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Electrolytic Polarisation of Pyrite Electrode

By

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With 14 text-figures.

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Abstract

If a pyrite electrode is cathodically polarised in dilute H_2SO_4 with a current of sufficient density, the dissolved oxygen in the electrolyte and the pyrite itself act, in turn, as the depolariser before the cathode potential reaches that of iron-hydrogen alloy, and the potential-change occurs in three steps.

On the other hand, in an anodic polarisation of pyrite in dilute H_2SO_4 , the depolarising action of the pyrite itself occurs before the anode potential settles to a practically constant value.

The effects of current density, acidity or alkalinity of electrolyte, and the effect of a preliminary electrolysis of the opposite sense upon the course of polarisation and upon the final settled potential in both cathodic and anodic polarisations were measured, and some chemical explanations were given to them.

Introduction

Electrolytic polarisation of pyrite was first studied by R. C. WELLS,¹⁾ who observed some rise or fall of potential when it was polarised either as an anode or as a cathode. C. SCHLUMBERGER²⁾ describes that a counter electromotive force of the order of 1.5 volts is produced when an electric current passes through an underground ore body, which is, of course, surrounded by the ground water. According to his explanation, the end of the ore body into which the current enters becomes a hydrogen-electrode, while the end from which the current leaves it becomes an oxygen-electrode so that a detonating gas cell is temporarily formed there.

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1. R. C. WELLS, U. S. Geol. Surv. Bul. 548 (1914).
 2. C. SCHLUMBERGER, Étude sur la prospection électrique du sous-sol (1920).

J. TAKUBO¹ has found a characteristic potential change of some iron-bearing sulphide minerals when they were once anodically and then cathodically polarised by electrolysing a very small droplet of dilute sulphuric acid. Since he measured the potential change by measuring that of current intensity, the evaluation of the cathode potential could be reached only to the vicinity of null value owing to the difficulty arising from the gas evolution.

It seemed interesting to the writer to measure the lower cathode potentials with some appropriate method. Further it seemed desirable to continue WELLS' investigation and to elucidate fully the manner of polarisation when the electrode is freely immersed in a large excess of electrolyte as it may throw much light upon the study of polarisation under various special conditions.

A pyrite electrode is by no means unattackable as well in acid, neutral or in alkaline solution. In 1871 W. SKEY² published his opinion that when pyrite is cathodically polarised in dilute sulphuric acid or in neutral salt solution, sulphur goes into H_2S : and under certain conditions metal is left on the electrode surface.

According to I. BERNFELD³, sulphur in the mineral undergoes oxidation in various degrees according to the conditions, and iron goes over to hydroxide if the mineral is employed as an anode. When the mineral constitutes a cathode, SH' ions are produced if the solution be acid, while in an alkaline solution metallic iron remains on the electrode as a slime.

Pyrite-cathode in $n H_2SO_4$ dissolves markedly by the action of current, sending $FeSO_4$ and H_2S in the electrolyte⁴. An electrolyte of 2% H_2SO_4 is also reported to act in the same way⁵. The writer's experiments have revealed that metallic iron may be produced on a pyrite cathode if the acidity of sulphuric acid solution is not larger than ca. 0.05 normal and the current density is not smaller than ca. 3 milliamperes per sq. cm. It was also found that a velvet-black coating of FeS may be produced under other circumstances.

The nature of the chemical reaction and consequently of the resulting surface characters of the electrode differs, in this way,

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1. J. TAKUBO, These Memoirs. Vol. X, No. 1, (1934) 37.
 2. W. SKEY, Chem. News, vol. 23 (1871) 291.
 3. I. BERNFELD, Zeitschr. f. physk. Chem. Bd. 25 (1898) 46.
 4. A. MATSUBARA u. J. TAKUBO, Anniversary Volume dedicated to Masumi Chikashige. (1930) 311.
 5. K. FISCHBECK, Zeitschr. anorg. Chem. Bd. 148 (1925) 112.

according to the condition of electrolysis. So it is quite natural that the electrode potential should also show remarkable differences from case to case. It requires, then, to elucidate the conditions under which each chemical reaction occurs before we can systematize the polarisation phenomena of pyrite.

Since, in many methods of electric prospecting, current is passed through the ground where the ore body lies, we have to be well aware of the effect of electrolytic polarisation of the latter in order not to get an erroneous conclusion whenever we happen to use a direct current.

Interested in this problem, the writer has undertaken first to examine the polarisation phenomena of pyrite and accompanying chemical reactions, employing a special apparatus which enabled one to measure the electrode potential and at the same time the intensity of the polarising current.

Experimental Arrangement

In order to examine the polarisation phenomena under a definite current density, or to study the current-change at the same time with the accompanying potential-change, an apparatus was contrived in which the current circuit may be kept open while the potential circuit is left in the closed state for a short length of time, after which the latter is opened and then the former is closed and again they may be left standing in that state for another short length of time. This alternate opening and closing of each circuit may be repeated ca. 40 times a second by means of a motor-commutator.

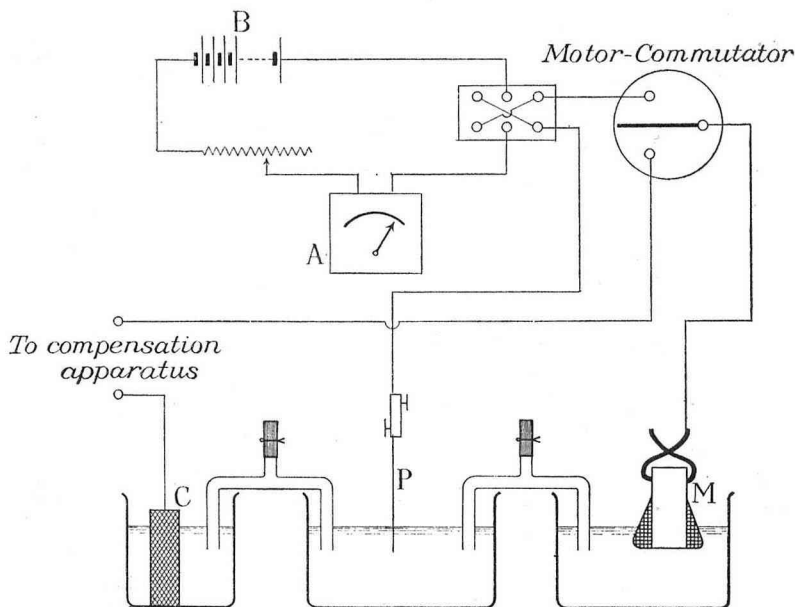
The above apparatus enabled one to measure the potential at any desired moment by the usual method of compensation without having any vibration of the galvanometer mirror, and the current intensity may be continuously measured or regulated to a definite magnitude without feeling any vibration of the needle of the milliammeter.

The ratio of the time during which the current circuit was kept open to that in the closed state was ca. 1/10 and the current intensity was reduced thereby to ca. 91 % of that of the continuous flow. This percentage could be kept constant by keeping the supplied current to the motor constant.

The essential part of the apparatus is schematically represented in Fig. 1.

The polarising current from a source of battery (B) could be measured with a milliammeter (A) to one or two thousandth of a milliampere when the current intensity was less than 1 milliampere, but the accuracy was reduced to 1/10 of it when the current in the range from 1 to 10 milliampere was measured.

Fig. 1



The electrode mineral (M) was first polished to a prismatic form and one half of its length was covered with hardened Canadabalsam. A plane nearly perpendicular to the edge of the prism was prepared by polishing the sealed end, and that was used as the electrode. The lateral cover of Canadabalsam (or sealing wax) was necessary as otherwise the lateral faces became irregularly wet with the electrolyte and the area of the active surface could not be accurately measured.

As the auxiliary electrode for the potential measurement, a broad, 60 mesh copper net (C), which was previously covered with a thick deposition of copper by electrolysis and immersed in a saturated, acidified CuSO_4 solution, was employed. The auxiliary electrode in the current circuit consisted simply of a fine platinum wire (P). In order to avoid the mixing of liquid, the bath of the platinum wire was always separated from that of the mineral by wicks. Since

the electrolyte was very dilute acid, it was often necessary to use two or three wicks in parallel in order to reduce the resistance.

Part I. Cathodic Polarisation

A. Cathodic polarisation of fresh pyrite

1) General course of polarisation

As soon as a pyrite electrode is cathodically polarised e. g. in 0.01 n H_2SO_4 with a current of a density of several milliamperes per sq. cm., the cathode potential falls first very rapidly, then the falling velocity fades gradually until it becomes practically null. It takes ca. 20 or 30 seconds before the potential reaches to a practically constant value, and afterwards it falls only very slowly.

If the polarising potential be kept constant, the current intensity decreases slightly at the beginning of the polarisation until it arrives

Table 1.

