.02 Bac12 /1000 H20	+ 0.005 SnCl ₂ + 0.013 ZnSO	+ 0.019 Co(N 4 + 0.015 CuS	103)2 + 304 + 0.	0.004 HgCl2 .021 Cr2(S04)	+
7.7 7.8	34.04 34.04	4.00 4.00	0.04 0.04	7.25	0.00170 0.00000	$\begin{pmatrix} + \\ - \end{pmatrix}$	Mn, Ca, Mn, <u>Ca</u> ,	Sr* Sr*
7.9 7.10	34.04 34.04	15.00 15.00	0.000	++ ++ 00	0.00410 -0.00005	$\begin{pmatrix} + \\ - \end{pmatrix}$	<u>Mn, Ca</u> , Ca,	Sr*Fe Sr*

#	0/00	Ę	Λ	A	M	Ь	Remarks
1S =	26.00 NaCl	+ 3.26 MgS	304 + 2.30	MgCl ₂ + 1.16	CaCl ₂ + 0.72 I	KC1 /100I	м 900 H ₂ 0
9.1	34.00	7.00	0.000	6.00	0.00060	(-)	Mn, Ca, Al , Sr
2 S =	30.00 NaCl	+ 3.50 MgS	304 + 2.30	MgCl ₂ + 1.20	CaCl2 + 0.72 I	KC1 /1001	и 900 Н ₂ 0
9.2	37.70	9.00	0.000	6.00	0.00070	(-)	Mn, Ca, Al , <u>Sr</u>
3S =	20.00 NaCl	+ 4.00 MgS	304 + 2.30	MgCl2 + 1.20	cacl ₂ + 0.70 I	KC1 /1001	1 900 Н ₂ 0
9.3	28.20	8.00	0.000	6.00	0.00332	(-)	Mn, <u>Ca</u> , <u>Al</u> , Sr*
4S =	15.00 NaCl	+ 4.00 MgS	304 + 3.00	MgCl ₂ + 1.00	KC1 /100M 900	H ₂ 0	
9.4	23.00	10.50	0.000	6.00	0.00520	(-)	Mn, Ca, <u>Al</u> , Sr
5S =	32.00 NaCl	+ 5.00 MgS	304 + 3.00	MgCl ₂ + 1.00	CaCl2 + 1.00 I	KC1 /1001	и 900 Н ₂ 0
60. 100.	42.00	8.00 44.50	0.000	6.00 6.00	-0.00018 -0.00028	(+ -)	Mn, <u>Ca</u> , Al, Sr <u>Mn</u> , Ca, Al*
	Let A =	3.26 MgSO4	+ 2.30 Mg	Cl ₂ + 1.16 Ca	C12 + 0.72 KC)	Ц	
6S =	A + 26.00 N	aCl + 0.56	MnCl ₂ / 1	000 H ₂ 0			
9.7	34.00	7.50	0.000	6.00	0.00268	(-)	Mn, Ca, <u>Al</u> , Sr

TABLE 9.--

9Continued	
TABLE	

#	00/0	E	Λ	A	M	പ	Remarks
7S = A	+ 25.00 N	laCl + 1.56	MnCl2/ 100	00 H ₂ 0			
9.8	34.00	10.50	000.0	6.00	0,00285	(-)	Mn, Ca, <u>Al</u> , Sr
8S = A	+ 26.50 N	laCl + 0.06	MnCl ₂ / 100	00 H ₂ 0			
9.9	34.00	8.50	000.0	6.00	0,00099	(-)	Mn, Ca, Al [*] , Sr
9S = A	+ 24.00 N	laCl + 2.56	MnCl ₂ / Ju	000 H ₂ 0			
9.10	34.00	8.50	000.0	6.00	0.00289	(-)	Mn, Ca, Al ; Sr
10S = f	1 + 20.00	NaCl + 6.5($5 \text{ Mncl}_2/1$	000 Н ₂ 0			
9.11 9.12	34.00 34.00	9.25 44.25	0.000	6.00 6.00	0.00384 -0.00086	(+ -	Mn, Ca, Al, Sr Mn, Ca, Al, Sr*

