

On the Electrolytic Polarization of Some Iron Minerals

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With Plates I—II and 7 Text-figures

(Received April, 23, 1934)

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I. Introductory

When a mineral whose component is electrically oxidisable or reducible is polarized as an electrode, certain characteristic potential changes due to the electrochemical oxidation or reduction occur. Experimental investigation on this line has hitherto been made only by R. C. WELLS¹⁾. He found a considerable increase of the potential of pyrite electrode due to the anodic polarization and a considerable

1) R. C. WELLS. "Electric Activity in Ore Deposits." *Bulletin U. S. G. S.*, 548 (1914).

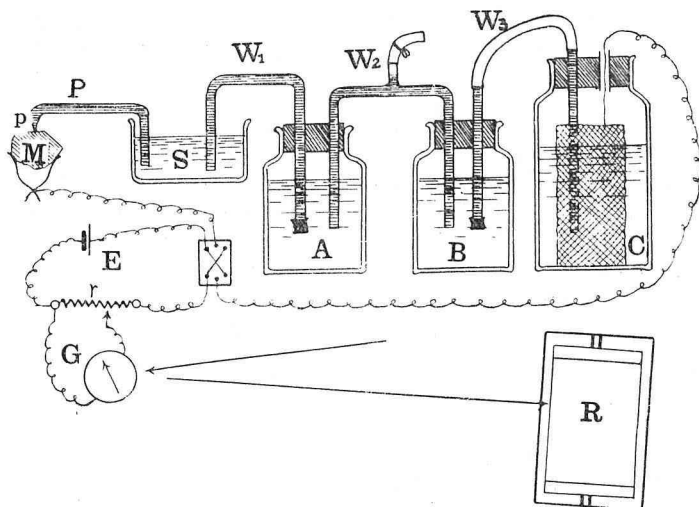
decrease of the potential due to the cathodic polarization. According to his opinion, this fact is ascribed only to the variation of ferric ion concentration owing to the electrical oxidation or reduction.

The writer's experiments have suggested that the cathodic polarization takes place in a characteristic manner if the mineral is previously polarized anodically. In this paper, some details of the investigation and an interpretation of the characteristic potential change are reported.

II. The Method of the Experiments

The samples for the experiments were selected from the collection consisting of more than three hundred separate crystals from Tsunatori. Particular care was taken to select only those specimens which had perfectly smooth and shining crystal faces free from all mechanical and chemical defects such as striation, tarnish, and minute etched engraving resulting from chemical action of secondary nature. The crystal faces were wiped with absorbent cotton moistened with water and ether, in order to remove any adhering grease. The experiments were carried out by the apparatus shown in Fig. 1.

Fig. 1.



The pyrite M was held by a metallic holder. The pick P consisted of a small glass tube one end of which was so narrow that the inner cross section was found to be only 0.009 sq. cm. when

the area of the figure, which was produced on a crystal face by the electrolytic etching, was measured by means of the camera lucida and planimeter. A solution of H_2SO_4 was chosen as the electrolyte. It was placed in a dish S and the pick P was filled with the same solution. By keeping the level of the solution in the dish at the same height as p, the solution in the pick could be kept stationary by capillary force.

After fixing the crystal face, the dish and pick were cautiously moved downwards so that the solution at the end of the latter touched gently on the crystal face. By this procedure, one could utilize any desirable part of the crystal face as the electrode, and the experiment could be repeated on one and the same crystal face. A copper electrode C was used as an auxiliary. This consisted of a roll of fine broad copper net partly dipped in a saturated copper sulphate solution whose acidity was twentieth normal with respect to sulphuric acid. The electrical connection between pyrite and copper electrode was accomplished by means of three wicks W_1 , W_2 , and W_3 . W_1 was filled with the solution of H_2SO_4 , which was protected from diffusion by tightly covering both ends with bladder membrane. The solution in W_3 was the same as that in contact with the copper electrode, and was protected from diffusion in the same manner as W_1 . The two intermediate bottles A and B contained a dilute solution of potassium chloride.

As a source of the polarizing current, a battery E was inserted in the external circuit of this cell. Though the strength of the applied current was as small as 10^{-5} amp., galvanometer G was too sensitive for the direct measurement. So the latter was put in a shunt circuit parallel to an appropriate resistance r . The resistance was restricted within a limit of twenty ohms in order to prevent as much natural vibration of the galvanometer as possible.

The variation of the current strength could be observed by the change of the deflection of the galvanometer. To make the observation easy and accurate, a photographic apparatus R was so adjusted that the reflected ray from the mirror of the galvanometer could be projected on the rolling photographic paper whose axis of rotation was perpendicular to that of the mirror. Thus all the investigations on this subject could be registered on the photographs.

The galvanometer which was used throughout these experiments had the period of vibration of 1.6 second. To determine the relation between the current strength and the deflection of the galvanometer, the latter was introduced as a shunt at various points of a uniform

resistance wire through which the constant current had been flowing. The curve representing the relation between the deflection and the resistance of wire at which the galvanometer was introduced showed perfect proportionality within a limit of 24 cm. of deflection. In the actual measurement, the deflection was restricted within 14 cm. and the distance of the photographic paper from the mirror was always 60 cm. while in the above test it was ca. 40 cm. So the proportional relation between the deflection and the current strength was quite trustworthy.

Here we must notice that the photographic paper differed from the curved scale in that it was a plane. Therefore, the corresponding correction had to be made whenever the current strength was evaluated from the photographic curves.

III. The Polarization of the Auxiliary Electrode

To examine the polarization of the pyrite electrode itself, it is necessary to know the effect of the copper auxiliary electrode. As a preliminary experiment of the polarization an attempt was made with a cell consisting of two copper electrodes under a current of similar strength as those used in the actual experiments. In order to determine the electromotive force of the above cell, the following procedure was followed. Two values of the potential drop caused by the two resistances, namely 10,000 ohms and 1,000 ohms were continuously measured one after the other for thirty minutes after the circuit was closed. If R be the total resistance, E , the effective electromotive force, e_1 and e_2 , the potential drop caused by the resistances r_1 and r_2 respectively, and r_1 and r_2 be so small compared to R that E may be regarded as a constant, we get

$$\frac{E}{(R+r_1)} = \frac{e_1}{r_1} \quad \dots\dots\dots(1)$$

$$\frac{E}{(R+r_2)} = \frac{e_2}{r_2} \quad \dots\dots\dots(2)$$

By combining (1) and (2), we get

$$\frac{e_1}{r_1}(R+r_1) = \frac{e_2}{r_2}(R+r_2)$$

$$R = \frac{e_1 - e_2}{\frac{e_2}{r_2} - \frac{e_1}{r_1}}$$

Substituting (3) in (1), we get

$$E = \left\{ \left(\frac{e_1 - e_2}{\frac{e_2}{r_2} - \frac{e_1}{r_1}} \right) + r_1 \right\} \frac{e_1}{r_1}$$

For the accurate computation of R and E , it is necessary to know the values of e_1 and e_2 . This can be accomplished only by the interpolation with two curves which represent the variations of e_1 and e_2 with the time as shown in Fig. 2. The experimental values of e_1 and e_2 are shown in Table I and interpolated e_1 and e_2 together with the calculated values of R , E and $\frac{E}{R}$ in Table II.