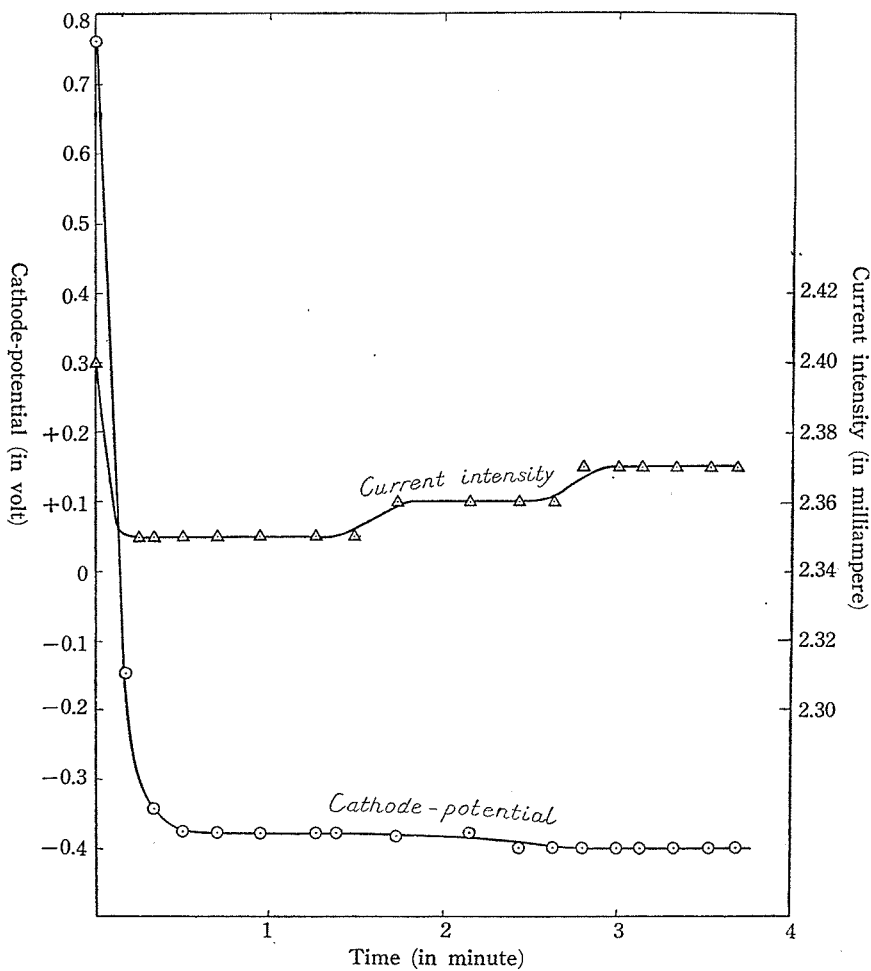
Cathodic polarisation of pyrite in 0.01 n H_2SO_4 . Initial current density: 5.04 milliamperes per sq. cm. Room temperature: 30°C.

Time		Scale reading of potentiometer	Cathode potential in volt	Current intensity in milliamperes
minute	second			
	0	7.22	+0.760	2.40
	10	26.82	-0.148	"
	15	"	"	2.35
	20	34.11	-0.343	"
	30	35.35	-0.376	"
	42	35.40	-0.377	"
	57	35.47	-0.379	"
1	16	"	"	"
	29	"	"	"
	44	35.65	-0.384	2.36
2	9	35.49	-0.379	"
	26	36.29	-0.401	"
	38	"	"	"
	48	"	"	2.37
3	0	"	"	"
	8	"	"	"
	20	"	"	"
	32	"	"	"
	41	"	"	"

at a constant magnitude just at the time when the potential change practically ceases. The flow of the current at this constant depressed state continues for some time, and then begins to show a very slow rise. The reason for this current change will be discussed later.

As an example, an experimental result is shown in Table 1 to illustrate the above changes, and the same result is graphically represented in Fig. 2.

Fig. 2.



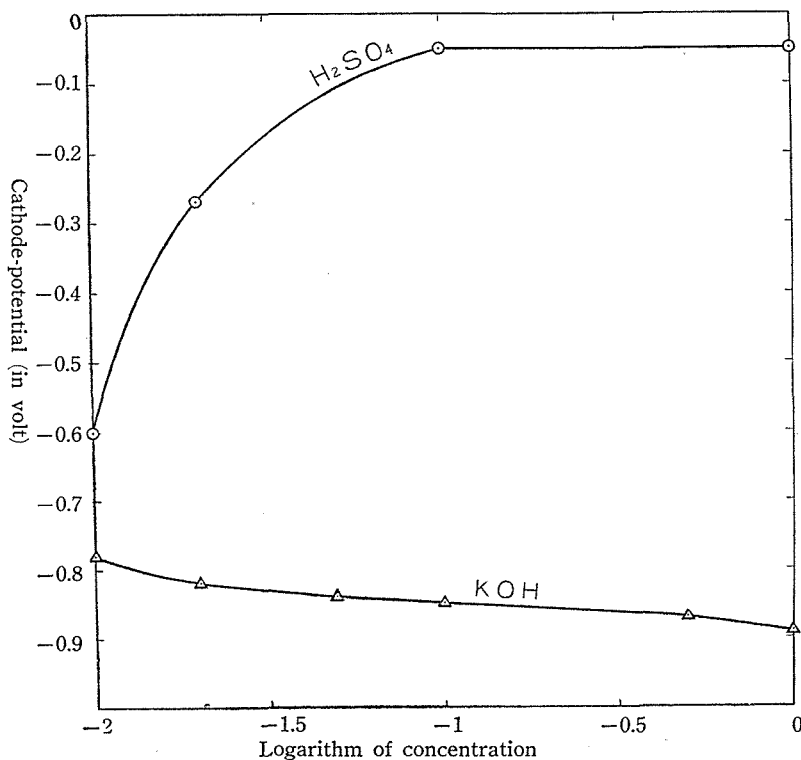
2) Effect of acidity and alkalinity

The settled potential differs according to the acidity or alkalinity of the electrolyte. The more concentrated the acid, the higher is the settled potential. On the contrary, the more concentrated alkali is the electrolyte, the more conspicuous is the potential fall.

Table. 2

Electrolyte	Settled cathode potential in volt	Electrolyte	Settled cathode potential in volt
1.0 n H_2SO_4	-0.03	0.01 n KOH	-0.78
0.1 n „	-0.05	0.02 n „	-0.82
0.02 n „	-0.27	0.05 n „	-0.84
0.01 n „	-0.60	0.1 n „	-0.85
		0.5 n „	-0.87
		1.0 n „	-0.89

Fig. 3



The relation between the settled potential and the concentration of electrolyte in a case when the current density is 3.45 milliampere per sq. cm. is shown in Table 2.

These relations are represented in two curves in Fig. 3 in which the potential is taken in the ordinate and the logarithm of concentration is taken in the abscissa. One will notice, in the figure, that the effect of the concentration of acid is very conspicuous especially in the dilute side. In the concentrated side, however, the curve is almost horizontal, for reasons which will be discussed later.

In cases when the current density is relatively large, the general form of the time-potential curve is also affected by acidity and alkalinity. The settlement of potential becomes slower when the acid concentration is smaller. In the case of 0.01 n H_2SO_4 , the potential once settled begins to rise slowly after about 20 minutes' electrolysis. In alkaline solution, the settlement of potential is generally rapid, but the potential-rise begins to take place after a few minutes' electrolysis.

Fig. 4 represents an example of time-potential curve in the case when the current density is 3.34 milliampere per sq. cm. and the electrolyte is 0.01 n H_2SO_4 . Fig. 5 is that of the case of 0.02 n KOH under the same current density.

Fig. 4.

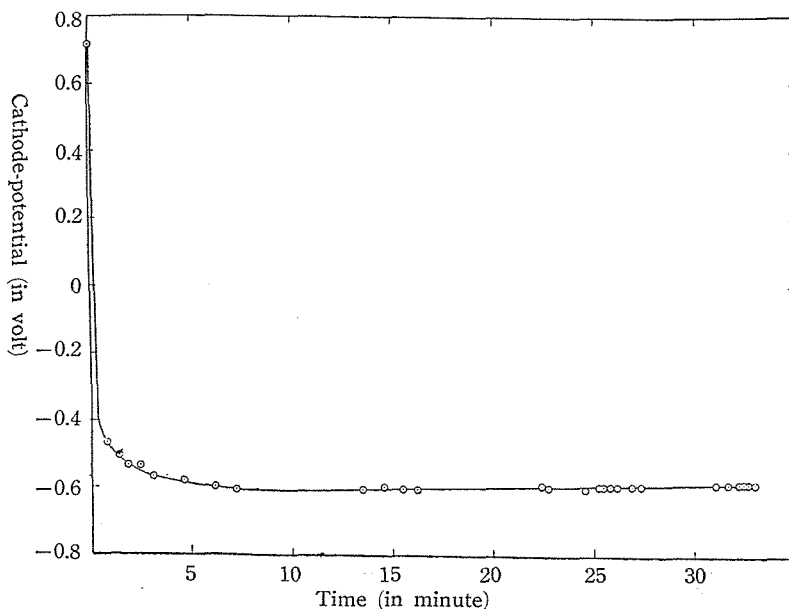
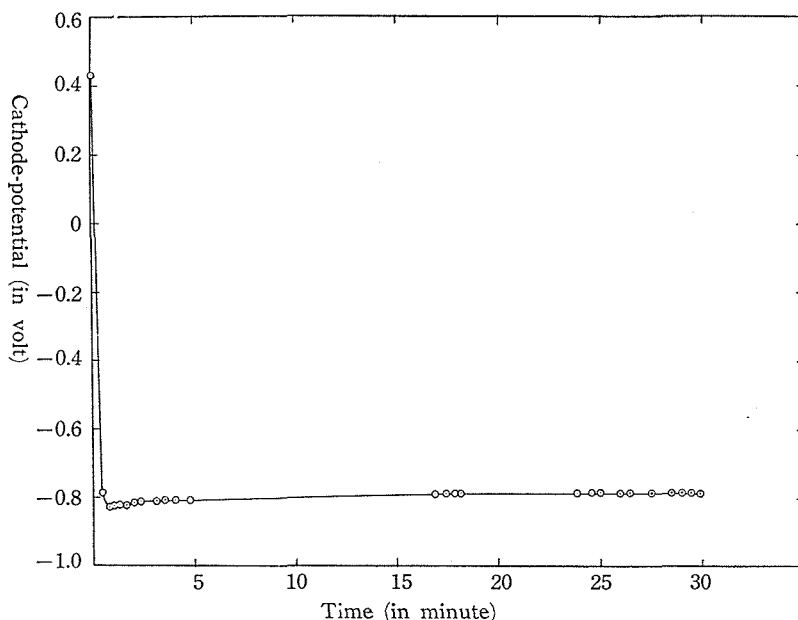


Fig. 5



3) Effect of current density

The influence of current density upon the settled potential is even more strong than that of the acidity and the alkalinity. In order to examine it, a series of experiments was carried out with various current density ranging from 0.078 to 9.91 milliampere per sq. cm. The electrolyte was 0.01 n H_2SO_4 .

The electrode which is once electrolytically polarised is apt to show somewhat abnormal potential even when its surface is thoroughly polished. Therefore, in each experiment of this series, a new, fresh electrode known never to have been polarised was employed. The dilute sulphuric acid in the cathode bath once used in an experiment was rejected, and an entirely fresh solution was used in the next experiment in order to avoid any disturbing effect of a minute quantity of dissolved substance. The temperature was maintained at $22 \pm 1^\circ\text{C}$. The current intensity in each experiment was maintained constant by hand regulation of rheostat.