9Continued
TABLE

Remarks		Ca, <u>Al</u> , Sr		Ca, Al; Sr		Ca, Al; Sr		Ca, <u>Al</u> , Sr <u>Ca</u> , <u>Al</u> ; Sr*
		, uM		e ul		, MN		Mn, Mn
Ч		(-)		(-)		(-)		-+
м		0.00285		0,00099		0.00289		0.00384 -0.00086
A	000 H ₂ 0	6.00	00 H ₂ 0	6.00	1000 H ₂ 0	6.00	1000 Н ² 0	6.00 6.00
Λ	5 MnCl2/ 10	0,000	$5 \text{ MnCl}_2/10$	0.000	5 MnCl ₂ / :	0.000	56 Mncl ₂ / :	0.000
Ē	VaCl + 1.50	10.50	VaCl + 0.00	8.50	VaC1 + 2.54	8.50	NaCl + 6.	9.25 44.25
0/00	+ 25.00 N	34.00	1 + 26.50 N	34.00	1 + 24.00 N	34.00	A + 20.00	34.00 34.00
#	7S = A	9.8	8S = A	9.9	9S = A	9.10	10S =	9.11 9.12

Trace ions	Salt of trace ions
*Zn	ZnS0 ₄
*Cu	CuSO ₄
*Fe	FeS0 ₄
Ba	BaCl ₂
*Cr	Na ₂ Cr ₂ 07
В	Na ₂ B ₄ 0 ₇
NO 3	NaN03
Ca	CaC0 ₃
Sn	SnCl ₂
*Co	Co(NO ₃) ₂
Hg	HgCl ₂
^{C0} 3	CaC0 ₃

TABLE 10.--Basic sea water mixture: 26.00 NaCl + 3.25 MgSO₄ + 2.30 MgCl₂ + 0.72 KCl + x MnCl₂.

*often found in manganese nodules

show almost all the trace elements in the test solutions simutaneously. Table 10 is a summary of the added trace elements. The only trace element plated was iron (7.1 and 7.9) and extraction took place only on the negative electrode. The fact that iron was not detected more often may have been the result of a colloidal precipitate that formed in most of the solutions, probably due to a reaction with the sulfate ions, and possibly through interactions with variety of the other ions present in the solution.

Scavenging effects were not noticed in the experimental results. The large variety of ions introduced (Table 10) which might have been scavenged were all electropositive, and most have oxidation potentials below that of manganese and calcium. Thus they were repelled by the manganese and calcium, and the other electropositive ions, and the action of the negative ions moving towards the positive pole would act as a shield for these less active ions. The colloidal layer that developed in some of the solutions, see Tables 7 through 9, may have prevented many of the trace ions from plating. Some elements could have been extracted in amounts below the sensitivity limit in the spectral region covered and were not detected in the analysis.

Table 9 represents a diversion from Tables 6 through 8. The test solution used is the same as the last solution indicated in Table 8 with the exception that the NaCl has been either decreased or increased and, has been adjusted to the changes in the NaCl so that the solutions in the first part of the Table (9.1 - 9.6) show both high and low salinities with a constant amount of $MnCl_2$. The second half of the tests employed a constant amount of $MnCl_2$. The second half of the tests employed a constant salinity with the addition of $MnCl_2$ to off set the reduction in NaCl. This experimentation did not alter the concept that plating is a function of the salinity. This will be seen in Figure X and discussed with respect to that figure.



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Since the voltage and current are directly related, the choice of amperage, for most of the graphs, was made because of the greater accuracy of the instrument. Figure II shows a graph plotting weight increase per time against the current in amps for the negative electrodes found in Tables 6 through 9. The result was not much better than that shown in Figure I.

From work in electrochemistry, the rate at which plating takes place in a commercial cell depends on the molar concentration of the solution. The molarity of the test solution would be similar to the salinity; therefore, the salinity factor was introduced in the denominator. The greater the salinity, the higher the current because of the increase in the number of ions, and this resulted in an increase in the weight extracted per unit time and surface area. Figure III is a plot of the same results as used in Figure II with the salinity factor introduced in the denominator. The points that are enclosed in triangles in Figure II and III were the ones most affected by the introduction of the salinity factor. The plot in Figure III enabled a better line to be drawn than in Figure II.