Table I

Time (min. Sec.)		Potential drop (volt)	
		e_1	e_2
	40	0.08746	
1	45		0.009107
3	15	0.08762	
5	0		0.009128
6	35	0.08792	
7	40		0.009142
9	0	0.08792	
10	15		0.009154
11	30	0.08803	
12	40		0.009166
14	0	0.08813	
15	10		0.009178
16	15	0.08823	
17	45		0.009186
19	10	0.08832	
20	30		0.009196
21	50	0.08842	
23	0		0.009206
24	10	0.08850	
25	30		0.009215
27	10	0.08860	
28	30		0.009227
29	50	0.08869	
30	45		0.009234

Fig. 2

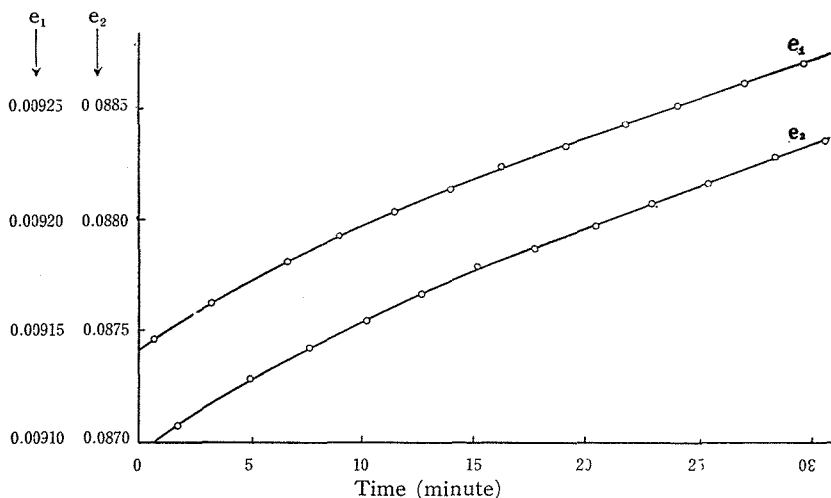


Table II

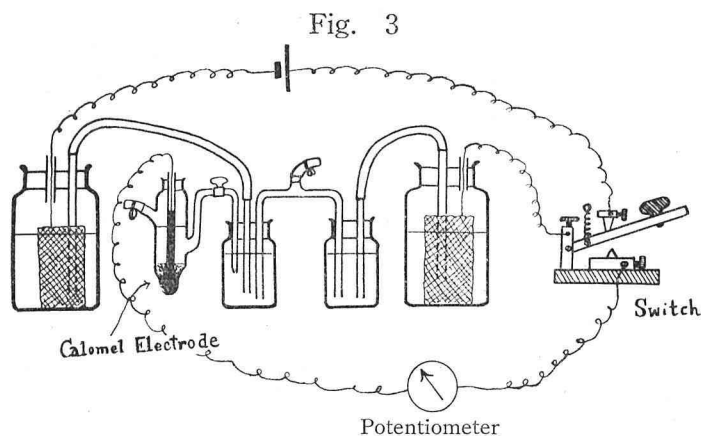
Time (Minute)	e_1 (volt)	e_2 (volt)	R (10^3 ohm)	E (volt)	E/R (10^{-5} amp.)
5	0.087720	0.0091278	2.209	2.025	0.917
10	0.087963	0.0091527	2.211	2.033	0.919
15	0.088173	0.0091754	2.206	2.033	0.922
20	0.088357	0.0091947	2.205	2.037	0.924
25	0.088527	0.0092127	2.203	2.039	0.926
30	0.088693	0.0092310	2.197	2.037	0.927

If the term e stands for the potential value of the copper electrode which corresponds to the ordinary state; ϵ_1 , its potential decrease resulting from the cathodic polarization; ϵ_2 , its potential increase resulting from the anodic polarization; and E_0 , the electromotive force of the battery, then the effective electromotive force E may be regarded as $E = E_0 + (e - \epsilon_1) - (e + \epsilon_2) = E_0 - (\epsilon_1 + \epsilon_2)$.

Although the electromotive force of the battery was not absolutely constant, it was experimentally confirmed that the variation was not quite negligible under a current strength of an order of 10^{-5} amp. By using the value 2.076 volt for E which was separately determined at the currentless state, we get, after 10 minutes' polarization, $\epsilon_1 + \epsilon_2 = 2.076 - 2.033 = 0.043$ volt as the resultant of both effects, assuming that E_0 remained unchanged (see Table II).

The above effect was determined by another operation under the same conditions. That is, the single potential of the copper

electrode at the polarized state, anodic or cathodic, was respectively measured in the usual way soon after the polarizing current was opened. Generally, the potential of the polarized electrode undergoes a considerable variation at the moment when the polarizing current is opened and afterwards its variation is continued until the potential recovers the value of ordinary state. However, by means of the specially designed switch shown in Fig. 3, the potential measurement could be taken simultaneously with opening of the current.



By the above experiment, the writer has obtained 0.578 volt as the potential of a cathodically polarized electrode and 0.615 volt as the potential of an anodically polarized electrode. The difference of the two is $0.615 - 0.578 = 0.037$ volt, which coincides nearly with the values 0.043 volt above obtained. Therefore in calculating the potential of the mineral electrode, we adopted 0.615 volt as the potential of the anodically polarized copper electrode, and 0.578 volt as the potential of the cathodically polarized copper electrode.

IV. General Course of the Polarization of Pyrite Electrode

When pyrite was polarized as a cathode under the above conditions, the polarization phenomena exhibited itself in a quite different manner according to the manner of treatment of the mineral. For example, if the cathodic polarization was made after the anodic, the current strength underwent a considerable decrease in a characteristic manner, whereas in the case of the polarization with a fresh mineral, it showed only a gradual variation in the course of time. In the case of an anodic polarization, however, no such variation was

recognized when the polarization was undertaken not only with a fresh piece of the mineral but also with a piece which had been previously polarized cathodically.

In the first case, the considerable decrease of current strength happened always in four steps (see Fig. 1 in Pl. I). In some experiments of this sort, however, the photograph showed some minute step besides four. From the results of a good many experiments, however, this appeared to have resulted from some unperceived imperfection of the crystal face. For the sake of brevity, the current strengths at the initial and the final points in the anodic curve are denoted by "Anode I" and "Anode II", and those which correspond to the respective steps in the cathodic curve by "Cathode I", "Cathode II", "Cathode III" and "Cathode IV".

The current strength is represented in terms of the deflection of the photographic image from the null point measured in centimeters. With regard to the Cathode IV, for example, the elongation of the curve meets with the perpendicular $t_4 c_4$, which passes through the transition point of the curve, at the point c_4' as is diagrammatically represented in Fig. 4. The distance from c_4' to the null point t_4 is taken as the current strength of that step. The current strengths thus measured in cm. at various steps are tabulated in the accompanying table, in which the current density is represented by the value corresponding to that at Anode II.