The experimental results are shown in the following tables :

Table 3

Current density: 9.915 milliamper per sq. cm.

Time		Scale reading of potentiometer	Cathode potential in volt
minute	second		
	0	+ 8.85	+0.805
	6	-35.80	-0.395
	16	-40.00	-0.507
	32	-41.12	-0.537
	44	-43.00	-0.588
	50	-43.69	-0.607
1	0	-44.38	-0.625
	16	-44.47	-0.627
	22	"	"
	46	-45.18	-0.619
2	6	-45.42	-0.653
	20	-45.69	-0.660
3	12	-45.80	-0.663
	34	"	"
	49	-46.00	-0.668
4	4	"	"
	16	"	"
	30	"	"
	44	"	"
5	2	"	"
	10	"	"

Table 4

Current density: 5.884 milliampere per sq. cm.

Time		Scale reading of potentiometer	Cathode potential in volt
minute	second		
	0	+ 8.15	+0.787
	8	-26.38	-0.147
	17	-27.82	-0.187
	25	-29.20	-0.224
	32	-31.10	-0.275
	40	-31.90	-0.297
	48	-33.25	-0.334
	52	"	"
1	20	-36.30	-0.416
	29	-37.52	-0.449
	41	-39.00	-0.490
	48	-40.42	-0.528
	52	-40.90	-0.541
2	0	-43.55	-0.613
	13	-44.40	-0.636
	20	"	"
	27	-44.89	-0.649
	42	-46.08	-0.681
	50	"	"
3	0	"	"
	10	-46.42	-0.691
	39	-47.00	-0.706
	50	"	"

Table 4

(Continued)

Time		Scale reading of potentiometer	Cathode potential in volt
minute	second		
4	0	-47.10	-0.709
	6	"	"
	13	"	"
5	47	"	"
	0	"	"
	23	-46.22	-0.685
6	33	-46.60	-0.695
	3	-46.50	-0.693
	13	"	"
7	47	-45.80	-0.674
	12	-46.20	-0.684
	30	-46.48	-0.692
8	46	"	"
	5	"	"

Table 5

Current density: 4.479 milliampere per sq. cm.

Time		Scale reading of potentiometer	Cathode potential in volt
minute	second		
1	0	+ 7.61	+0.771
	8	-37.38	-0.437
	20	-37.40	-0.438
	29	-37.72	-0.446
	36	-38.78	-0.475
	46	-39.91	-0.505
	58	-40.79	-0.529
	14	-40.90	-0.532
	27	-43.12	-0.592
	36	-43.90	-0.613
2	52	-44.21	-0.621
	6	-44.30	-0.623
	16	-44.83	-0.638
3	44	-45.30	-0.650
	0	"	"
	12	-45.28	-0.650
	29	-45.30	"
	50	"	"
4	10	"	"
	20	"	"
	20	"	"
5	0	-45.75	-0.662
	20	"	"
	40	"	"
	56	"	"
6	14	"	"
	30	"	"
	56	"	"
7	20	"	"
	20	"	"

Table 6

Current density: 3.306 milliampere per sq. cm.

Time		Scale reading of potentiometer	Cathode potential in volt
minute	second		
	0	+ 9.02	+0.809
	9	-27.93	-0.185
	18	-31.92	-0.293
	23	-34.41	-0.361
	34	-34.48	-0.362
	44	-37.25	-0.436
	56	-40.73	-0.536
1	2	-43.80	-0.612
	14	"	"
	26	-43.95	-0.617
	46	"	"
2	20	-44.11	-0.621
	42	-44.60	-0.634
3	0	-44.61	"
	20	-45.02	-0.645
	30	"	"
	47	"	"
4	6	"	"
	20	"	"
	44	"	"
5	12	"	"
	34	"	"
	46	"	"
6	6	"	"
	56	"	"

Table 7

Current density: 3.093 milliampere per sq. cm.

Time		Scale reading of potentiometer	Cathode potential in volt
minute	second		
	0	+ 7.70	+0.777
	23	-30.98	-0.281
	27	-32.12	-0.312
	32	-32.35	-0.318
	40	-32.65	-0.327
	53	-33.95	-0.362
	58	-34.18	-0.369
1	0	-36.65	-0.408
	20	-39.58	-0.516
	24	-39.92	-0.526
	30	-40.22	-0.534
	47	-40.10	-0.531
2	8	-40.25	-0.535
	20	-40.48	-0.541
	42	-41.21	-0.561
	56	-41.50	-0.569
3	24	-42.38	-0.593
	55	-42.62	-0.600
5	0	-42.83	-0.605
	25	-43.30	-0.618
	58	-43.30	-0.618

Table 7

(Continued)

Time		Scale reading of potentiometer	Cathode potential in volt
minute	second		
6	10	-43.30	-0.618
	27	"	"
	47	"	"
7	0	"	"
	17	"	"
	35	"	"
	48	"	"
8	0	"	"

Table 8

Current density: 2.826 milliampere per sq. cm.

Time		Scale reading of potentiometer	Cathode potential in volt
minute	second		
	0	+ 6.35	+0.737
	9	-26.80	-0.153
	22	-27.30	-0.167
	44	-29.62	-0.229
	56	-31.61	-0.282
1	13	-32.12	-0.296
	32	-32.58	-0.308
2	0	-33.22	-0.326
	34	-33.22	-0.326
3	51	-33.12	-0.323
	6	-33.12	-0.323
	40	-33.30	-0.328
4	56	"	"
	6	"	"

> Remained unchanged until 15' 50".

Table 9

Current density: 2.496 milliampere per sq. cm.

Time		Scale reading of potentiometer	Cathode potential in volt
minute	second		
	0	+ 6.70	+0.748
	13	-25.68	-0.125
	30	-29.32	-0.223
	40	-30.60	-0.258
	54	-31.81	-0.290
1	16	-32.28	-0.303
	30	-32.35	-0.305
	46	-32.35	-0.305
2	4	"	"
	30	"	"
3	46	"	"
	0	-32.60	-0.312
	12	"	"
	26	"	"
	42	"	"
	56	"	"
4	20	"	"
5	24	-33.00	-0.322
6	36	-33.75	-0.343

Remained unchanged until 13' 27".

Table 10

Current density: 2.041 milliamperes per sq. cm.

Time		Scale reading of potentiometer	Cathode potential in volt
minute	second		
	0	+ 8.90	+0.806
	8	-14.48	+0.178
	16	-24.30	-0.086
	27	-25.29	-0.116
	46	-26.49	-0.148
1	0	-27.30	-0.167
	20	-29.12	-0.216
	32	-30.74	-0.259
2	20	-32.06	-0.295
	34	-32.00	-0.293
	49	-32.00	-0.293
3	6	"	"
	22	-32.20	-0.299
	49	"	"
4	27	"	"
5	0	-32.52	-0.307
	36	-32.59	-0.309
6	20	-33.19	-0.325
7	16	"	"
	24	"	"
8	4	"	"
	30	"	"
	40	"	"
	54	"	"
9	20	"	"
	49	-33.02	-0.321
10	0	"	"
	16	"	"

Table 11

Current density: 1.689 milliamperes per sq. cm.

Time		Scale reading of potentiometer	Cathode potential in volt
minute	second		
	0	+ 7.49	+0.772
	8	-20.49	+0.006
	13	-23.82	-0.085
	32	-24.30	-0.098
	40	"	"
	55	-24.62	-0.107
1	2	-25.32	-0.126
	10	-25.81	-0.140
	21	-27.00	-0.173
	36	-27.00	-0.173
	42	-27.80	-0.194
2	2	-29.00	-0.227
	8	-29.42	-0.239
	17	-30.71	-0.274
	27	-31.15	-0.286
	36	-31.21	-0.288
	48	"	"

Table 11

(Continued)

Time		Scale reading of potentiometer	Cathode potential in volt
minute	second		
3	13	-31.21	-0.288
	45	-31.52	-0.296
4	0	-31.52	-0.296
	40	"	"
5	13	"	"
	36	-32.29	-0.317
	59	-31.80	-0.304
6	5	"	"
	16	"	"
	42	-31.91	-0.307
7	8	-31.58	-0.298
	36	-32.28	-0.317
8	0	-31.90	-0.307

Table 12

Current density: 1.237 milliamperes per sq. cm.

Time		Scale reading of potentiometer	Cathode potential in volt
minute	second		
	0	+ 7.60	+0.775
	15	-24.60	-0.106
	26	-25.52	-0.131
	40	"	"
	44	"	"
1	0	"	"
	14	-25.82	-0.140
	26	"	"
	42	"	"
2	1	-26.49	-0.158
	15	-27.31	-0.180
	20	-28.42	-0.211
	31	-29.15	-0.231
	40	-29.98	-0.254
	54	-30.38	-0.265
3	11	-31.50	-0.295
	18	-31.83	-0.304
	32	-31.85	-0.305
4	11	-31.85	"
	28	"	"
5	17	-31.38	-0.292
	26	"	"
	40	"	"
6	10	"	"
	45	"	"
7	0	-31.70	-0.300
	36	"	"
8	5	"	"
	15	"	"

Table 13

Current density: 0.999 milliamperere per sq. cm.

Time		Scale reading of potentiometer	Cathode potential in volt
minute	second		
	0	+ 6.45	+0.741
	20	-23.41	-0.065
	34	-23.65	-0.071
	46	-23.70	-0.073
1	10	-24.01	-0.081
	26	-24.20	-0.086
	46	"	"
2	0	-24.72	-0.100
	14	-24.78	-0.102
	33	-24.82	-0.103
3	3	-25.33	-0.117
	24	-25.50	-0.121
	44	-25.72	-0.127
4	20	-26.12	-0.138

Remained unchanged until 7' 0".

Table 14

Current density: 0.993 milliamperere per sq. cm.

Time		Scale reading of potentiometer	Cathode potential in volt
minute	second		
	0	+ 8.69	+0.800
	20	-26.12	-0.135
	30	-26.00	-0.135
1	10	"	"
	44	-26.12	-0.135
2	4	"	"
	16	"	"

Remained unchanged until 5'.

