

FTD-HT- 67-233

# EDITED TRANSLATION

THE PROTECTIVE ACTION OF CALCIUM-MAGNESIUM COATINGS DURING CATHODIC PROTECTION OF STEEL AND IRON IN SEA WATER

By: Chung-tao Tai, Ming-tang Chi and Ching-cheng Koo

English pages: 19

SOURCE: Hai Yang Yu Hu Chao (Oceanologia et Limnologia Sinica) (Oceanology and Limnology). Vol. 8, No. 1, 1966, pp. 51-59.

Translated under: Contract AF33(657)-16410

СН/0105-66-008-001

TP7001443

THIS TRANSLATION IS A RENDITION OF THE ORIGI-NAL FOREIGN TEXT WITHOUT ANY ANALYTICAL OR EDITORIAL COMMENT. STATEMENTS OR THEORIES ADVOCATED OR IMPLIED ARE THOSE OF THE SOURCE AND BO NOT NECESSARILY REPLECT THE POSITION OR OPINION OF THE FOREIGN TECHNOLOGY DI-VISION,

PREPARED BY

TRANSLATION DIVISION FOREIGN TECHNYLOGY DIVISION WP-APB, ONIO.

FTD- HT - 67-233

Dete 20 Sep 19 67

01 Acc Nr 68 Translation Nr 65 X Ref Acc Nr 76 Reel/Frame Nr TP7001443 HT6700233 AP6022632 1881 1279 97 Header Clas 63 Clas Control Markings 64 94 Expansion 4C Ctry Info UNCL, UNCL 0 CH 02 Ctry 03 Ref 04 Yr 05 Vol 10 Date 06 Iss 07 B. Pg. 45 B. Pg. CH 0105 008 6É 0001 0051 0059 NONE Transliterated Title NONE AVAILABLE 09 English Title THE PROTECTIVE ACTION OF CALCIUM-MAGNESIUM COATINGS DURING ·CATHODIC PROTECTION OF STEEL AND IRON IN SEA WATER **43 Source** (CHINESE) HAI YANG YU HU CHAO 42 Author 98 Document Location TAI, CHUNG-TAO (2071/6945/6670) 16 Co-Author 47 Subject Codes 11. 13 CHI, MING-T'ANG (1323/2494/1016) 16 Co-Author 39 Topic Tags: low alloy steel, steel corrosion, cathode polarization, KU, CHIN-CH'ENG (7357/6930/1004) protective coating, sea water corrosion, 16 Co-Author corrosion protection, metal coating NONE 16 Co-Author NONE ABSTRACT : The protective action of white films formed on iron and steel surfaces in sea water under conditions of cathodic protection was studied. Three series of tests were performed with 16 Mn low-alloy steel supplied by the Peking Iron and Steel Institute. In the first series, specimens were exposed either to natural sea water or to 3% NaCl solution, and protected with a constant current. In the second series the specimens were first exposed to stagnant or stirred sea water and for 3 days protected with a high density, 40  $\mu a/cm^2$ , current to form uniform films and then current applied periodically in 24-hr cycles. Specimens of the third series were tested either in natural or artificial sea water with various current densities. The artificial sea water contained either Mg and Ca (pH = 7.7), Mg alone (pH = 7.8), Ca alone (pH = 8.0), or no Mg and Ca (pH = 7.8). Experimental results showed that protection can be achieved in natural sea water at 25  $\mu$ a/cm<sup>2</sup> and in 3% NaCl solution at 35  $\mu$ a/cm<sup>2</sup>. Specimens pretreated with a higher current can be protected at  $3.5 \ \mu a/cm^2$ . The .periodically applied current should have a density of 15-20  $\mu$ a/cm<sup>2</sup>. Polarization of Ca-Mg films is 5-8.8 times that of Ca or Mg films, while polarization of Mg films is higher than that of Ca films. Polarization characteristics are affected by current density applied in forming the film, Film formation is more difficult on rusted metal surfaces and more complete in stirred sea water. Films formed at a pH exceeding 10 provide protection for metals; films formed at pH = 9 fail to protect. The authors conclude that calcium-magnesium films have a certain protective ability which makes it possible to use lower current densities in cathodic protection and a shorter period of current application. The dissociation of Mg(OH), in films plays an important role in protection of metals when the current is discontinued. The authors are deeply indebted to Hua Pao-ting of the Applied Chemistry Institute of the Chinese Academy of Sciences for reviewing the