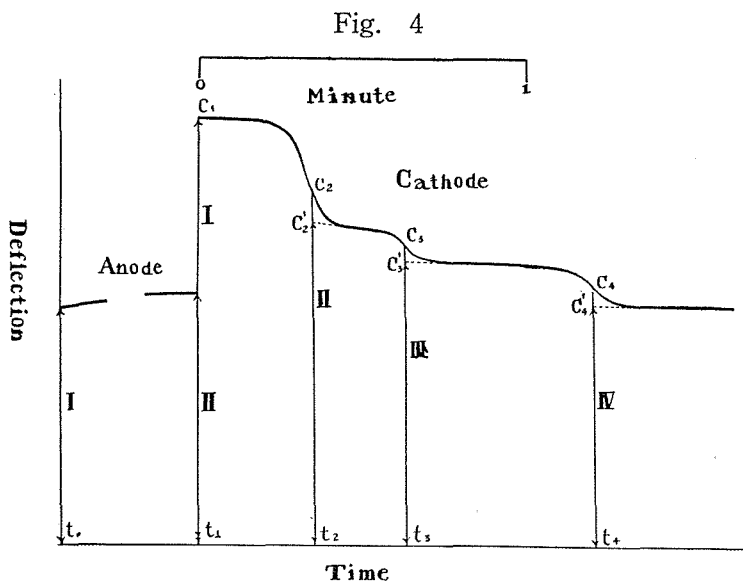


Table III

Electrode: (100) of pyrite from Tsunatori. Current density: 1.13×10^{-3} amp./sq. cm. Applied electromotive force: ca. 2 volts. Time of previous anodic polarization: 10 minutes.

a) Electrolyte: $n/100\text{-H}_2\text{SO}_4$

Exp. No.	Anode		Cathode			
	I	II	I	II	III	IV
1	6.75	7.22	12.25	9.33	8.37	7.09
2	6.81	7.27	12.28	9.32	8.44	7.14
3	6.73	7.21	12.19	9.34	8.36	7.06
4	6.67	7.21	12.22	9.21	8.35	7.06
Mean	6.74	7.23	12.24	9.30	8.38	7.09

b) Electrolyte: $n\text{-H}_2\text{SO}_4$

Exp. No.	Anode		Cathode			
	I	II	I	II	III	IV
1	7.01	7.29	11.81	9.18	8.36	6.76
2	7.12	7.26	11.78	9.22	8.45	6.76
3	6.96	7.19	11.67	9.10	8.26	6.77
4	7.01	7.29	11.79	9.12	8.21	6.81
5	6.96	7.23	11.79	9.12	8.21	6.76
Mean	7.01	7.25	11.77	9.15	8.30	6.77

Even on the same crystal face, perfect coincidence of these values can not be expected owing to such inevitable differences as the contact area or the diffusion of the electrolyte. In spite of these facts, the results thus obtained by the same surface do not show any noticeable deviation. All figures shown by the electrolyte of $n\text{-H}_2\text{SO}_4$ differ somewhat from those shown by the electrolyte of $n/100\text{-H}_2\text{SO}_4$. Whatever the figures may be, it is always possible to perceive the same fundamental character in the manner of the current variation.

1. Effect of the current density. In order to determine the effect of the current density on the step-wise variation, other experiments were carried out under various current densities. The results are summarized in the following table, where the current density is represented by the value of the Anode II as was stated before.

Table IV

Electrode: (100) of pyrite from Tsunatori. Applied electromotive force: ca. 2 volts. Electrolyte: $n/100\text{-H}_2\text{SO}_4$. Time of the previous anodic polarization: 10 minutes

Exp. No.	Current density (10^{-5} amp./sq. cm.)	Anode		Cathode				Sample
		I	II	I	II	III	IV	
1	1.15	7.03	7.42	12.69	9.66	8.69	7.31	} S ₁
2	"	6.95	7.43	12.69	9.70	8.76	7.30	
3	"	6.96	7.36	12.64	9.56	8.60	7.26	
4	"	6.97	7.37	12.64	9.68	8.65	7.24	
5	"	6.89	7.36	12.66	9.62	8.65	7.27	
6	"	6.96	7.33	12.57	9.63	8.62	7.25	
Mean		6.96	7.38	12.65	9.64	8.66	7.27	
7	2.08	6.82	7.71	13.16	9.96	8.94	7.48	} S ₂
8	"	6.92	7.75	13.27	10.12	9.05	7.61	
9	"	6.99	7.72	13.19	9.94	8.92	7.56	
10	"	7.01	7.75	13.23	10.00	8.92	7.58	
11	"	7.13	7.85	13.29	10.06	9.07	7.67	
Mean		6.97	7.76	13.23	10.02	8.98	7.58	
12	0.94	6.71	6.96	11.94	9.06	8.09	6.67	} S ₃
13	"	6.61	6.95	11.91	8.95	8.09	6.82	
14	"	6.61	6.92	11.89	9.00	8.13	6.78	
15	"	6.63	6.92	11.90	8.92	8.13	6.82	
16	"	6.68	6.92	11.90	9.09	8.19	6.87	
Mean		6.65	6.93	11.91	9.00	8.13	6.79	
17	0.70	6.10	6.23	10.56	8.11	7.32	6.14	} S ₄
18	"	5.97	6.28	10.71	8.06	7.28	6.10	
19	"	5.99	6.24	10.67	8.10	7.18	6.14	
20	"	6.06	6.26	10.71	8.08	7.23	6.09	
21	"	6.05	6.28	10.77	8.12	7.36	6.14	
Mean		6.03	6.26	10.63	8.09	7.27	6.12	

Since the shunt resistance in which the galvanometer was inserted had to be changed according to the current density in order to adjust the deflection for the suitable amount, the comparison of the figures given by the respective samples is quite meaningless.

For the sake of comparison, all figures above mentioned are recalculated in proportion that the Anode I is always 7.00 cm.

Results are summarized in Table V. Those obtained from the previous experimental results shown in Table III a) are also included in this table.