Table 15

Current density: 0.705 milliamperere per sq. cm.

Time		Scale reading of potentiometer	Cathode potential in volt
minute	second		
	0	+ 8.21	+0.788
	10	-13.39	+0.208
	26	-23.32	-0.058
	36	-23.73	-0.069
	44	-23.91	-0.074
	56	"	"
1	16	-24.40	-0.087
	26	-24.40	"
	38	-24.62	-0.093
	46	"	"
2	53	"	"
	10	"	"
	26	"	"
	42	"	"
	56	"	"
3	14	"	"
	34	-25.11	-0.106
	52	-25.25	-0.109

Remained unchanged until 7' 7".

Table 16

Current density: 0.495 milliamere per sq. cm.

Time		Scale reading of potentiometer	Cathode potential in volt
minute	second		
1	0	+ 7.72	+0.777
	6	-15.60	+0.142
	18	-23.32	-0.068
	46	-23.30	-0.068
	2	"	"
	11	"	"
	24	-23.25	-0.067
2	33	"	"
	0	"	"
	26	-23.38	-0.070

Remained unchanged until 6'.

Table 17

Current density: 0.2587 milliampere per sq. cm.

Time		Scale reading of potentiometer	Cathode potential in volt
minute	second		
1	0	+ 7.52	+0.762
	12	+ 2.22	+0.627
	19	- 2.68	+0.495
	40	-13.95	+0.192
	50	-17.80	+0.089
	0	-18.81	+0.062
	16	-19.95	+0.031
	34	-20.78	+0.009
	46	-21.80	-0.018
	56	"	"
2	10	-22.06	-0.026
	30	-22.57	-0.039
	46	-22.73	-0.044
3	10	-22.75	-0.044
	27	-23.11	-0.054

Remained unchanged until 10' 59".

Table 18

Current density: 0.0777 milliampere per sq. cm.

Time		Scale reading of potentiometer	Cathode potential in volt
minute	second		
1	0	+ 7.50	+0.772
	8	- 0.02	+0.562
	23	- 3.58	+0.469
	32	- 3.92	+0.460
	44	- 6.02	+0.375
	57	- 7.70	+0.367
	8	- 8.91	+0.324
	25	-10.92	+0.269
	46	-13.25	+0.206
	51	-14.47	+0.173
2	8	-15.65	+0.140
	28	-17.82	+0.081
	53	-19.71	+0.029

Table 18

(Continued)

minute	Time		Scale reading of potentiometer	Cathode potential in volt
	second			
3	18		-19.80	+0.027
	51		-20.02	+0.021
4	0		-20.11	-0.018
	18		"	"
	31		"	"
5	45		"	"
	17		"	"
	50		"	"
6	8		"	"
	25		"	"
7	13		-20.91	-0.003
	25		"	"
	35		-21.08	-0.008

Remained unchanged until 10'.

Table 19

Current density: 0.00219 milliamperes per sq. cm.

minute	Time		Scale reading of potentiometer	Cathode potential in volt
	second			
1	0		+7.89	+0.776
	42		+5.50	+0.715
	10		+4.20	+0.680
2	30		+3.89	+0.671
	12		+3.68	+0.666
	40		+3.60	+0.664
3	10		+3.45	+0.660
	20		+3.31	+0.656
4	4		+3.20	+0.653
	49		+3.00	+0.648
5	36		"	"
	10		"	"
	30		"	"
6	49		"	"
	16		"	"
	46		"	"
7	54		+2.95	+0.646
	30		"	"
	46		"	"
8	4		+2.61	+0.637
	29		"	"
9	40		"	"
	4		"	"
10	22		"	"
	42		"	"
11	14		"	"
	40		+2.71	+0.640
12	0		"	"
	0		"	"

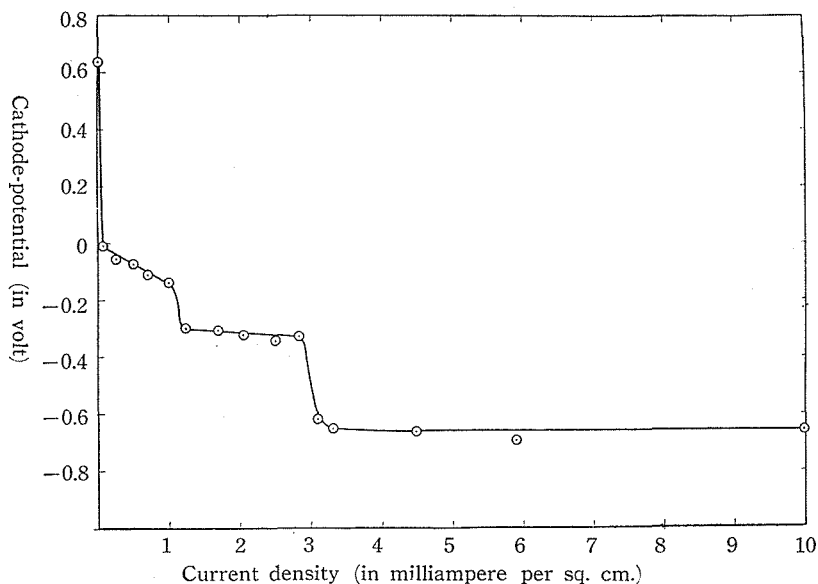
The relation between the settled potential and current density is summarized in the following table:

Table 20

Current density in milliampere per sq. cm.	Potential in volt	Current density in milliampere per sq. cm.	potential in volt
9.915	-0.668	0.999	-0.138
5.884	-0.692	0.993	-0.135
4.479	-0.662	0.705	-0.110
3.306	-0.645	0.495	-0.070
3.093	-0.618	0.259	-0.054
2.826	-0.328	0.078	-0.008
2.496	-0.343		
2.041	-0.321		
1.689	-0.307		
1.237	-0.300		

The above relation is plotted in a current density-potential curve in Fig. 6. One will notice at once in the figure that the curve has

Fig. 6



two nearly horizontal portions. One of them, extending from ca. 1.2 to 3 milliampere in current density, shows a potential of ca. -0.32 volt. The other is the lowest horizontal and extends from ca. 3 milliampere towards the higher current density. The potential at this horizontal is ca. -0.65 volt.

Near the left end of the curve where the current density is very small, there is a turning point at the potential of -0.05 volt. From this turning point up to the current density of 1 milliampere, the curve shows a relatively small inclination.

4) Chemical change in cathodic polarisation

If a pyrite electrode be cathodically polarised in $0.01\text{ n H}_2\text{SO}_4$, e. g. with a current of the density of 30 milliampere per sq. cm., the electrode surface is distinctly covered by metallic iron. Under this condition, however, there remains always a part of the electrode surface which is not covered by the metal but is seriously etched, and fresh pyrite crystals are always exposed. This part seems to supply the solution with ferrous ions, and the metallic iron seems to be deposited electrolytically on the other part of the surface. The writer thought at first that iron atoms in the crystal lattice might be reduced in situ to the metal, but this does not seem to be the case.

After a long run of the electrolysis, a black substance begins to be deposited. A qualitative analysis of this substance has proved that it contains sulphur besides iron so that it may possibly be FeS. Since a good deal of hydrogen sulphide is produced by the cathodic reaction of the fresh part of pyrite surface, its concentration in the solution may finally become large enough to convert the depositing iron into FeS as soon as the hydrogen ion concentration is sufficiently reduced by the cathodic reaction.

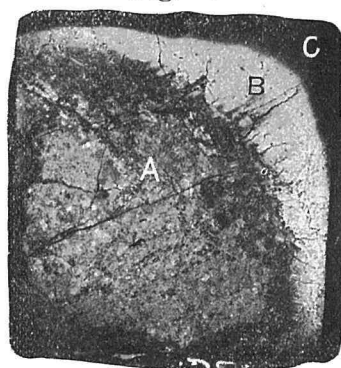
If the surface of pyrite electrode be placed on a pile of sheets of filter paper placed on a glass or ebonite plate, and $0.01\text{ n H}_2\text{SO}_4$, which is previously soaked in the paper, is electrolysed by employing the pyrite as the cathode, hydrogen ions in the solution, which is in contact with the electrode surface, are consumed rapidly and the solution soon becomes saturated with H_2S , owing to the small quantity of electrolyte and the incompleteness of diffusion. This should be the best condition for the production of FeS. As a matter of fact, a rich precipitation of FeS is at once formed between the pyrite and the filter paper.

As the deposition of metallic iron, FeS seems to be also deposited from the solution, for it is formed on the part of the electrode surface which is completely covered by metallic iron. In many cases one can expose the underlying, shining metallic surface by polishing

the blackened surface. Therefore, it may safely be concluded that FeS is not the residual skeleton of the crystal.

Fig. 7 is a reproduction from a photograph of a face of pyrite cathode partly covered by metallic iron, which is, in turn, partly covered by FeS. In the photograph, A is the fresh part of pyrite, B is the part covered by iron, and C that by FeS.

Even when the deposit of iron is very thin, its presence can be easily confirmed by washing the electrode surface with warm acetic acid and by examining the resultant solution for iron. Pyrite and FeS show no appreciable solubility in acetic acid by the similar treatment.



The deposition of metal is markedly hindered by the acidity of the electrolyte. In normal and 0.1 normal H_2SO_4 , no trace of iron can be deposited. The deposition occurs only when the acidity is smaller than 0.05 normal. It is quite natural, then, that K. FISCHBECK'S¹ experiments with 2% H_2SO_4 have not proved the formation of iron. In J. TAKUBO'S² experiment, sufficient quantity of sulphur may have been oxidised to sulphuric acid during the preliminary anodic treatment to render the minute droplet of electrolyte too acidic to allow the deposition of iron.

When metallic iron begins to deposit, the surface area of the electrode may be gradually widened by the deposition of fine crystals, which must necessarily cause the decrease of current density and resistance. The gradual rise of current intensity, which is observed in Fig. 1, as well as the gradual rise of potential in Fig. 5 may well be explained by this effect.