FTD FEE 67 0-90

ITIS INDEX CONTROL FORM

1981 - 1580

TP7001443

HT6700233

6.

manuscript and valuable suggestions, to Chi Ming-hou of the Oceanography Institute for showing interest and assistance, and to Fan Shou-an for taking part in the experiment. Orig. art. has: 5 tables and 6 figures. English Translation: 20 pages. This paper attempts to study the composition and function of calcium magnesium coatings, their effectiveness, and their effects on the polarization characteristics of steel samples. In addition, studies were also made of the surface structure of the metals, and the effect of the speed of sea water current to the formation of the coatings.

# A. RELATIONSHIP OF THE SURFACE STRUCTURE OF STEEL SAMPLES, COMPOSITION OF THE COATINGS AND CONDITIONS OF THE MEDIA WITH POLARIZATION AND PROTECTIVE ACTION.

# I. Test Procedure

Sixteen Mn low-alloy steel<sup>2</sup> was used for testing. Samples of three specifications were made according to the requirements of the experiment (see following tables). All separation lines were sealed with acetylene. Surfaces of the samples were polished with diamond sandpapers to such a degree that no scratch marks could be seen with the naked eye.

# 1. Protection by electric current

Samples used were of rectangular shape  $(2 \times 7 \times 0.3 \text{ mm})$ , placed separately in 1,000 cc of stable natural sea water and 3% NaCl solution to receive cathodic protection under a constant electric current. The sea water was changed every three days. After the test samples were acid-cleaned and dried, they were weighed. The difference between these weights and the weights before the test was the amount of weight lost. A comparison of the weight lost by protected samples and corresponding samples indicated the degree of protection. The procedure for acid cleaning is as follows: samples were put into an acid cleaning solution composed of 20% HCL and 1% hexa-methyl quaternary ammonium. They were cleaned with a bamboo scraper for three minutes, and then neutralized in 5% Na<sub>2</sub>CO<sub>3</sub> solution; rinsed in water, two minutes in 20% NaNO<sub>2</sub> solution, then rinsed in distilled water. The sample was weighed after drying for 24 hours. Corresponding samples went through the same acid cleaning pro-

FTD-HT-67-233

<sup>&</sup>lt;sup>2</sup>See page 18

cedure so any alterations could be noted.

### 2. Intermittent protection.

Samples were cylindrical in shape (0.46 mm diameter, 7.0 mm long). A cathode current of 40  $\mu$ A/cm<sup>2</sup> was turned on for three days while the sample was immersed in 1,000 cc of stable or stirred-up natural sea water, until a white, even coating of calcium-magnesium appeared over the surface of the sample. Then the sea water was replaced with fresh sea water, and the electric current was reduced, or an intermitent current was used every 24 hours for protection. Otherwise, the acid cleaning procedure and the method used to determine the degree of protection were the same as  $\underline{1}$ .

# 3. <u>Study of the effect of the coating on</u> polarization characteristics

Area of sample:  $5 \text{ cm}^2$  (double face). Put separately in natural sea water and artificial sea water of different compositions, using electric currents of different intensities (other conditions same as 2), until the calcium-magnesium precipitate coating has formed, then measured cathode polarizations to plot curves. fook readings of electrical potential every 10 minutes when they did not exceed 2 mV. In the secondary polarization curve, when differences in potential values of various reference points did not exceed 10 mV, mean values were taken.

All tests were conducted under a constant temperature of 25°C. Platinum electrodes were used as auxiliary electrodes. Saturated mercury electrodes were used as reference electrodes (all converted to standard hydrogen electrode when plotting diagrams). The potentiometer used was of the UJ type.

Artificial sea water was prepared according to Brujwicz's formula [4]. According to the requirements of the experiments, the calcium-magnesium content was changed as follows:

- a) both calcium and magnesium (pH = 7.7)
- b) magnesium only, no calcium (pH = 7.8)

FTD -HT-67-233

c) calcium only, no magnesium (pH = 8.0)

d) no calcium, no magnesium (pH = 7.8)

Any other shortage of elements was rectified by proper additions of NaCl. There was no change in other elements.