Table V

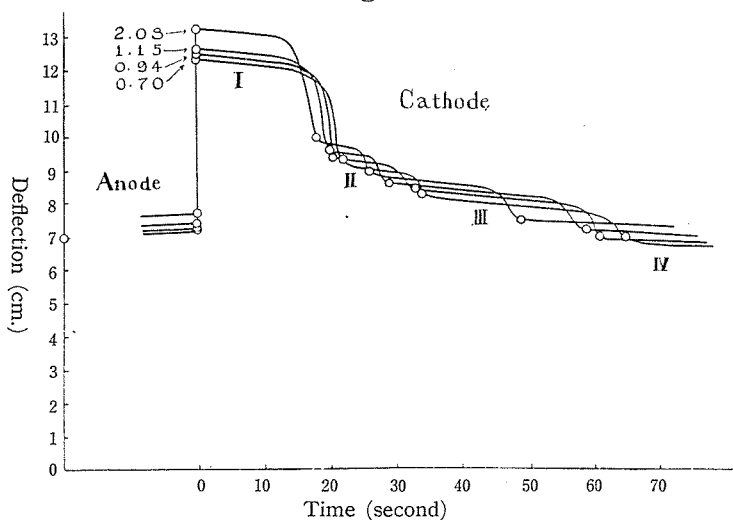
Current density (10^{-5} amp./sq.cm.)	Anode		Cathode				Sample
	I	II	I	II	III	IV	
2.08	7.00	7.91	13.51	10.22	9.18	7.66	} S ₁
"	"	7.84	13.42	10.24	9.15	7.70	
"	"	7.73	13.21	9.95	8.93	7.57	
"	"	7.74	13.21	9.99	8.91	7.57	
"	"	7.71	13.05	9.88	8.90	7.53	
Mean		7.79	13.28	10.06	9.01	7.61	
1.15	7.00	7.39	12.64	9.62	8.65	7.28	} S ₂
"	"	7.48	12.78	9.77	8.82	7.35	
"	"	7.40	12.71	9.61	8.65	7.30	
"	"	7.40	12.69	9.72	8.69	7.27	
"	"	7.48	12.86	9.77	8.79	7.39	
		7.37	12.64	9.69	8.67	7.29	
Mean		7.42	12.72	9.70	8.71	7.31	
1.13	7.00	7.49	12.70	9.68	8.68	7.35	} S ₃
"	"	7.47	12.62	9.58	8.68	7.34	
"	"	7.50	12.68	9.71	8.70	7.34	
"	"	7.57	12.82	9.67	8.76	7.41	
Mean		7.51	12.71	9.66	8.71	7.36	
0.94	7.00	7.26	12.46	9.45	8.44	6.96	} S ₃
"	"	7.36	12.61	9.48	8.57	7.22	
"	"	7.33	12.59	9.53	8.61	7.18	
"	"	7.31	12.56	9.42	8.58	7.20	
"	"	7.25	12.47	9.53	8.58	7.20	
Mean		7.30	12.54	9.48	8.56	7.15	
0.70	7.00	7.15	12.12	9.31	8.40	7.05	} S ₄
"	"	7.36	12.56	9.45	8.54	7.15	
"	"	7.29	12.47	9.47	8.39	7.18	
"	"	7.23	12.37	9.33	8.35	7.03	
"	"	7.27	12.46	9.39	8.52	7.10	
Mean		7.26	12.40	9.39	8.44	7.10	

The transition time of the respective steps was obtained from a number of the polarizing curves, and its mean values are given in the following table. The effect of the current density on the cathodic polarization is diagrammatically illustrated in Fig. 5.

Table VI

Current density (10 amp./sq. cm.)	Transition time (second)		
	I→II	II→III	III→IV
2.08	18	26	49
1.15	20	29	59
0.94	21	33	61
0.70	22	34	65

Fig. 5



The greater the polarizing current strength is, the higher the value of each step is not only in anodic but also cathodic polarization, although the variation is very small. And the transition time becomes shorter as the current density increases. Whatever the above effect may be, it is certain that the essential character of the variation is by no means affected by the current density.

2) **Influence of the duration of the anodic polarization.** The results of the experiments to determine the effect caused by the change of time taken in the anodic polarization on the step-wise variation are given in Table VII.

Table VII

Electrode: (100) of pyrite from Tsunatori. Current density: 0.91×10^{-3} amp./sq. cm. Applied electromotive force: ca. 2 volts. Electrolyte: n- H_2SO_4

Time (minute)	Anode		Cathode			
	I	II	I	II	III	IV
2	6.43	6.52	9.88	7.74	7.22	6.05
5	6.42	6.55	9.88	7.80	7.21	6.05
10	6.39	6.52	9.94	7.81	7.20	6.04
20	6.37	6.62	9.96	7.77	7.22	6.10
30	6.50	6.89	10.46	8.00	7.35	6.25

The results are recalculated in proportion that the Anode I is always 7.00 cm.

Table VIII

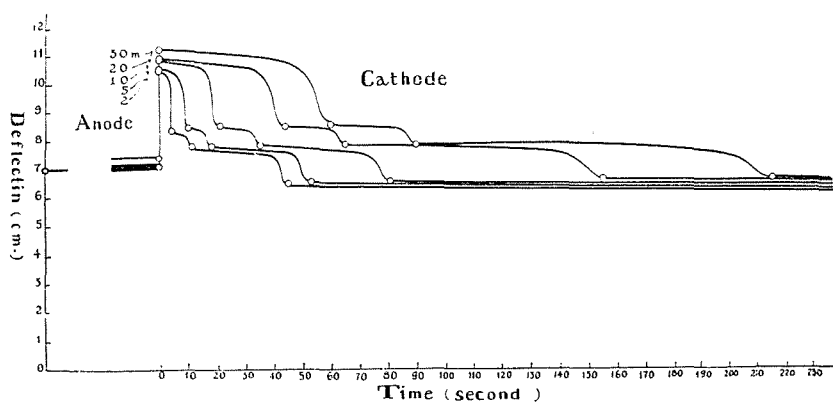
Time (minute)	Anode		Cathode			
	I	II	I	II	III	IV
2	7.00	7.10	10.76	8.43	7.86	6.59
5	„	7.14	10.77	8.50	7.86	6.60
10	„	7.14	10.89	8.56	7.89	6.62
20	„	7.27	10.95	8.54	7.93	6.70
30	„	7.42	11.26	8.62	7.92	6.73

Two facts are evident from these experiments: (1) that the current strength at each step both in the anodic and the cathodic polarization acquires somewhat higher value, although the variation is very small; and (2) the transition time of each step becomes longer by a considerable degree with the increase of the time of anodic polarization. When pyrite was subjected to the anodic polarization for 30 minutes, for example, more than 3 minutes were required to accomplish the whole variation; whereas in the case of 10 minutes' anodic polarization, the variation took only about one minute. The transition times of the respective steps observed in the foregoing experiments are given in the following table, and all results are graphically expressed in Fig. 6.

Table IX

Time (minute)	Transition time (second)		
	I→II	II→III	III→IV
2	4	12	45
5	10	18	53
10	21	35	81
20	44	65	155
30	60	90	217

Fig. 6.



3) **Influence of the applied electromotive force.** In order to corroborate the effect of a change of applied electromotive force several other experiments were undertaken with various degrees of applied electromotive force but with the same current strength. Results are tabulated in the following table, in which the current density is represented by the values corresponding to that at Anode II.

Table X

Electrode: (100) of pyrite from Tsunatori. Electrolyte: $n/100\text{-H}_2\text{SO}_4$.

Current density (10^{-3} amp./sq. cm.)	Applied e. m. f. (volt)	Anode		Cathode			
		I	II	I	II	III	IV
1.12	2.090	6.65	7.16	11.97	8.92	8.12	6.85
1.15	4.057	6.96	7.10	9.12	7.83	7.50	6.95
1.13	6.066	8.30	8.34	9.84	8.88	8.64	8.22
1.18	10.051	7.32	7.35	8.13	7.63	7.51	7.35

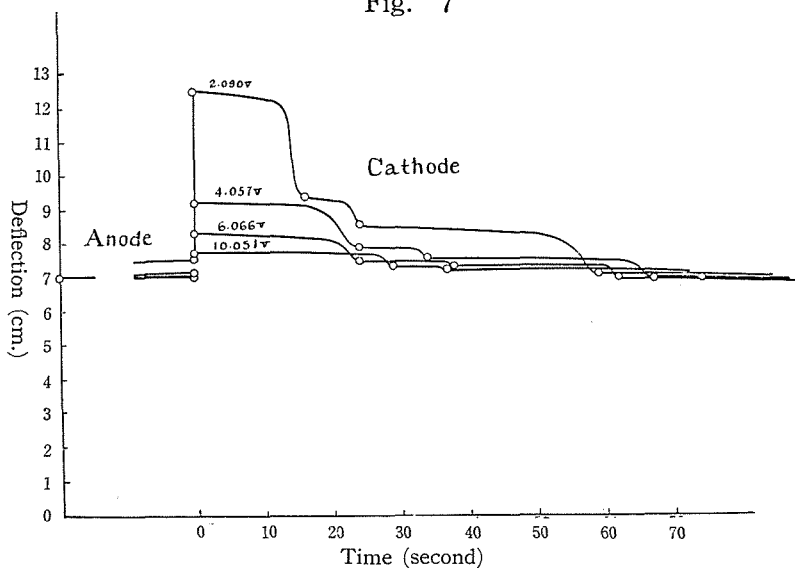
For the sake of comparison, all figures above mentioned are recalculated in proportion that the Anode I is always 7.00 cm. Results are shown in Table XI.