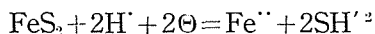
When the current density is smaller than ca. 1 milliampere, the potential fall of the cathode is not sufficient to overcome the oxidising action of dissolved oxygen in the solution. Therefore, the potential at this state may be regarded as a kind of "air potential." The chief factors which control the actual potential value at this state may be current density, acid concentration, and temperature.

1. K. FISCHBECK, *op. cit.*
2. J. TAKUBO, *op. cit.*

The oxidising velocity of the dissolved oxygen differs according to the temperature, and the velocity of reduction is, of course, determined by the current density. The affinity of sulphur atoms to unite with H⁺ ions in the solution, which is one of the chief origins of the high potential of pyrite¹, is determined by the hydrogenion concentration of the solution.

If we use an electrolyte of a definite acid concentration, e. g. 0.01 n H₂SO₄, a balance may be established soon after the beginning of the electrolysis in which the oxygen-concentration in the diffusion layer is kept constant at a certain lower magnitude than that of the currentless condition, and the supply of oxygen to the layer by the diffusion is equal to the consumption of the same by the current. As long as the latter is small as compared with the former, no conspicuous depression of oxygen-concentration can occur, and the balancing point of the concentration will be gradually lowered with increase of current density. This will explain the small inclination of that portion of the curve in Fig. 6.

At the next horizontal portion of the current density-potential curve, the potential which is originated from sulphur anions in the electrode seems to appear as the final settled potential. Sulphur anions consume the discharging hydrogen to form H₂S according to the equation



so that in this case they act as a depolariser. As long as the depolariser is not covered by an iron film of sufficient thickness, the potential due to sulphur anions should appear, no matter how the current density may change.

Under the above condition, the desulphurized iron atoms on the electrode surface are probably not reduced to metallic state or else the metal is dissolved as soon as it is formed so that the fresh surface of pyrite is always exposed to the electrolyte. If the velocity of this dissolution is larger than that of the production of the metal, the latter will have no chance to cover the electrode surface.

If the current density becomes large enough, and consequently the velocity of the deposition of metal is large enough to surpass that of the dissolution, iron film will soon begin to cover the elec-

1. A. MATSUBARA, Jap. Journ. of Geol. and Geograph. Vol. VII, No. 2 (1930) P. 59.

2. A. MATSUBARA and J. TAKUBO, *op. cit.*

trode. When the latter becomes sufficiently thick to exhibit its own potential, it becomes the counter-electrode in the potential measurement, because, as the potential of iron is much lower than any uncovered fresh portion of the electrode surface, it is iron and not the fresh pyrite which acts as the counter-electrode to the referring electrode of copper net whose single potential measures +0.567 volt.

For the above reason, the cathode potential is always the same, namely -0.65 volt, no matter how large the current density may be. And this potential is nothing other than that of a cathodically polarised iron.

B. Cathodic Polarisation preceded by Anodic

1) General course of polarisation

If a pyrite-electrode be first anodically polarised, e. g. in 0.01 n H_2SO_4 with a current of the density of a few milliampere per sq. cm. and then cathodically by suddenly reversing the current, the time-potential curve for the cathodic polarisation receives a certain modification. When the current density is large enough to deposit iron, the curve shows turning points both at the air potential and at the sulphide potential before it finally arrives at the horizontal of the iron potential.

Another characteristic feature of the time-potential curve is that it shows a turning point corresponding to the oxide-potential at the beginning of the polarisation. This can be clearly observed especially when the current density is relatively small.

When the current density is not large enough to deposit iron, one or two of the above mentioned turning points can not be observed, and the final settled potential is either the sulphide- or the air-potential. Therefore the final state is exactly the same as in the case of simple cathodic polarisation.

2) Effect of current density

In order to examine the effect of current density and the course of polarisation especially at the early period, a series of experiments was carried out employing 0.01 n H_2SO_4 as the electrolyte. The experimental conditions were the same as in the previous series except that the temperature was ca. $28^\circ C$. and the preliminary anodic polarisation was executed for 4 minutes with the current of the same density as in the succeeding cathodic polarisation. The results are

Table 21

Current density in m. a./sq. cm.	Settled cathode potential in volt	Current density in m. a./sq. cm.	Settled cathode potential in volt
0.0986	-0.008	2.081	-0.265
0.197	-0.025	2.412	-0.282
0.658	-0.234	2.741	-0.314
0.548	-0.085	2.847	-0.554
0.602	-0.101	3.067	-0.637
0.986	-0.276	4.166	-0.648
1.535	-0.318	5.476	-0.631

summarized in Table 21.

The above relation precisely coincides with that of Table 20, i. e., the current density-potential curve plotted from the above data is identical with that of Fig. 6. This fact suggests that the preliminary anodic oxidation can not modify the final settled potential; the presence of an oxidation product neither facilitates the deposition of iron nor modifies the value of the air potential.

3) Chemical change

The effect of the preliminary anodic polarisation may be observed principally at the early period in the time-potential curve. In order to compare the time-potential curves for various current densities, three experimental results are plotted in Fig. 8.

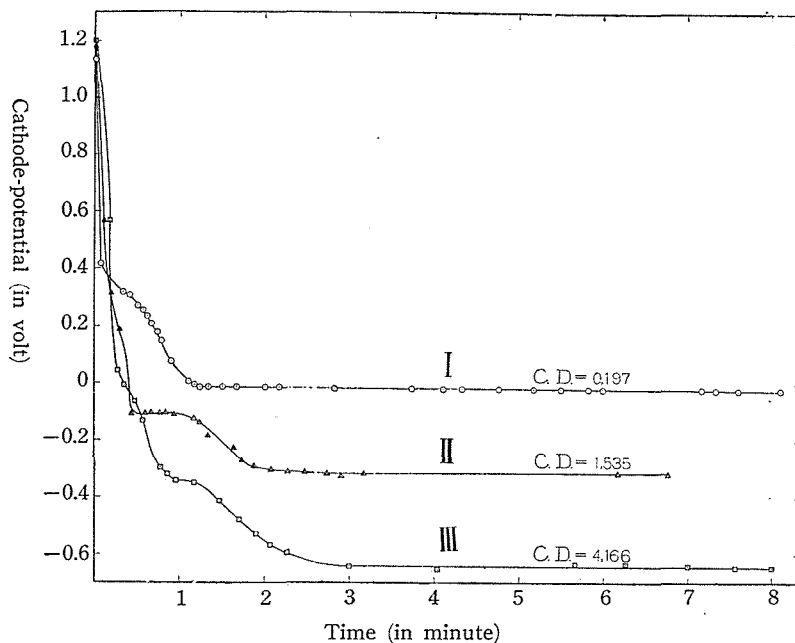
Curve I in Fig. 8 shows a distinct turning point at the beginning of polarisation. This corresponds to the ferric-ferrous potential which was never recognized in the polarisation of fresh pyrite. The second turning of the curve leads to the final horizontal of the air potential.

As the result of the anodic polarisation, there is formed some oxidised crust, which, brown in colour, is probably ferric oxide. In the succeeding cathodic polarisation, this oxidation product should react as the depolariser. In more precise words, it sends out some ferric ions in the diffusion layer as the result of which the ratio $[Fe^{III}]:[Fe^{II}]$ in the solution has a tendency to increase to a certain equilibrium concentration. By the cathodic reduction, on the contrary, the concentration of ferric ion is always reduced with a velocity corresponding to the current density.

As long as Fe^{III} ions are supplied by the oxidised crust, the velocity of the decrease of the above ratio should be to a certain

extent retarded and consequently the drop of the pyrite potential is retarded to that extent, as the latter is very seriously affected by the value of the above ratio, being nobler in the solutions rich in Fe^{+++} ions.

Fig. 8



Curve II in Fig. 8 shows that after the above depolarisation continues for about 25 seconds, next the air potential is established for about half a minute, and then the reduction proceeds further to the horizontal of the sulphide potential.

In curve III, the turning point for the ferro-ferri potential can scarcely be recognized, as the reaction is completed too rapidly. However, a slight but distinct turning point for the air potential and that of the sulphide potential may be observed, and at last the potential settles to that of the cathodically polarised iron.

Part II. Anodic Polarisation

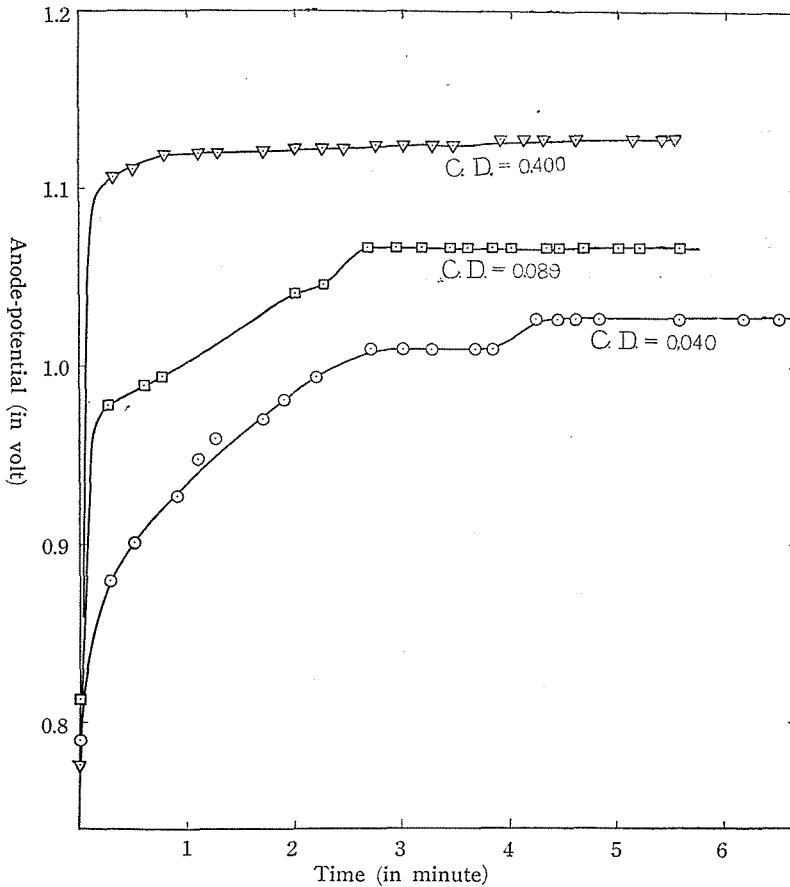
A. Anodic polarisation of fresh pyrite

1) General course of polarisation

By an anodic polarisation with a current of several milliamperes per sq. cm., the potential of pyrite electrode rises at first very quickly and then settles to a practically constant value. The velocity of potential rise increases with increase of the concentration of electrolyte in the case when the latter is acid, but in the case of alkaline electrolytes it decreases with an increase of concentration.