## II. Test Results

From Table 1, we can see that when the intensity of electric current reaches  $25 \ \mu A/cm^2$  in natural sea water, complete protection has been achieved. On the other hand, it takes  $35 \ \mu A/cm^2$  to achieve the same degree of protection in 3% NaCl solution. The reason is that samples in natural sea water form a calcium-magnesium coating quickly, thereby requiring a smaller amount of protective electric current.

If a stronger current was applied to the surface of the sample to produce a layer of calcium-magnesium coating, the protective current could be reduced, then the intensity of electric current needed to achieve the same degree of protection can be reduced to  $3.5 \ \mu\text{A/cm}^2$  (Table 2), only one-tenth of the amount required in the 3% NaCl solution. If the electric current was cut off for 24 hours every 24 hours (protection to be provided by the calcium-magnesium coating alone), then the amount of electric current is reduced to  $15-20 \ \mu\text{A/cm}^2$ . All these results, except the value for the minimum protective current, are close to those in the references [3, 5, 9, 19]. (Reference only listed narrative descriptions without systematic figures.) All these seem to prove calcium-magnesium coatings do possess excellent protective functions.

According to spectral analysis, the main components of precipitation from natural sea water after cathodic protection are calcium and magnesium, plus a small amount of titanium, borax and silicon. To study the effects of calcium and magnesium (the main components) after their precipitation, on the polarization action of steel samples, we prepared artificial sea water to measure the polarization of the precipitations.

The cathode polarization curves of the precipitations from both natural sea water and artificial sea water coincide with each other, except for static potential

light yellow rust, incomplete thin сĽ gray, hard coating on surface, no incomplete grayish-white conting on surface. complete grayish-white coating and light yellow rust stain on corrosion concentrated around serious corrosion on surface. surface, with white spots; cotton-like rust on edges. yellow rust on surface; purplish-black color Remarks partly corroded. corrosion; rust on edges. surface; coating; edges. 72 hours -0.5201 -0.4908 -0.7516-0.6060 -0.4579 -0.4712 -0.4557 -0.4614 -0.6909 -0.4721 Change in potential (equivalent to standard hydrogen electrode) 24 hours 48 hcurs -0.6618-0.5233 -0.4558 -0.4524 -0.5805 -0.5350 -0.4571 -0.7189-0.5715 -0.5193 -0.4914 -0.4695 -0.4689 -0.6212 -0.4657 -0.6390 -0.6319 -0.5597 -0.6262 12 hours -0.5178 -0.4896 -0.4737 -0.5783 -0.4728 -0.6096 -0.4628 -0.6377 -0.6390 -0.5999 46.78 94.30 87.56 29.61 82.92 67.17 83.13 100 100 Trotection, X 00 Degree of 1.6710 3.2470 2.2860 2.2856 0.0956 1.0730 0.5503 0.4044 Corroston rate, gram/day.m2 1.7285 0 ی sea water; 3% NaCl sea water; 3% NaCl sea water; sea water; sea water; sea water; Medium 3X NaCl 3X NaCl NaCI NaCl 3% 34 current uA/cm<sup>2</sup> gaittoetorg 0 5 20 2 25 g Intensity of

CATHODIC PROTECTION OF 16 Mn STEEL SAMPLE IN SEA WATER, 3% NaCl SOLUTION.

**GINE WEITE** 

TABLE 1.

5

•

. .

TABLE 1. CATHODIC PROTECTION OF 16 Mn STEEL SAMPLE IN SEA WATER, 3% NaCl SOLUTION. (Continued)

-

2

Remarks		grayish-white coating on sur- face, no corrosion; lost original luster, dark brown spots appeared.	bright, no corrosion.
valent trode)	72 huurs	-0.7646 -0.6863	-0.7256
Change in potential (equiv to standard hydrogen elect	48 hours	-0.7340 -0.6893	-0.7445
	24 hours	0.6882 -0.7262	-0.7364
	12 hours	-0.6903 -0.7496	-0.7234
Degree of protection, Z		92.63 100	100
сотгозіоп тасе, gram/day•m <sup>2</sup>		0.1235 0	0
Medium		sea water; 3% NaCl	sea water; 3% NaCl
Intensity of protecting current µA/cm2		35	40