Table XI

Applied e. m. f. (volt)	Anode		Cathode			
	I	II	I	II	III	IV
2.090	7.00	7.54	12.60	9.39	8.55	7.21
4.057	„	7.14	9.17	7.88	7.54	6.99
6.066	„	7.03	8.30	7.49	7.29	6.93
10.051	„	7.03	7.77	7.30	7.18	7.03

Results thus obtained are diagrammatically summarized in Fig. 7.

Fig. 7



As is shown in Fig. 7, the differences of the current strength between the successive steps are more and more contracted with the increase of applied electromotive force (see Fig. 2 in Pl. I). This important fact suggests that the step-wise variation is principally based upon the variation of the effective electromotive force, that is, of the single potential of pyrite.

4) Polarization of some sulphide minerals other than pyrite.

With various other minerals such as galena, chalcopyrite, chalcocite and arsenopyrite, some experiments were undertaken

under similar conditions as above described. With respect to the chalcopyrite and arsenopyrite, the curves of the current variation were quite analogous with that of pyrite (see Figs. 2 and 3 in Pl. I); but the remaining minerals gave very different curves. Results with regard to these minerals are given in the following table.

Table XII

a) Electrode: Chalcopyrite from Ani. Current density: 1.20×10^{-3} amp./sq. cm. Applied electromotive force: ca. 2 volt. Electrolyte: n/100- H_2SO_4 . Time of previous anodic polarization: 2 minutes.

Exp. No.	Anode		Cathode			
	I	II	I	II	III	IV
1	5.75	5.85	8.33	6.52	not clear	4.35
2	5.70	5.70	8.14	6.41	„	4.39
3	5.73	5.71	8.20	6.39	„	4.37
4	5.68	5.65	8.15	6.43	„	4.38
5	5.71	5.72	8.17	6.50	„	4.43
6	5.63	5.53	7.95	6.26	„	4.20
Mean	5.70	5.69	8.16	6.42		4.35

b) Electrode: Arsenopyrite from Awashiro. Current density: 1.16×10^{-3} amp./sq. cm. Applied electromotive force: ca. 2 volt. Electrolyte: n/100- H_2SO_4 . Time of previous anodic polarization: 5 minutes.

Exp. No.	Anode		Cathode			
	I	II	I	II	III	IV
1	5.46	5.94	7.92	not clear	4.48	3.86
2	5.50	5.93	8.03	„	4.48	3.90
3	5.42	5.92	7.90	„	4.42	3.94
4	5.45	6.03	7.91	„	4.60	3.97
Mean	5.46	5.96	7.94		4.50	3.92

For the sake of comparison, the above mean values are recalculated in proportion that Cathode I is always 12.65 cm., which was actually obtained as the mean value with pyrite electrode under the current density of 1.15×10^{-3} amp./sq. cm. as shown in Table IV. The results are cited in the following table.

Table XIII

Electrode	Current density (10^{-3} amp./sq. cm.)	Cathode			
		I	II	III	IV
Pyrite	1.15	12.65	9.64	8.66	7.27
Chalcopyrite	1.20	„	9.95	—	6.74
Arsenopyrite	1.16	„	—	7.17	6.25

In the case of chalcopyrite, a step corresponding to the Cathode III of pyrite is not distinct, but the others nearly correspond to those of pyrite. Of the arsenopyrite, a step correlated to the Cathode II can not be clearly recognized and, moreover, both Cathode III and IV are somewhat less than those of pyrite. But it shows, as a whole, a variation quite analogous to pyrite.

At all events, it would be impossible to attempt an exact correlation with pyrite solely from the variation of the current strength because of the fact that each mineral is of different chemical nature.

Whatever the current strength may be, it may easily be perceived that the step-wise variation shown by iron minerals is of the same character, so that the phenomenon may well be ascribed to the iron content of minerals.

5) **Effect of $Fe_2(SO_4)_3$ -content of the electrolyte.** In the next place, two experiments were performed in order to examine the effect of the $Fe_2(SO_4)_3$ -content in the electrolyte.

a) The cathodic polarization was carried out in a solution of $n/20-H_2SO_4$ in the same manner as before.

b) The trace of a solution of $n-Fe_2(SO_4)_3$, which was so acidified that its acidity was $1/20$ normal with respect to H_2SO_4 , was added

Table XIV

a) Electrode; (100) of pyrite from Tsunatori. Applied electromotive force: ca. 2 volt. Electrolyte: $n/10-H_2SO_4$. Time of the previous anodic polarization: 10 minutes.

Exp. No.	Cathode			
	I	II	III	IV
1	8.84	6.76	6.02	4.91
2	8.89	6.68	6.00	4.93
3	8.86	6.66	5.94	4.93
4	8.76	6.60	5.87	4.76
5	8.76	6.62	5.92	4.88
Mean	8.82	6.66	5.95	4.88

- b) Electrode: (100) of pyrite from Tsunatori. Applied electromotive force: ca. 2 volt. Electrolyte: $n/20\text{-H}_2\text{SO}_4$ in which a trace of $n\text{-Fe}_2(\text{SO}_4)_3$ had been added

Exp. No.	Cathode			
	I	II	III	IV
1	8.86	—	—	4.70
2	8.67	—	—	4.70
3	8.62	—	—	4.72
4	8.79	—	—	4.76
5	8.75	—	—	4.70
Mean	8.74	—	—	4.72

to the solution at the end of the pick by means of a platinum wire; and the cathodic polarization was so undertaken that the polarizing current began to pass at the same time that the pick was touched to the electrode surface. Both results are tabulated in Table XIV. (see Fig. 6 in Pl. II).

In the case of (b), only two steps are observed, and their values almost correspond respectively to the Cathode I and Cathode IV of (a). Moreover, a step corresponding to Cathode I is easily prolonged according to the quantity of the solution of $\text{Fe}_2(\text{SO}_4)_3$ added. Such distinct behaviors can be principally ascribed to the fact that, in the case of (b), only $\text{Fe}_2(\text{SO}_4)_3$ reacts as a depolarizer, whereas in the case of (a), not only $\text{Fe}_2(\text{SO}_4)_3$ but also some iron oxide on the electrode surface takes part in the depolarization. From this fact, it may be positively stated that in the step-wise variation in the cathodic polarization after the anodic, the step of the Cathode I results from the presence in the solution of $\text{Fe}_2(\text{SO}_4)_3$; and the steps of the Cathode II and Cathode III result from some iron oxide on the electrode surface because of the fact that the Cathode IV almost coincides with the initial current strength in the cathodic polarization in the case of a fresh mineral.