With a current of somewhat smaller densities, the period of the quick rise of potential is followed by a somewhat slower but nearly constant potential rise, and finally the last period comes when the

Fig. 9



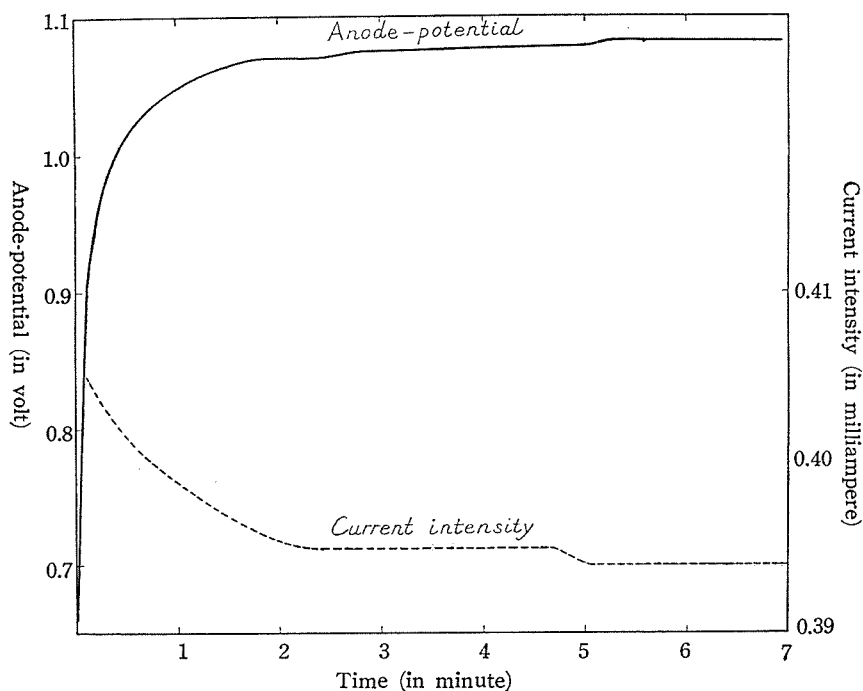
potential settles to a practically constant value showing only very slow gradual rise if the electrolyte is an acid solution. In alkaline electrolyte the initial quick rise is generally small, but the above described second period lasts for a long time, especially when the solution is concentrated.

Three examples of time-potential curve for the electrolyte of 0.01 n H_2SO_4 are shown in Fig. 9, experimental data for which is given in Tables 29, 30 and 31.

2) Change of current intensity

The current intensity undergoes a slight decrease at the beginning of polarisation if a constant polarising potential is applied. In order to examine the manner of current change and the accompanying potential change under the above condition, an experiment such as that which gave the data of Table 1 was carried out. The current intensity was read exactly at the same instant as the establishment of the compensation in each potential measurement which was reported by a vocal signal of the observer. The electrolyte was

Fig. 10



0.01 n H₂SO₄; the initial current density was 0.262 milliampere per sq. cm; and the temperature was 31°C. The results follow:

Table 22

Time		Current intensity in milliampere	Scale reading in potentiometer	Anode potential in volt
minute	second			
	0		+ 7.05	0.659
	6	0.405	12.32	0.903
	12	0.404	13.89	0.946
	18	0.403	15.40	0.987
	27	0.402	15.90	1.001
	34	0.401	16.60	1.020
	41	0.400	17.03	1.032
	49	"	17.23	1.037
1	0	0.399	17.66	1.049
	8	0.398	17.72	1.051
	14	"	17.98	1.058
	24	0.397	18.10	1.061
	30	"	18.19	1.064
	37	"	18.29	1.066
	43	0.396	18.39	1.069
	53	"	"	"
2	0	"	18.40	1.069
	6	0.395	"	"
	10	"	"	"
	24	"	18.43	1.070
	32	0.394	18.48	1.071
	44	0.395	18.60	1.075
	54	"	"	"
3	0	0.394	18.61	1.075
	10	0.395	18.65	1.076
	24	"	"	"
	30	"	"	"
	42	"	"	"
	48	"	"	"
	54	"	"	"
4	10	"	"	"
	18	"	"	"
	23	"	"	"
	34	"	"	"
	49	"	18.70	1.078
	59	0.394	18.72	"
5	6	"	18.78	1.080
	12	"	18.88	1.082

Remained unchanged until 7' 56".

The above results are graphically represented in Fig. 10. This figure shows that the manner of current change is quite reciprocal to that of potential change: the decrease of the former is rapid when the rise of the latter is rapid and vice versa. This fact suggests that the potential rise is principally caused by the increase of resistance as the result of the formation of less conducting crust over the electrode surface, i. e., by the mechanical passivation of the latter.

3) Effect of current density

In order to examine the effect of current density upon the manner of polarisation and the settled potential, a series of experiments was carried out in which 0.01 n H_2SO_4 was used throughout as the electrolyte and a new pyrite electrode was employed in each experiment in order to eliminate the effect of the previous treatment. Current intensity was maintained constant in each experiment by hand regulation of the rheostat. The temperature of the anode bath was ca. 30°C . Some of the results are shown in the following tables:

Table 23

Current density: 108.77 milliamperes per sq. cm.

Time		Scale reading of potentiometer	Anode potential in volt
minute	second		
	0	+ 8.10	+0.784
	20	+21.12	+1.132
	38	+23.33	+1.191
2	20	+23.75	+1.202
	41	+24.00	+1.209
3	0	"	"
	33	"	"
	55	"	"
4	7	"	"
	42	"	"
5	0	"	"

Table 24

Current density: 19.88 milliamperes per sq. cm.

Time		Scale reading of potentiometer	Anode potential in volt
minute	second		
	0	+ 8.23	+0.780
	16	+23.40	+1.173
	25	+23.42	+1.174
	56	+24.42	+1.199
1	14	+24.42	+1.199
	25	"	"
	41	"	"
	53	"	"
2	0	+24.51	+1.202
	25	+24.58	+1.204
	41	"	"
3	7	"	"
	17	"	"
	30	"	"
	42	"	"
4	0	"	"
	10	"	"
	55	"	"

Table 25

Current density: 5.252 milliampere per sq. cm.

Time		Scale reading of potentiometer	Anode potential in volt
minute	second		
	0	+10.73	+0.863
	8	+21.59	+1.163
	16	+22.82	+1.197
1	39	"	"
	17	"	"
Remained unchanged until 6' 0".			

Table 26

Current density: 4.95 milliampere per sq. cm.

Time		Scale reading of potentiometer	Anode potential in volt
minute	second		
	0	+ 9.12	+0.818
	10	+17.50	+1.050
	14	+22.79	+1.196
	27	+22.80	+1.196
1	46	"	"
	22	"	"
Remained unchanged until 5' 0".			

Table 27

Current density: 3.067 milliampere per sq. cm.

Time		Scale reading of potentiometer	Anode potential in volt
minute	second		
	0	+ 9.60	+0.819
	16	+22.23	+1.150
	29	+23.31	+1.179
	46	+23.52	+1.184
1	0	"	"
	10	+23.61	+1.186
	36	"	"
2	0	"	"
	26	"	"
	40	"	"
3	0	+23.90	+1.194
	20	"	"
	34	"	"
	44	"	"
	54	"	"

Table 28

Current density: 1.029 milliampere per sq. cm.

Time		Scale reading of potentiometer	Anode potential in volt
minute	second		
	0	+10.21	+0.838
	21	+20.40	+1.109
	27	+20.50	+1.112
	42	+20.71	+1.117
	46	+21.00	+1.125
1	10	+21.03	+1.126
	35	+21.21	+1.131
	50	+21.25	+1.132
2	6	+21.39	+1.135
	20		
	47	+21.49	+1.138
	58		
3	10	+21.69	+1.144

Remained unchanged until 5' 20".

Table 29

Current density: 0.400 milliampere per sq. cm.

Time		Scale reading of potentiometer	Anode potential in volt
minute	second		
	0	+ 7.80	+0.776
	19	+20.11	+1.106
	30	+20.32	+1.111
	47	+20.58	+1.118
1	6	+20.60	+1.119
	17		
	42	+20.68	+1.121
2	0	+20.70	+1.122
	15		
	27		
	45	+20.79	+1.124
3	0		
	16		
	28		
	54	+20.93	+1.128

Remained unchanged until 6' 0".

Table 30

Current density: 0.0886 milliampere per sq. cm.

Time		Scale reading of potentiometer	Anode potential in volt
minute	second		
	0	+ 8.99	+0.813
	16	+15.00	+0.978
	36	+15.39	+0.989
1	26	+15.60	+0.994
2	0	+17.31	+1.041
	16	+17.50	+1.046
	40	+18.25	+1.067

Remained unchanged until 5' 34".

Table 31

Current density: 0.0404 milliampere per sq. cm.

minute	Time		Scale reading of potentiometer	Anode potential in volt
	second			
		0	+ 8.15	+0.790
		16	+11.41	+0.879
		30	+12.20	+0.901
1		54	+13.13	+0.927
		6	+13.91	+0.948
		16	+14.33	+0.959
		42	+14.71	+0.970
		54	+15.13	+0.981
2		12	+15.60	+0.994
		42	+16.19	+1.010
3		0	"	"
		16	"	"
		40	"	"
4		50	"	"
		12	+16.79	+1.027

Remained unchanged until 6' 30".