•

TABLE 2. CATHODIC PROTECTION STATUS AFTER 16 Mn SAMPLES HAVE ACQUIRED CALCIUM MAGNESIUM COATINGS IN SEA WATER

1

The second second second

•

•

Remarkıs			no corrosion observed: possible error					no corrosion observed; possible error	no corrosion observed: possible error		
ctrodej	8th day	elec- trícíty on			120th hr.						
rogen ele	7th day	elec. tricity off	-0.5098		96th hr.			-0.8389	-0.8730		
ndard hvd	6th day	elec- tricity on -0.8606	-0.8502		72nd hr.	-0.5023	-0.7244	-0.7301	-0.8081		
nt to sta	Sth dav	elec- tricity off -0.4525	-0.5204	-0.5082	48th hr.	-0.4670	-0.7125		-0.7810	-0.5211	
(equivale	4th day	elec- tricity on -^.\$162	-0.9094	-0.9125	24th hr.	-0.4586	-0.6803	-0.7937	-0.5514	-0.5253	
tial (V)	3rd day	elec- tricity off -f. <sup>290</sup>	-0.5001	-0.4815	10th hr.	-0.4567		-0.6587			
in poten	2nd day	elec- tricity on .7593	-0.8632	-0.8870	5th hr.						
Change	lst dav	elec- tricity off -۱.۵۹۵	-0.4383	-0.5590	lst hr.	-0,3909					
iee of See of	prot Degr	an <b>.</b> 5	97.8	<b>∽</b> 100		39.6	100	97.7	∽ 100	0	
on, gram on, gram suors	74 42 1801 1802	0.2904	0.675	0.0157		1.8504	U	0.0701	0.0351	3.0670	
fo yjten scitas (su) jns.	cm2) cnrr prot Inte	6.CI	0.21	20.0		2.5	3.5	5.0	10.0	0	
ι (24 hour pro- μττεπτ pro- Μετhod of ιτεπτ elec-		τετπίττεητ ίς current ction (24	cy tr tn tn	- ג	jien Detec	brd Iatei	ς σεττέπτ ους ίον ί	continue eiectrie tion	corre- sponding samples		

.

.

(Figure 2). But there are appreciable differences between these curves and the polarization curves of single element calcium coatings and magnesium coatings. To reach a standard polarization voltage of 0.6 V, both coatings formed by natural sea water and artifical sea water required 3  $\mu$ A/cm<sup>2</sup>, with an average polarization efficiency of 0.2 V/ $\mu$ A·cm<sup>2</sup>; coatings containing only calcium need 26.5  $\mu$ A/cm<sup>2</sup> with an average polarization efficiency of 0.023 V/ $\mu$ A·cm<sup>2</sup>; coatings containing only calcium need 26.5  $\mu$ A/cm<sup>2</sup>; corresponding blank samples need 30  $\mu$ A/cm<sup>2</sup>, with an average polarization efficiency of 0.02 V/ $\mu$ A·cm<sup>2</sup>. The polarization of a combination calcium-magnesium coating in 5 to 8.8 times that of just a calcium or magnesium coating.



Figure 1. Effects of calcium and magnesium on polarization characteristics. (1) cathode polarization curve of steel samples without calciummagnesium coating; (1') anode polarization curve of steel samples without calciummagnesium coating; (2) cathode polarization curve of steel samples with calcium magnesium coating; (2') anode polarization curve of steel samples with calcium magnesium coating.



Figure 2. Cathodic polarization curve of 16 Mn steel in different media after formation of coatings (coating formation current 40  $\mu$ A/cm<sup>2</sup>; time required, 3 days. Media: (1) natural sea water (0); (2) artificial sea water with both calcium and magnesium (X); (3) artificial sea water with magnesium, no calcium (•); (4) ertificial sea water without calcium and magnesium (X); (5) artificial sea water with calcium, no magnesium ( $\Delta$ ); (6) artificial sea water with no coatings (corresponding samples ) (0).



Figure 3. Cathode polarization curve -- after coatings formed using different coating-forming current intensities (medium, natural sea water). (1) coatingforming current intensity, 46.6  $\mu$ A/cm<sup>2</sup> for 3 days; (2) coatingforming current intensity, 40.0  $\mu$ A/cm<sup>2</sup> for 3 days.