The weight loss due to chipping when clamping wires onto the electrodes played an important part when low plating accumulation figures were obtained. To correct this undesirable effect, the (G) factor was established. This correction factor was an average of the electrodes showing

TABL	E 11	E	Lect	rode.	Factors	
------	------	---	------	-------	---------	--

	Electrodes affected	by the (G) factor
6.11	+0.00091	corrected = $+ 0.00180$
7.1	0.00000	corrected = + 0.00079
9.1	+0.00060	corrected = + 0.00139
9.2	+0.00070	corrected = $+ 0.00149$
9.5	-0.00018	corrected = + 0.00061
9.9	+0.00099	corrected = + 0.00188
	Electrodes affected	by the (H) factor
6.13	+0.02235	corrected = + 0.00235
7.3	+0.01065	corrected = + 0.00200
5.5	+0.02603	corrected = + 0.00603



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Current in Amps

an abnormal or negative weight after exposure. The calculated correction was found to be 0.00079 grams. This number was added to the weights of the affected electrodes. Table 11 is a list of those electrodes corrected with the (G) factor. Those chipped were noted when chipping tools place and only these were corrected. Figure IV is a plot of the electrodes (-) from Tables 6 through 9 with the addition of the (G) factor to those electrodes listed in Table 11. The effect on the positions of the corrected plots was slight.

Since the surface area of the electrodes could not be effectively measured, a correction factor (H) was devised to smooth out the variation. Certain electrodes were found to deviate an abnormal extent from the plot in Figures III and IV. These abnormal plots have a triangle around them in Figure IV. In all cases they displayed an increase in weight that was not proportional to their associated electrodes at the same potentials. The (H) factor is a negative number on the order of 0.02000 grams. It was derived arbitrarily from the time exposed, the potential, and the accumulative weight of electrodes at or near the same potential and time. The electrodes corrected by the (H) factor are listed in Table II.

Figure V is a plot of the grams/(time) (salinity) against the current in amps with both the (G) and (H)

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factor correcting the appropriate weights. The resulting plot is the type that can be predicted from electrochemistry.

The time factor seemed to be one of the major causes of abnormal weights. Weights accumulated over short periods of time at low currents did not deviate from linearity. Figure VI is a plot of those points that did not deviate from a straight line.

To correct for the polarization effect, (time) was substituted be (time)². The resulting curve (Figure VII), was plotted from the same data used in Figure V, was much better. The points were now brought into fair linear agreement.

Figure VIII was plotted from the data of Figure V, but $(time)^3$ was substituted for (time). This appeared to be an over correction, and the resulting plot lost some of its linear aspect.

The $(time)^2$ plot (Figure VII) may have been an over correction, and the best curve might be found at some intermediate value between $(time)^2$ and (time). Several trial curves were plotted using (1/2 time), (3/2 time), and (1/4 time). None of these curves appeared to be as good as the $(time)^2$ relationship.

Figure IX represents a complete plot of all the data with reference to the negative electrodes using the basic sea water test solution. The data may be found in Tables 3 through 9. The (G) and (H) factor were included for these electrode weights that were affected by these corrections.

The weight + (G) + (H) divided by $(time)^2$ (salinity) was plotted against the current in amps.

The rate of accumulation would seem to depend a great deal on the time factor. Extrapolating the final curve obtained in Figure IX to zero, and multiplying by a power of ten to counteract the time squared effect, the rate of accumulation at very low potentials falls in the range of 10^{-7} grams per hour.

The time squared factor lowers the value of the electrical current, which is necessary for good curve agreement. At the higher currents a polarization effect can be seen by the block of points that is off the curve around 10 amps. The polarization effect is the tendency of the ions to arrange themselves in the solution much as the ions of the NaCl space lattice are arranged. The positive ions crowd near the negative electrode, and the negative ions near the positive electrode. Through this arrangement the ions in the solution became more stable and thus resist the passage of the electrical current. At low currents the polarization effect does not take place, and the time squared factor would not be needed. When the duration of the current was small, the polarization effect was a minimum. This was seen in Figure VI. The electrical currents generated in the ocean would not be large enough to produce a polarization effect.

A brief experiment was conducted holding the current and the salinity constant. This may be seen in the data



in Table 11. The electrodes (9.7-9.12) were treated the same as the previous electrodes in all other respects. The test solutions were varied between the NaCl and the MnCl₂ concentration. Since the currents were not high, and the time period was short, the polarization effect should not have been noted. Figure X is a plot of weight per time against the concentration of MnCl₂/1000 H₂0. The curve has a negative slope towards the zero concentration which shows that the rate of accumulation does depend on the concentration of manganese ion in solution. The fact that the curve is not steep may mean that the overall effect of a trace amount of manganese in sea water does not have an important effect on the accumulation of the manganese nodules.