Table 32

Current density: 0.0111 milliampere per sq. cm.

minute	Time		Scale reading of potentiometer	Anode potential in volt
	second			
		0	+ 9.80	+0.830
		18	+11.93	+0.887
1		30	"	"
		0	+11.80	+0.884
		17	"	"
2		46	+11.90	+0.887
		50	+12.11	+0.892
3		25	+12.21	+0.895
		46	+12.52	+0.903
4		8	+12.58	+0.905
5		16	+12.98	+0.916
		34	"	"
6		0	+13.10	+0.919
		15	+13.10	+0.919
		51	+13.23	+0.922

Remained unchanged until 8' 25".

Table 33

Current density: 0.00349 milliampere per sq. cm.

minute	Time		Scale reading of potentiometer	Anode potential in volt
	second			
		0	+8.55	+0.802
		22	+8.56	+0.802
1		46	"	"
		20	"	"
		42	"	"
		10	"	"
2		30	+8.58	+0.803
		6	+8.81	+0.809
3		29	+8.90	+0.811

Table 33
(Continued)

Time		Scale reading of potentiometer	Anode potential in volt
minute	second		
4	10	+9.02	+0.815
	20	"	"
	36	"	"
5	14	+9.21	+0.820
	30	"	"
	44	"	"
	56	"	"
6	10	"	"
	25	"	"
	40	"	"
	56	"	"
7	34	+9.37	+0.824
8	10	+9.50	+0.828
	29	+9.69	+0.833

Remained unchanged until 11' 14".

Many other experiments were made to examine the manner of potential variation and the settled potentials, but the tabulation of the results are omitted for lack of space. The relation between the settled potential and current density found in all the experiments of this sort is summarized in the following table :

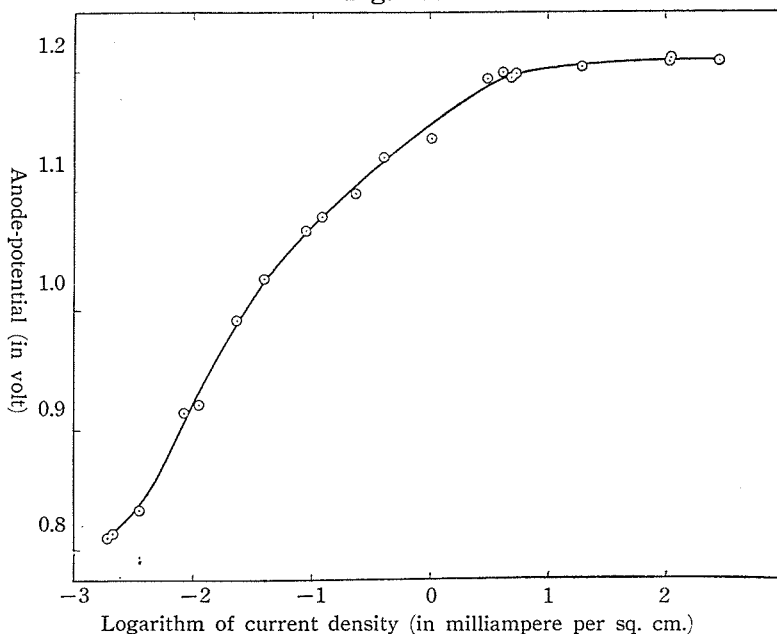
Table 34

Current density in m. a./sq. cm.	Settled anode potential in volt	Current density in m. a./sq. cm.	Settled anode potential in volt
293.9	1.209	0.400	1.123
111.7	1.212	0.232	1.098
108.8	1.209	0.122	1.079
51.72	1.234	0.088	1.067
19.88	1.204	0.0404	1.027
10.18	1.177	0.0225	0.992
9.961	1.227	0.0111	0.922
5.252	1.197	0.0084	0.915
4.950	1.196	0.0035	0.833
4.166	1.199	0.0021	0.813
3.067	1.194	0.0019	0.810
1.029	1.144		

The above results are plotted in a curve in Fig. 11. It may be seen in the figure that the potential rises with increase of current density in the range of the latter between 0.0084 and ca. 10 milli-ampere. Above this range, current density has little influence on the anode potential. The latter does not seem to rise much higher

than 1.22 at least under a current density smaller than ca. 500 milliamperes per sq. cm., and at a temperature of ca. 30°C.

Fig. 11



4) Influence of temperature

To examine the influence of temperature upon the anode potential, three fresh electrodes were polarised in turn in 0.01 n H_2SO_4 with the current density of ca. 5 milliamperes per sq. cm. under different temperatures. The results were as in Table 35.

Table 35

Temperature of anode bath °C.	Settled anode potential in volt
30	1.196
9.2	1.253
5.7	1.314

These results suggest that lower temperatures facilitate the establishment of higher anode potentials.

5) Influence of acidity and alkalinity

When a pyrite electrode is freely immersed in a bath of dilute sulphuric acid and anodically polarised, the final potential is slightly affected by the concentration of acid. The following table summarizes the results of experiment in which the current density is

kept constant at 3.34 milliampere per sq. cm. and the solutions of various acid concentration were employed, the temperature of the bath having been ca. 8°C.

Table 36

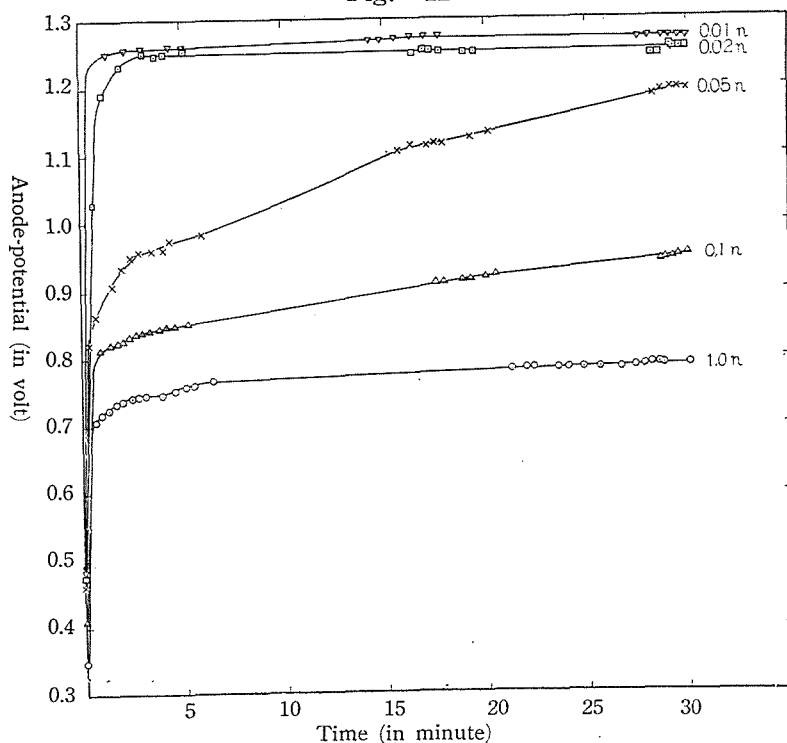
Concentration of H ₂ SO ₄ (normal)	Settled anode potential in volt
1.0	1.236
0.1	1.243
0.05	1.243
0.02	1.250
0.01	1.276

In the above determinations, the anode potential settled very quickly and remained almost constant for about 30 minutes in the case of 0.02 and 0.01 normal, while the slow potential rise was more conspicuous in the case of 0.1 and 1.0 normal. All the potential values shown in the table are

those measured after 30 minutes' electrolysis.

The effect of alkali concentration is somewhat more conspicuous. Table 37 summarizes the variation of anode potential due to the concentration of KOH. The conditions of the experiment were the same as above.

Fig. 12



These two series of experiments show that the anode potential rises with dilution of electrolyte both in the cases of acid and alkali.

In concentrated acid or alkali the transition of the period of the rapid potential rise to that of the slow rise occurs at relatively lower anode potential,

and the potential rise at the later period is conspicuous. To illustrate this condition, the time-potential curves for various concentrations of KOH are compared in Fig. 12.

Since concentrated solutions of either acid or alkali must react with pyrite more vigorously than do dilute solutions, the depolarising action of pyrite must be more vigorous.

6) Influence of H_2S and $FeSO_4$

If a pyrite electrode be anodically polarised in 0.01 n H_2SO_4 which is saturated with H_2S , the time-potential curve receives a slight modification due to the presence of H_2S . The potential and the accompanying current-change by a current of the initial density of 0.102 milliamperes per sq. cm. were as follows:

Table 38

Temperature of the anode bath: 22°C
(Polarising potential is maintained constant)

Time		Anode potential in volt	Current intensity in milliamperes
minute	second		
	0	0.356	
	4	0.428	0.0711
	10	0.509	0.0690
	13	0.530	0.0677
	30	0.576	0.0621
	42	0.841	0.0573
	49	0.876	0.0541
1	0	0.886	0.0523
	14	0.927	0.0500
	20	0.955	0.0484
	27	0.962	0.0479
	36	0.976	0.0470
	46	0.994	0.0464
	52	1.003	0.0460

Table 37

Concentration of KOH (normal)	settled anode potential in volt
1.0	0.788
0.1	0.953
0.05	1.194
0.02	1.255
0.01	1.271