Figure 4. Cathode polarization curve -- after coatings formed under different surface conditions (conditions same as Figure 2; the medium was natural sea water). (1) cathode polarization curve of 16 Mn steel sample after coatings were formed -- bright surface; (2) cathode polarization curve of 16 Mn steel sample after coatings were formed -surface showing corrosion; (3) cathode polarization curve of 16 Mn steel sample before coatings were formed -- surface showing corrosion.

The electric current intensity during the formation of coatings has a great effect on the polarization characteristics of the coating. A coating-forming current of 46.6  $\mu$ A/cm<sup>2</sup> is apparently higher in polarization characteristics than one of 40  $\mu$ A/cm<sup>2</sup> (Figure 3).

It is more difficult to form coatings (Figure 4) on samples with harder corrosion shells. In stable sea water, the current intensity must be raised to 70  $\mu$ A/cm<sup>2</sup> and above in order to form a relatively complete calcium-magnesium coating.

The stirring conditions of the media also have direct effects on the formation of coatings. If we stablilize the current intensity at 46.6  $\mu$ A/cm<sup>2</sup>, and convert the revolving speed of the stirring rod to a linear speed (assuming it is equivalent

to the fluid speed) of 80-90 meters/hour, we noticed a very different situation in the formation of coatings, even better than that which could be achieved in stable sea water. Only a current intensity of 2.5  $\mu$ A/cm<sup>2</sup> was needed to reach a polarization voltage of -0.6 V during \_ mization, while 3.0  $\mu$ A/cm<sup>2</sup> was needed if the coating was formed in stable sea water. This is due to the fact that slow stirring improves the ionic diffusion requirement of calcium and magnesium. But if the stirring speed increased to the equivalent fluid speed of 470-520 meters/hour, then the same current intensity could not form a good coating, and the sample corroded quickly. This is because the pH value of the medium could not be quickly raised due to stirring, and in the meantime, depolarization due to oxygen was speeded up. But if the current was raised to 70  $\mu$ A/cm<sup>2</sup> and above, we could see the formation of good coatings again.

## B. OH PROTECTIVE ACTION OF CALCIUM-MAGNESIUM COATINGS.

# I. Test Procedure

Sixteen Mn cylindrically shaped samples (0.46 cm diameter, 7.0 cm long), were used. Direct current was introduced while sample was immersed in natural sea water (or artificial sea water (1 liter) at 40  $\mu$ A/cm<sup>2</sup> for 3 days, under a constant tempeerature of 25° C, until a white, even calcium-magnesium coating (thickness 0.1-0.3 mm) was formed. A scalpel was used to carve out small holes (diameter, 0.5-2 mm) along the axis line and spaced 1 cm apart, so that the basic metal was exposed. The sample was then immersed in fresh sea water, to observe its corrosion status.

The sample was gently flushed with distilled water, its calcium-magnesium coating removed (coatings from the corroded and noncorroded areas in the same sample were taken separately to conduct separate tests), 5-10 cc distilled water was added, and the coating was repeatedly stirred. After half an hour the pH value of the upper part of the clear solution was tested.

Type of Coating	Potenrial (Equivalent to Standard Hydrogen Electrode)			
	At Small Hole Area	Coating Area		
Calcium-magnesium coating	(1) -0.478	-0.479		
	(2) 0.487	-0.488		
Clear Lacquer	-0.435	-0.436		

# TABLE 4. POTENTIAL DIFFERENCE BETWEEN COATINGS ON STEEL SAMPLE SURFACES AND THE SMALL HOLES

## II. Test Results

In the experiment concerned with drilling holes through calcium-magnesium coatings on the sample surface, 8 tests were conducted and 40 holes were tested. Of these, only 3 revealed blue or yellow corrosion stains within 8 hours. The other part of the sample did not reveal any corrosion stains within this period of time. Furthermore, when stretched into longer periods, corrosion only developed at the original places. Other areas retained their bright metallic sheen. On the other hand, corresponding samples with three coats of clear varnish, from ten tests of 50 holes, revealed yellow or blue corrosion stains in 47 holes within 5 hours. In addition, when calcium-magnesium coatings were peeled off in patches to the point where their areas were one-third of the total area of the sample, corrosion stains began to occur within 2.5 hours. Therefore, it is not enough to explain this phenomenon from the viewpoint of physical shielding. The theory regarding the protective aftereffect of the coatings is also rather hazy, since it does not explain the real reason for the protective aftereffect.