V. Some Experiments to Elucidate the Chemical Mechanism Accompanying the Variation of the Polarizing Current Strength

1) **Anodic polarization.** To elucidate the cause of the current variation under the above circumstances, we have to take account of two fundamental variables: the effective electromotive force and total resistance of the circuit.

With reference to the effective electromotive force, the potential increase of pyrite due to the anodic polarization on the one hand, and the potential decrease of the copper electrode due to the cathodic polarization on the other, come under consideration since the electromotive force of the battery is practically constant. The resultant of these variations, however, should play a role of lowering the current strength. Therefore, the increase of current strength should be considered solely from the effect of the variation of the total resistance of the circuit.

Under the same procedure as that already taken in the previous experiment, the two values of the potential drops corresponding to the two definite resistances were continuously measured one after the other in the course of thirty minutes' polarization after closing the circuit. From this data, the total resistance, effective electromotive force, and the current strength at various times were calculated as before. The results are shown in Table XV.

Table XV

Electrode: (100) of pyrite from Tsunatori.
 Electrolyte: n/100-H₂SO₄.

Time (minute)	R (10 ⁵ ohm)	E (volt)	E/R (10 ⁻⁵ amp.)
5	1.387	1.450	1.045
10	1.380	1.464	1.061
15	1.368	1.467	1.072
20	1.358	1.468	1.031
25	1.347	1.465	1.038
30	1.343	1.467	1.092

According to the above data, the effective electromotive force is almost constant except at the time of 5 minutes; whereas the total resistance shows a gradual change in the course of time towards the lower value. This fact is more certainly recognized in the case of larger current strength. Table XVI represents the calculated results in a case in which the current strength is more than twice as large as that in the case of Table XV.

Table XVI

Electrode: (100) of pyrite from Tsunatori. Electrolyte: n/100-H₂SO₄.

Time (minute)	R (10 ⁶ ohm)	E (volt)	E/R (10 ⁻⁵ amp.)
5	0.641	1.397	2.181
10	0.625	1.397	2.236
15	0.616	1.397	2.270
20	0.610	1.400	2.293
25	0.605	1.398	2.311
30	0.602	1.401	2.320

These results prove that the course of the gradual increase of the current strength during anodic polarization may be ascribed merely to the decrease of the resistance. As the cause of the variation of the resistance, the anodic oxidation of the pyrite must be taken into account besides the diffusion of the electrolyte and the polarization of the copper electrode. In fact, when the pyrite is used as an anode, the electrolytes H₂SO₄ and Fe₂(SO₄)₃ are produced from the anodic oxidation of pyrite itself. Therefore it is quite natural to expect that these electrolytes render the solution more conductive. Moreover, the longer duration or the greater current density of the anodic polarization acquires a somewhat higher flow of current strength not only at Anode II but also at each step in the subsequent polarization, as we already noticed in the foregoing experimental results. In order to eliminate the effect of the change of resistance in the course of the anodic polarization, the mean values in Table IV are proportionally converted so that the Anode II is always 7.00 cm. Table XVII shows the results of this recalculation.

Table XVII

Current density (10 ⁻³ amp./sq. cm.)	Cathode			
	I	II	III	IV
2.08	11.93	9.04	8.10	6.84
1.15	12.00	9.14	8.21	6.90
0.94	12.03	9.09	8.21	6.86
0.70	11.94	9.05	8.13	6.84

The coincidence of the figures of this table tells us that, providing we eliminate the slight effect of resistance, the current

strength at each step of a cathodic polarization is practically independent of the current density in such a range of variation as is shown in the above table and that it shows nearly a constant value at each step. The same statement holds true in the case in which the duration of the anodic polarization was modified. This may only be explained by the constancy of the cathode potential at each step.

The effective electromotive force in the course of polarization shows nearly a constant from the beginning, as may be shown in Table XV. However we know that the pyrite potential assumes a far higher value than that of the ordinary state when it has been anodically polarized. At Anode II, after 10 minutes' polarization, the value reaches $2.083 + 0.578 - 1.464 = 1.197$ volts; where 2.083 volts is the electromotive force of the battery; 0.578 volts, the potential of copper electrode; and 1.464 volts, the effective electromotive force shown in Table XV. The value 1.197 volts is far higher than the values assumed against the normal ferric sulphate, which was so acidified that its acidity was twentieth normal with respect to the sulphuric acid. The latter are as follows:

1. Pyrite from Tsunatori	1.067 volt	}By the writer
2. "	1.078 "		
3. "	1.071 "		
Pyrite potential against an acidified normal ferric sulphate			
	1.10 "		By WELLS

These values are remarkably smaller than that calculated from the effective electromotive force in the state of the anodic polarization. Assuming the potential of pyrite against the $n/100\text{-H}_2\text{SO}_4$ is ca. 0.900 volts which was actually determined at 18°C , the increase due to the anodic polarization should amount to $1.197 - 0.900 = 0.297$ volts.

R. C. WELLS¹⁾, working with $n\text{-KCl}$ as the electrolyte, connected the pyrite electrode to the auxiliary copper electrode in copper sulphate. He polarized the mineral with a current of the strength of about 5×10^{-6} amp. Under these circumstances, the potential of pyrite rose to about 0.97 volts and afterwards remained constant as long as the polarization was anodic. When the pyrite was used as the cathode, the potential fell to 0.57 volts in 15 minutes and afterwards remained almost in the constant state.

According to his opinion, the pyrite potential depends in a minute degree on the ferric-ion concentration. The potential at the

1) *Loc. cit.*

constant state, therefore, corresponds to that determined by the maximum ferric-ion concentration; in the case of cathodic polarization, on the contrary, it corresponds to that determined by the highly reduced ferric-ion concentration.

It is a well known fact that the potential of the sulphide mineral electrode shows a great dependence also on the hydrogen ion concentration. Therefore the increase of the hydrogen ion concentration besides the ferric ion should contribute to the potential increase of the mineral electrode in the anodic polarization.

2) **Cathodic polarization.** To arrive at a consistent explanation for the change of the current strength in the cathodic polarization, the total resistance and the electromotive force at various times were calculated in the same way described before. These calculated values are recorded in Table XVIII.

Table XVIII

Electrode: (100) of pyrite from Tsunatori. Electrolyte: n/100-H₂SO₄.

Time (minute)	R (10 ⁴ ohm)	E (volt)	E/R (10 ⁻⁵ amp.)
10	1.195	1.395	1.168
15	1.209	1.397	1.156
20	1.216	1.397	1.149
25	1.219	1.393	1.143
30	1.227	1.394	1.136

Measurements within 10 minutes were almost impossible to carry out on account of the considerable change of the current strength.

According to the results, the effective electromotive force shows almost a constant in the course of polarization. The gradual fall of polarizing current as we see in this table, therefore, should be ascribed principally to the increase of the total resistance, since the solution becomes lower and lower in ion conductance in proportion to the decrease of free acid.