Since the rate of accumulation of a plated material is a function of the surface area, an approximate surface area was calculated from the equation for an Oblate Spheroid and divided by two.

Equation: surface area = $2 a^2 = \frac{b^2}{e} \log_e \frac{1+e}{1-e} = 80$ sqr. mm

a = 3.5 mm, b = 5 mm, e = 1.5 mm

If the value of 10⁻⁷ grams per hour per 80 square mm. is a valid figure for the rate of accumulation, as the graphs indicate, then the time given for the accumulation of the nodules in the original theory is too long. Based on the figure obtained from the experimental results, would take about 20,000 years to accumulate a 1000 gram nodule and no longer than 200,000 years at the lowest extrapolated currents. The smaller figure is probably more accurate because it was obtained from the more accurate data.

The validity of the experiment itself in relation to electrochemical procedures can be seen from the calculation of a hypothetical deposit from an ideal solution. This calculation is based on Faraday's Laws for electrolytic solutions. The basic equation is:

$$m = \frac{I t}{z F}$$

where:

m = mass accumulated M = atomic weight of the element z = valence number of the ion F = Faraday's number = 96,479 coulombs t = time I = current in amps

Substituting the values of (9.3) (Table 9) into the equation, the following value was obtained for manganese:

$$\frac{m}{25} = \frac{(6)(8)}{(4)(96,479)} = 0.00311 \text{ grams}$$

The observed value from the experimental results was (0.00332 grams).

Since none of the electrolytic solutions used in this experiment can be considered ideal, the results obtained by the calculation of Faraday's equation cannot be expected to coincide with the experimental results. Faraday's theory does not take into account the ionic mobilities which are a function of the molarity or salinity of the solutions. It does not account for the current fluctuations that would be found in nature, and that were present in the experiment. There was no relation to the size of the electrode which has an effect in nature on the rate of accumulation. The ionic activities and the ionic strength of the ions in solution were not accounted for. The types of ions plated were assumed by Faraday to be of only one type.

The relation calculated for this experiment was for manganese and not for the other ions that were plated. The fact that a large number of the experimental results do coincide rather well with the Farday value for manganese, as shown by the example, points out that the electrochemical theory of deposition for manganese nodules does have a sound theoretical basis.

CHAPTER VI

CONCLUSIONS

The deposition or extraction of manganese from a dilute aqueous solution by electrochemical procedures occurs. It has been shown that the rate of accumulation is a function of the salinity, the time, the magnitude of the potential, and the surface area exposed. The plated material was similar to a hydrous manganese oxide that may be found in the manganese nodules removed from the sea floor.

The salinity of the test solutions, which acted as an effective electrolytic medium, was similar to the salinity of sea water and extrapolation of the experimental data to conditions which might exist in a marine environment was reasonable. If the source of the manganese is held to be submarine vulcanism, then this same vulcanism could produce relatively strong bottom currents which would create the potential necessary for the plating of manganese. The catalytic action of the iron hydroxide would allow the manganese to form as an oxide. The need for a single electrode could be easily satisfied by a one directional current created by the submarine vulcanism. The rate of accumulation would be greater than previously

thought, on the order of 10^{-7} grams per hour per 80 square mm. The scavenging effect does not seem to be an important part of the electrochemical process for the extraction of copper, cobalt, and nickel.

CHAPTER VII

SUGGESTIONS FOR ADDITIONAL RESEARCH

There is a need for more advanced and detailed work on this project. Instruments accurate to very low voltages and amperages should be used. A means of determining the surface area of the exposed electrodes should be worked out. The concentration of iron in the electrolytic solutions should be made proportional to that of the manganese in order to determine if the plated proportion of iron to manganese is comparable with the observed proportions found in the natural manganese nodules.

The creation of an electrical potential by the motion of sea water parallel to a magnetic field should be attempted. A recycling system should be constructed which would create a steady flow of artificial sea water around an electrode. A magnetic field should be induced around the electrodes of the same intensity of the earth's as has been measured by geophysical methods. Conditions could then be made similar to those thought to be found in nature, and a more accurate prediction could be made as to the environment of the sea bottom at the time of plating. The next step would be to find an area of the sea that is currently experiencing submarine vulcanism

and to attempt to measure the bottom currents produced by this action and to analysis the bottom water to see if the concentration of manganese has been locally increased. The use of this collected sea water in the laboratory experiment would also be desirable.

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