Calcium-magnesium coatings, in addition to their mechanical shielding action, also exhibit other types of protective action.

Because sea water possesses good electrical conductivity, there are no appreciable differences between the voltages of the coating area and the small hole

TABLE 5. RELATIONSHIP BETWEEN THE PROTECTIVE ACTION OF CALCIUM-MAGNESIUM COATINGS AND PH.

ere taken pH Corrosion at small hole Remarks Value areas	<pre>test; 8.19 in 8 tests, within 8 hours, est; 8.13 only 3 out of 40 holes coating samples taken and y coating. 10.20 showed yellow rust. 0th- ers preserved their bright rent cut off. metal sheen.</pre>	test; 8.08 in 1 test, within 8 hours, coating samples analyzed test;	test; 8.24 in 4 tests, within 5 hours, coating samples analyzed test;	<pre>test; 7.60 within 5 hours, large area coating samples unalyzed :est; 7.53 (more than 1/3) showed yel- after soaking in natural y coating. 9.12 low rust. Coating provides sea water for 2 days after no protective action.</pre>
Where samples were taken from	sea water before test; { sea water after test; { solution formed by coating. 10	sea water befor test; sea water after test; solution formed by coating without corrosion; solution formed by coating with corrosion.	sea water before test; { sea water after test; solution formed by coating 10 without corrosion; solution formed by coating 9 with corrosion.	sea water before test; sea water after test; solution formed by coating.
Medium in which cost- ing was formed	natural sea water	artificial sea water (contains both cal- cium and magnesiun)	artificial sea water (contains only magne- sium)	artificial sea wauer (rontains only cal- cium).

.

•

•

٩

.

ings of different compositions seemed to be constant. pH values of coatings containing magnesium maintained a constant pH value of around 10.2, while coatings containing only calcium maintained a constant pH value of around 9.1. This is close to the pH values when the coatings began to precipitate as stated in reference [3]. In addition, calcium-magnesium coatings that have shown corrosive stains on the samples maintained a constant pH value around 9.1.

#### C. DISCUSSION

1. Possible reaction on the surface of the steel when the electric current was turned on:

$$O_1 + 4e + 2H_2O \rightarrow 4OH^-$$

Because of these reactions, the surface of the steel was coated with a layer of precipitated coating.

In Figure 1 we notice that the above-mentioned cathode precipitation mainly affects the cathodic process and static voltage. When electricity is turned on, it essentially performs the mechanical covering function, as stated in the references, which impedes the diffusion of oxygen, reduces the cathode area, and thus increases the polarization efficiency, and saves appreciably on protective current (saves about 9/10 of the protective current). It also affects the anodic process. The presence of the costing prevents the outward diffusion of the metal ions.

The fact that a combined calcium-magnesium coating is 5-8.8 times higher in polarization efficiency than a single coating of calcium or magnesium is probably due to the following reasons. The mixture of differently-structured precipitations probably forms a tighter and denser coating than the precipitation of a single

structure (gaps in structure mutually filled up), and thereby greatly increases polarization efficiency.

2. We feel, however, that during the time of electricity cut-off, such calciummagnesium coatings possess OH<sup>-</sup> protective action, in addition to their mechanical protective-coating function. This kind of coating is porous, therefore, due to the gradual decomposition of its hydroxides and carbonate salts; a solution of higher pH fills these small pores.

 $\begin{array}{rcl} \mathrm{Mg(OH)}_{2} & \xrightarrow{} & \mathrm{Mg^{**}} + 2\mathrm{OH^{-}}\\ \mathrm{Mg(O_{1}+H_{2}O)} & \xrightarrow{} & \mathrm{Mg^{**}} + \mathrm{HCO_{2}^{-}} + \mathrm{OH^{-}}\\ \mathrm{Co(OH)}_{2} & \xrightarrow{} & \mathrm{Ca^{**}} + 2\mathrm{OH^{-}}\\ \mathrm{CaCO_{3}} + 2\mathrm{HO} & \xrightarrow{} & \mathrm{Ca^{**}} + \mathrm{HCO_{2}^{-}} + \mathrm{OH^{-}} \end{array}$ 

Therefore, even after the electricity cut-off, such coatings, due to their own dissolution, can still release a certain amount of base, which affects the solution in the pores and the thin layer of relatively stable solution on the surface of the sample (approaching the pH value when the coating reaches decomposition equilibrium), or can even form a new thin layer of precipitation around the small holes (we observed that during the experiment it could be formed by calcium carbonate) to protect the metal within the small holes.