Here we have 2.083 volts as the electromotive force of the battery; 0.615 volts, as the potential of the copper electrode; and 1.395 volts, as the effective electromotive force after 10 minutes; therefore, the potential of pyrite amounts to $1.395 + 0.615 - 2.083 = -0.073$ volts.

It is also well-known that when hydrogen sulphide is passed into the solution, in general the potential of sulphide mineral against

it shows a considerable fall.¹⁾ With regard to the case of pyrite in $n/100\text{-H}_2\text{SO}_4$, for example, saturation brought the potential down to ca. 0.40 volts, a figure far greater than -0.071 volts, which was obtained from the effective electromotive force. Therefore we should imagine the medium at the state of much more reduced hydrogen ion concentration than $n/100\text{-H}_2\text{SO}_4$. In summary, the following two facts might be considered as the causes of the decrease in the potential during this polarization :

a) The decrease of the hydrogen ion concentration due to the cathodic discharge.

b) Hydrogen sulphide produced in the solution owing to the cathodic reduction of the pyrite material.

3) **Cathodic polarization after the anodic.** The characteristic current variation in the course of this polarization is principally due to the change in the potential of the pyrite electrode. This important statement is confirmed by the following experimental results already mentioned.

a) The current strength at each step in this polarization is nearly a constant regardless of the variation of current density, as we eliminate the slight effect of the variation of the resistance in the anodic polarization.

b) The differences of current strength between the successive steps decrease with the increase of applied electromotive force.

c) Cathode I and Cathode IV invariably appear in the cathodic polarization of a pyrite electrode without the previous anodic treatment if a trace of the solution of $\text{Fe}_2(\text{SO}_4)_3$ had been added to the electrolyte.

Now the total resistances at various times were calculated through the same procedure detailed before. Table XIX shows the

Table XIX

Electrode: (100) of pyrite from Tsunatori. Electrolyte: $n/100\text{-H}_2\text{SO}_4$.

Polarization Time (minute)	Total resistance (10^5 ohm)	Current density (10^{-5} amp./sq. cm.)
Anodic	5	1.15
	10	
	15	
	20	
	25	
Cathodic.....	30	1.32
	5	1.13

1) A. MATSUBARA. "On the Self-electrification of Sulphide Orebodies," *Japanese Journ. of Geol. and Geog.*, Vol. VII, No. 2, 1930.

results which were obtained in the course of the cathodic, subsequent to the anodic, polarization.

From this table we see that, in the anodic polarization, the total resistance undergoes a gradual fall with the time. An abrupt change, which occurred at the interval of 20 and 25 minutes, may be an experimental error. If we consider that the resistance after 5 minutes in the subsequent cathodic polarization nearly corresponds to that at the state of Cathode IV, the increase of the resistance through the step-wise variation amounts to $(1.329 - 1.318) \times 10^5 = 0.011 \times 10^5$ ohm according to the above data. This amount, however, could not have an influence upon the deflection of the galvanometer of more than 0.8 mm. assuming the resistance at the Cathode I as 1.318×10^5 ohm and the deflection as 12.65 cm. (see Table IV). The step-wise variation, in fact, is completed in less than 4 minutes in the case of 30 minutes' anodic polarization as shown in Table IX. So the real variation of the resistance in this interval, therefore, would be so small that its effect could practically be neglected in the whole variation.

If we assume that the current variations depend alone on the change of the electromotive force of the cell, the latter and the potential of pyrite are easily computed from the current strength.

Table XX

Applied e. m. f. (volt)	Anode	Cathode				
	II	I	II	III	IV	
2.090	Current strength (cm.)	7.16	11.97	8.92	8.12	6.85
	Effective e. m. f. (volt)	1.471	2.459	1.833	1.668	1.407
	Potential of pyrite (volt)		0.984	0.358	0.193	-0.068
4.057	Current strength (cm.)	7.10	9.12	7.83	7.50	6.95
	Effective e. m. f. (volt)	3.438	4.416	3.791	3.632	3.365
	Potential of pyrite (volt)		0.974	0.349	0.190	-0.077
6.066	Current strength (cm.)	8.34	9.84	8.88	8.64	8.22
	Effective e. m. f. (volt)	5.447	6.427	5.800	5.643	5.369
	Potential of pyrite (volt)		0.976	0.349	0.192	-0.082
10.051	Current strength (cm.)	7.35	8.13	7.63	7.51	7.30
	Effective e. m. f. (volt)	9.432	10.433	9.791	9.637	9.368
	Potential of pyrite (volt)		0.987	0.355	0.201	-0.068
Mean of the potential of pyrite			0.983	0.353	0.194	-0.074

The calculation may be made from the figures shown in Table X, assuming the potential of pyrite electrode at Anode II as 1.197 volt (see p. 57).

The pyrite potential at Cathode I is not accordant with that at Anode II: the latter is greater than the former by $1.197 - 0.983 = 0.214$ volt. Therefore it should be supposed that the potential at Anode II undergoes such variation in a moment when the polarization is commutated.

It has already been noticed that the characteristic current variation results from the previous anodic polarization and never from the cathodic itself. And Cathode I, moreover, may be ascribed to the presence of $\text{Fe}_2(\text{SO}_4)_3$ produced by the anodic oxidation.

The value of 0.983 volt at Cathode I is nearly in accord with the value of ca. 1.0 volt, which was actually obtained as the pyrite potential in $n\text{-Fe}_2(\text{SO}_4)_3$. Moreover, the value of -0.074 volt almost coincides with that of -0.073 volt which was obtained in the foregoing experiment with a fresh mineral surface (see p. 58). This is naturally expected from the fact that the polarization curve obtained with a fresh mineral surface exactly coincides with that of Cathode IV on the photograph.

VI. Conclusion

1) When pyrite is polarised as an anode in a very small amount of not agitated electrolyte, the potential of pyrite rises to about 1.197 volt after 10 minutes polarization. This development of potential should be established very soon after the polarising current begins to pass.

2) In the cathodic polarization, the phenomena of polarization depend upon the previous treatment of the mineral. If the polarization is undertaken with a piece which was previously polarized anodically, the current strength shows a characteristic step-wise variation. In the case of the polarization of a fresh mineral, on the other hand, no such variation is displayed.

3) The step-wise variation in the former case happens always in four steps. The longer the duration of anodic polarization, the longer the transition time of the respective step; but the fundamental character of variation is by no means influenced by the duration.

4) The current strength at each step acquires slightly higher values with increase of the duration of anodic treatment or the

current strength. If we eliminate the effect of the variation of the resistance due to the previous anodic polarization, the current strength at each step is practically constant regardless of the duration of anodic treatment or the current density in a certain range.

5) The difference of the current strength between the successive steps decreases more and more with increase of applied electromotive force.

6) The characteristic step-wise variation of the current strength is principally caused by the potential variation of the mineral owing to the cathodic reduction of the anodically oxidized products such as $\text{Fe}_2(\text{SO}_4)_3$ in the solution and some iron oxide on the electrode surface.

7) The pyrite potentials corresponding to the four steps are calculated approximately as 0.983, 0.353, 0.194 and -0.074 volt respectively.