The self-dissolution of the coating begins with the hydroxides of the magnesium. At this time the pH value of the surface of the sample is always maintained above 10 (shortly after the electricity cut-off, pH value should be higher than the time of decomposition equilibrium due to the existence of excessive OH<sup>-</sup>), which provides protective action to iron and steel. When the hydroxides of the magnesium in all of the local areas begin to dissolve, the calcium salts begin to dissolve. pH value by this time drops to about 9.1, losing its protective action to iron and steel, and corrosion in spots and larger areas begins to appear.

3. Krasnoyarskiy maintains that a calcium-magnesium coating exhibits a protec-



Figure 5. Time versus voltage curve, when electricity was cut off after steel sample was polarized for 48 hours under an electric current of 25  $\mu$ A/cm<sup>2</sup>. (1) 30 g/liter of NaCl; (2) 3.74 g/liter of MgSO<sub>4</sub>, 2.76 g/ liter MgCl<sub>2</sub>, and 1.5 g/liter CaCl<sub>2</sub> [according to Krasnoyarskiy]. Key: (a) potential (according to K, H,); (b) hours.



Figure 6. Change in the relative ratio of calcium and magnesium in the coating with the change of electric intensity [according to Krasnoyarskiy]. Key: (a)  $\mu$ A/cm<sup>2</sup>.

tive aftereffect, but this does not explain why a "protective aftereffect" still exists in NaCl solution without the formation of a calcium-magnesium coating (Figure 5) [7]. We feel this is due to the effect of electricity. A highly concentrated <sup>OH-</sup> layer is produced around the electrode, which makes it possible to maintain protective action for a definite period even after the electricity cut-off when no calcium-magnesium coating has been formed.

In the meantime, we feel that Krasnoyarskiy's theory that cathode polarization causes the protective aftereffect of a calcium-magnesium coating only explains the superficial phenomenon. A fuller explanation should be: since a calcium-magnesium coating contains a larger concentration of OH<sup>-</sup> (excess and decomposed), it causes the metal to maintain a higher negative voltage. The concentration of OH<sup>-</sup> begins to diminish with the passage of time, while in the meantime oxygen has permeated through the coating to reach the metal surface. Both factors cause the change in voltage, and eventually the sample loses its protective action.

4. For practical purposes, we hope the magnesium content of the coating can be increased. The ratio of calcium compounds to magnesium compounds depends on the

intensity of the electric current. When we raise the current intensity, the relative quantity of magnesium compounds can be raised (Figure 6) [7].

#### D. CONCLUSION

The calcium-magnesium coating formed on the surface of iron and steel during cathodic protection in sea water posses distinct protective functions, which can save 9/10 of the protective electric current and half of the time required for protection. A calcium-magnesium coating is more densely constructed than simply a calcium or magnesium coating, therefore it has a higher polarization efficiency. A magnesium coating has a higher polarization efficiency than & calcium coating.

Many authors abroad maintain that this kind of coating only produces a mechanical protective-coating action. The authors of this paper feel that such a theory is not complete. The correct explanation should be as follows: when the electric current is on, it essentially produces a mechanical protective-coating action. When the electric current is turned off, it still maintains protective action provided by OH<sup>-</sup>. When the pH value of the ccating is maintained above 10 (equivalent to the decomposition equilibrium pH value for  $Mg(OH)_2$ ), the voltage is maintained at the proper negative value, causing no corrosion of the iron. When the pH value of the coating drops below 9 (equivalent to decomposition equilibrium pH value of  $CA(OH)_2$ ), the voltage readings become positive, which causes corrosion to appear. The OH<sup>-</sup> protective action of the coating is provided by the decomposition of  $Mg(OH)_2$ . Calcium coating does not have protective action.

The surface condition of the metal, current speed of the sea water and the intensity of the electric current also have strong effects on the precipitation of the coating and its protective action.