In conclusion, the writer wishes to express his hearty thanks to Prof. Dr. A. MATSUBARA under whose kind guidance and encouragement the present experiments were performed.

Explanation of Plates

- Pl. I. Fig. 1. The current variation during the cathodic polarization after 10 minutes of anodic polarization with pyrite electrode in contact with $n/100\text{-H}_2\text{SO}_4$ under the applied electromotive force of 2.090 volts.
- Fig. 2. The same, except that the applied electromotive force has been raised to 6.066 volts.
- Fig. 3. The current variation during the cathodic polarization after 35 minutes of anodic polarization with pyrite electrode in contact with $n/100\text{-H}_2\text{SO}_4$ under the applied electromotive force of ca. 2 volts.
- Fig. 4. The current variation during the cathodic polarization with a fresh piece of pyrite in contact with $n/20\text{-H}_2\text{SO}_4$ in which a trace of acidified $n\text{-Fe}_2(\text{SO}_4)_3$ had been added.
- Pl. II. Fig. 5. The photograph given in Fig. 4 was overlapped on another which was obtained during the cathodic polarization after 10 minutes of anodic polarization with pyrite electrode in contact with $n/20\text{-H}_2\text{SO}_4$ under the applied electromotive force of ca. 2 volts.
- Fig. 6. The current variation during the cathodic polarization after 5 minutes of anodic polarization with chalcopyrite electrode in contact with $n/100\text{-H}_2\text{SO}_4$ under the applied electromotive force of ca. 2 volts.
- Fig. 7. The current variation during the cathodic polarization after 5 minutes of anodic polarization with arsenopyrite electrode in contact with $n/100\text{-H}_2\text{SO}_4$ under the applied electromotive force of ca. 2 volts.
- Fig. 8. The current variation during the cathodic polarization after 1 minute of anodic polarization with chalcosite electrode in contact with $n/100\text{-H}_2\text{SO}_4$ under the applied electromotive force of ca. 2 volts.

Fig. 1

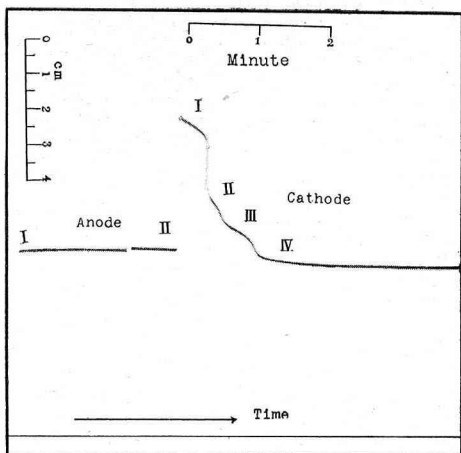


Fig. 2

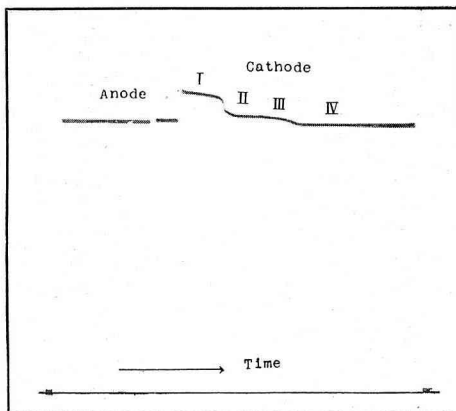


Fig. 3

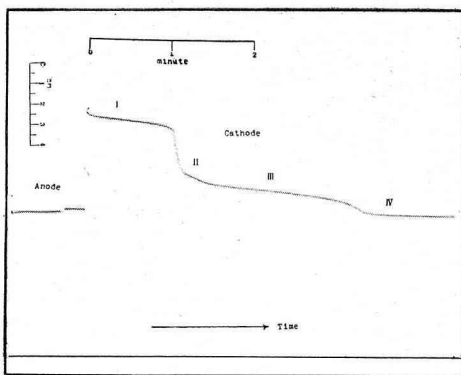
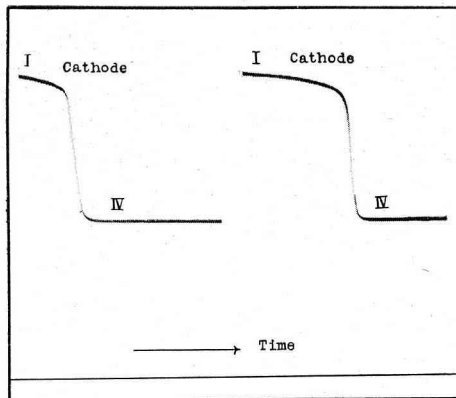


Fig. 4



J. TAKUBO Photo.

Fig. 5

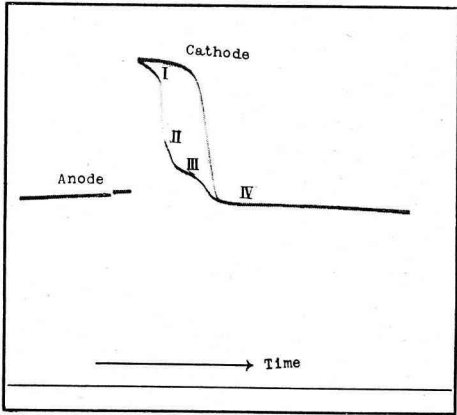


Fig. 6

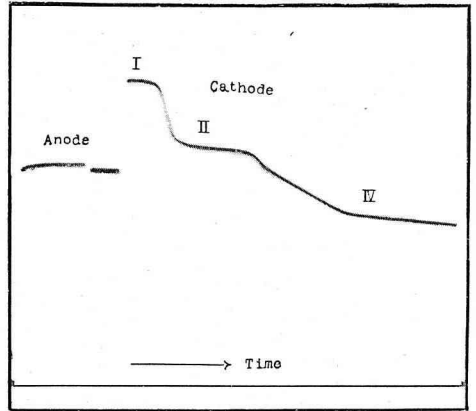


Fig. 7

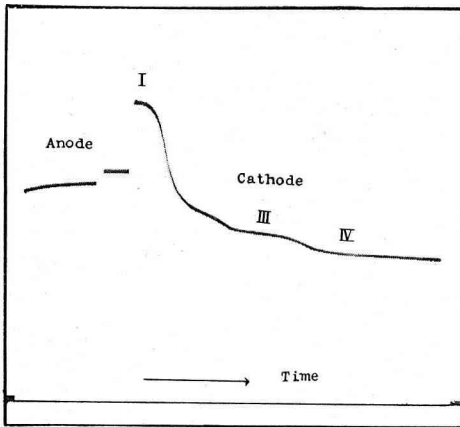
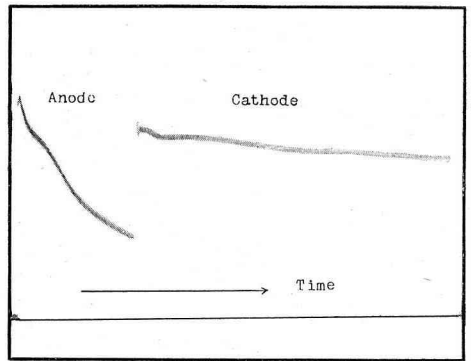


Fig. 8



J. TAKUBO Photo.