# Footnotes

- 1. to p. 1. Research report No. 113, Oceanographic Research Institute, Academia Sinica. This paper was presented to the Third National Correction Prevention and Protection Conference in 1964. Amendments and revisions were made after the conference. Acknowledgement and appreciation are given here to: Mr. Paoting Hua, Applied Chemistry Research Institute, Academia Sinica, for proofreading and offering many valuable suggestions for revision; Mr. Ming-hou Chi of this Institute for his great encouragement and assistance; Mr. Shou-an Fan for participating in part of the experimental work.
- to p. 2. Acknowledgement and thanks are given here to the Iron and Steel Research Institute of Peking for supplying the samples.

FTD-HT-67-233

### Bibliography

- Tomashov, N. D.: Metal Corrosion and Its Protection Theories. 1959. Translated by Hua Pao-ting et al., China Industrial Publishing Society, 1964, pp. 206-211.
- 2. Akimov, G. V.: Theories of Metal Corrosion and Their Research Methods. 1945. Translated by Yu Pai-nien, Science Publ-ishing Society, 1958, pp. 128-296.
- Rozenfeld, I. L. et al.: Reports on Metal Corrosion and Their Prevention. Translated by Metal Corrosion and Prevention Coordinating Subcommittee, Mechanical Committee, Science and Technical Commission, Mechanical Industry Publishing Society, 1959, pp. 124-131.
- 4. Sphedrupu et al.: Sea and Ocean. 194 Translated by Mao Chin-lee, Science Publishing Society, 1958, Vol. 1, p. 157.
- Grigor'yev, V. P.: Dependence of the intensity of protective currents on the conditions for calcium deposition. *Zhurnal Prikladnoy Khimii*, Vol. 34, pp. 182-186, 1961.
- Krasnoyarskiy, V. V.: Electrochemical method of protection from sea-water corrosion and the properties of "salt deposit". (Protection of Sea-going Vessels Against Corrosion.) Izd. "Morskoy Transport," Moscow, 1958, pp. 75-78.
- Krasnoyarskiy, V. V.: Elektrokhimicheskiy metod zashchita metallov ot korrozii. (Electrochemical Method of Protecting Metals Against Corrosion.) 1961, pp. 45-61.
- Ulanovskiy, I. B.: Processes of the formation and destruction of coatings in the case of cathode protection of steel surfaces in sea water. *Zhurnal Prikladnoy Khimii*, Vol. 29, No. 7, pp. 1056-1062, 1956.
- 9. Farkhadov, A. A.: Katodraya zaschita ot korrozii stal'nykh sooruzheniy v morskoy vode. (Cathode Protection of Steel Structures Against Corrosion in Sea Water.) 1962, pp. 156-160.

FTD-HT-67-233,

- 10. Atkin, G. R.: Soft water corrosion and calcium carbonate saturation. S. African Ind. Chemist. Vol. 8, pp. 104-111, 1954.
- 11. Denison, I. A.: Corrosion of galvanized steel in soils. J. Research NBS, Vol. 49, pp. 299-300, 1952.
- Dvorocek, L. M.: Effect of pH on anodic behavior of carbon stcel in sodium chloride solutions containing ammonia. Corrosion, Vol. 10, pp. 303-306, 1964.
- Evans, U. R.: Metallic Corrosion Passivity and Protection. Butler and Tanner, Ltd., London, England, 1937, p. 720.
- 14. Evans, U. R.: The corrosion and oxidation of metals: scientific principles and practical applications. pp. 160-162, 165, 1960.
- 15. Humble, R. A.: Cathodic protection of steel in sea water with Mg anodes. Corrosion, Vol. 4(7), pp. 358-370, 1948.
- Logan, K. H.: The protection of pipes against soil action. Trans. Electrochem. Soc., Vol. 64, pp. 137-149, 1933.
- Pearson, J. M.: Fundamentals of cathodic protection. In: Ullig, N. H., p.
  933, Corrosion Handbook. By John Wiley and Sons, Inc., New York, p. 1192.
- Speller, F. N.: Corrosion, Causes and Prevention. McGraw-Hill Book Co. Inc., New York, p. 621.
- 19. Schwerdtfeger, W. J. and R. J. Manuels: Coatings formed on steel by cathodic protection and their evaluation by polarization measurements. J. Research Natl. Bur. Standards, Vol. 65C, pp. 171-181, 1961.
- 20. Uhlig, H. H.: Corrosion and corrosion control. pp. 102-105, 1963.

FTD-HT-67-233