Table 38

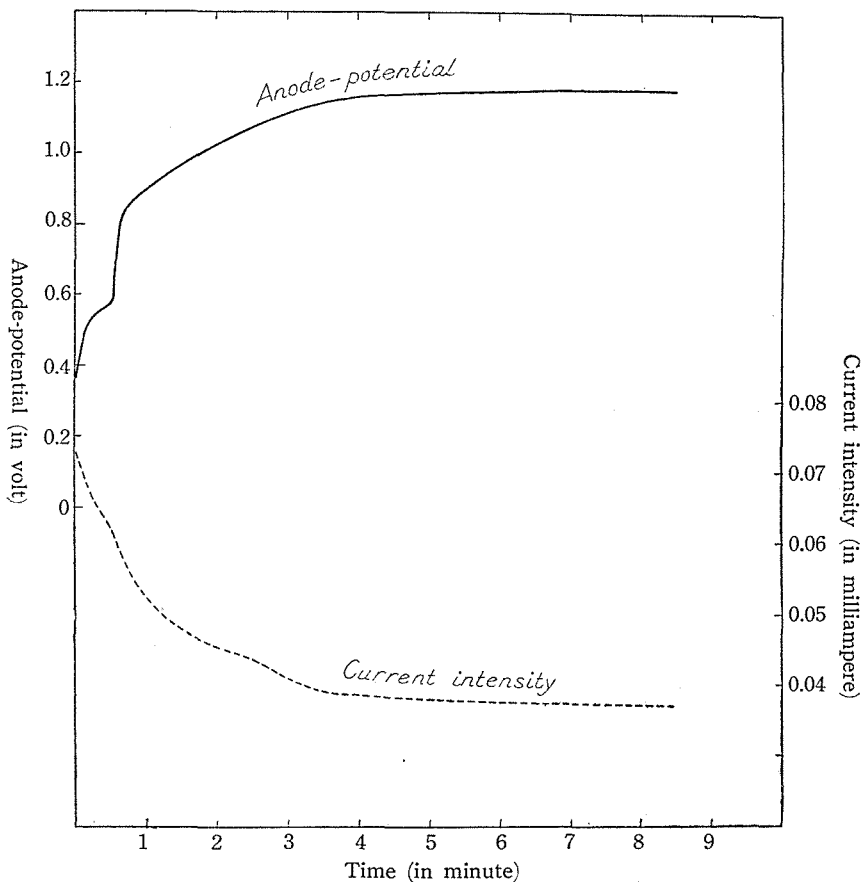
(Continued)

Time		Anode potential in volt	Current intensity in milliamere	
minute	second			
2	1	1.022	0.0452	
	13	1.044	0.0444	
	20	1.060	0.0440	
	30	1.077	0.0432	
	42	1.093	0.0428	
	53	1.108	0.0415	
3	0	1.118	0.0407	
	14	1.128	0.0401	
	24	1.132	0.0395	
	31	1.147	0.0390	
	40	1.150	0.0387	
	47	1.154	0.0386	
	53	"	0.0385	
4	10	1.157	0.0384	
	14	1.163	0.0385	
	24	1.167	"	
	36	"	0.0384	
	49	1.171	0.0382	
	57	"	0.0380	
	5	2	1.173	0.0378
	10	"	"	
	16	"	"	
	23	"	"	
	40	"	"	
	47	"	0.0377	
	52	"	0.0376	
	6	0	"	0.0375
	7	7	1.177	0.0374
	14	1.179	"	
	22	1.184	"	
	30	"	0.0373	
	36	"	"	
	40	"	"	
	47	"	"	
	53	"	"	
	7	0	"	0.0372
	6	"	"	
	12	"	0.0371	

Remained unchanged until 8' 24".

The above results are plotted in curves in Fig. 13. A comparison of this figure with either Fig. 10 or 9 will at once reveal that

Fig. 13



the effect of H_2S is visible during the time between 15 to 30 seconds after the close of the circuit, when both the potential rise and the current fall are slightly retarded by the depolarising action of S'' or SH' . The potential of the reaction $\text{S}'' - 2\Theta = \text{S}$ is therefore ca. 0.5 volt under the above current density.

In order to examine the effect of FeSO_4 , ca. 1 n solution of the latter, which is 0.01 n with respect to H_2SO_4 , was used as the electrolyte and a pyrite electrode was polarised anodically at the temperature of 22°C . The polarising potential was maintained constant as before. The result was as follows:

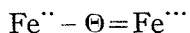
Table 39

Initial current density: 0.100 milliampere per sq. cm.

Time		Anode potential in volt	Current intensity in milliampere
minute	second		
	0	0.792	0.172
	6	0.796	"
	16	0.801	"
	29	0.802	"
	37	0.805	"
	51	0.805	"
1	6	0.808	"
	14	0.809	"
	27	0.810	"
	42	0.811	"
	52	0.812	"
2	0	"	"
	10	"	"
	24	0.813	"
	38	"	"
	51	"	"
3	10	"	"
	26	"	"
	46	0.815	"
4	4	"	"
	16	0.816	"
	34	"	"
	46	"	"
5	0	"	0.171
	14	"	"
	30	"	0.170
	42	"	0.169
	54	"	"
6	4	"	"
	16	0.817	"

Remained unchanged until 7' 16".

The above results show that the oxidising reaction



under the above mentioned current density occurs at the potential of ca. 0.81 volt which is about 0.3 volt higher than the oxidation potential for sulphide ion.

It is quite clear, now, that the oblique portion of the time-

potential curve of Fig. 13 corresponds to the period of retardation of polarisation by the depolarising action of ferrous iron, for the turning point of the curve is ca. 0.8 volt.

7) Chemical change

We are now in a position to consider the chemical change accompanying the anodic polarisation. Since the retardation of potential rise due to the depolarising action of ferrous iron causes the time-potential curve of Fig. 13 to form the oblique portion, those oblique portions of the curves in Fig. 9 may well be considered to have a similar origin. It follows, then, that the oxidation of ferrous iron to ferric begins at higher anode potential if the current density is larger.

Ferrous ions are delivered by the electrode to the diffusion layer at the same time that they are oxidised to ferric by the action of current. The ratio $[\text{Fe}^{3+}]:[\text{Fe}^{2+}]$ in the layer is determined by the relative magnitude of the velocity of these chemical changes. If the delivery of Fe^{2+} ion is plentiful as compared with its oxidation, the retardation of the increase of the above ratio by the delivery will begin to occur at a relatively Fe^{2+} -rich medium. On the contrary, under a larger current density and hence under a larger velocity of oxidation, the above ratio will acquire a relatively high value before the retardation can occur.

Since the ratio $[\text{Fe}^{3+}]:[\text{Fe}^{2+}]$ is one of the most important factors which determine the potential of pyrite, the increase of the current density may well be the reason of the higher potential at which the retardation of the potential rise begins to occur.

The gradual rise of the anode potential at the oblique portion of a time-potential curve is probably due to the gradual decrease of the velocity with which Fe^{2+} ions are delivered from the electrode surface as the result of the thickening of the oxidised crust.

The depolarising action of sulphur anion, which takes place at the potential of ca. 0.5 volt, seems to be indistinct both in acid and in alkali solutions. Probably no sufficient amount of sulphide ion is produced at one time to arrest the anode potential at such a low value as 0.5 volt, because the corruption of crystal lattice can not occur as long as ferrous atoms on the surface layer remain unchanged; and a small amount of sulphur atom, which is oxidised to free state, covers the crystal surface.

When the electrode surface is completely covered by the oxi-

dised crust, so-called mechanical polarisation should take place provided that the current density is sufficiently large. This may also be a reason of the gradual rise of potential.

At the final state, a rich formation of iron sulphate takes place on the electrode surface. This may be actually witnessed by observing the streams of dense solution flowing from the electrode surface down to the bottom of the anode bath when they are seen, by the aid of a magnifying lens, through the side wall of the bath of thin crystallizing dish against a well illuminated or well reflecting back.

Sulphur atoms, which may be oxidised only to the free state at the lower potentials, may be oxidised to sulphuric acid at the final period owing to the high potential of the electrode.

The evolution of oxygen gas can not be observed even under a considerable current density. However, if we polarise one and the same electrode repeatedly as anode, it acquires finally a character of unattackable electrode and the anode potential may be raised even to that of the oxygen-electrode, namely to 1.4 volts. This interesting phenomenon resembles the passivation of iron electrode and requires some further investigation to elucidate its chemical mechanism. A fresh pyrite electrode can never be brought to such a noble state no matter how long it may be anodically polarised and how large the current density may be.

B. Anodic Polarisation preceded by Cathodic

1) General course of polarisation

A preliminary cathodic polarisation may bring the electrode surface to various different states according to the current density. The electrode may remain surrounded by a solution rich in oxygen, or it may come in contact with a solution containing ferrous sulphate and hydrogen sulphide. The electrode itself may be covered by ferrous sulphide or even by an iron-hydrogen alloy.

All the above enumerated reaction products should react as depolariser in the succeeding anodic polarisation. As a matter of fact, the depolarisation takes place in four steps provided that the preliminary cathodic treatment is sufficiently strong.

As an example, the potential-change and corresponding current change in the case when the polarising potential was kept constant is reported in Table 40. In this experiment, the preliminary cathodic polarisation was executed for 6 minutes with a current of

the density of 6.33 milliamperere per sq. cm., while the initial current density in the succeeding anodic polarisation was 0.092 milliamperere per sq. cm. The electrolyte was 0.01 n H_2SO_4 .

Table 40

Time		Scale reading of potentiometer	Anode potential in volt	Current intensity in milliamperere
minute	second			
	0	-52.40	-0.859	
	4	-31.32	-0.285	0.0795
	10	-30.29	-0.257	0.0791
	16	-29.95	-0.248	0.0773
	21	-28.41	-0.206	0.0751
	28	-26.18	-0.145	0.0663
	34	-26.03	-0.141	0.0602
	41	-21.32	-0.013	0.0557
	47	-17.42	+0.093	0.0519
	54	-12.53	+0.229	0.0500
1	1	-11.40	+0.257	0.0481
	9	- 8.65	+0.332	0.0469
	14	- 6.71	+0.384	0.0460
	22	- 5.91	+0.406	0.0455
	30	- 4.40	+0.447	0.0449
	37	- 3.51	+0.471	0.0440
	44	- 2.42	+0.501	0.0435
	49	- 1.25	+0.533	0.0430
	54	- 0.79	+0.546	0.0420
2	1	- 0.11	+0.565	0.0409
	9	+ 2.00	+0.621	0.0394
	15	+ 5.23	+0.709	0.0386
	21	+ 5.25	+0.710	0.0380
	30	+ 6.51	+0.744	0.0372
	36	+ 7.31	+0.766	0.0365
	45	+ 8.10	+0.787	0.0360
	51	+ 8.80	+0.806	0.0356
	59	+ 9.72	+0.831	0.0351
3	6	+10.40	+0.850	0.0345
	15	+10.80	+0.861	0.0339
	24	+12.55	+0.908	0.0332
	31	+13.00	+0.921	0.0330
	40	+13.79	+0.942	0.0328
	48	+14.00	+0.948	0.0326
	54	+14.10	+0.951	0.0323

Table 40

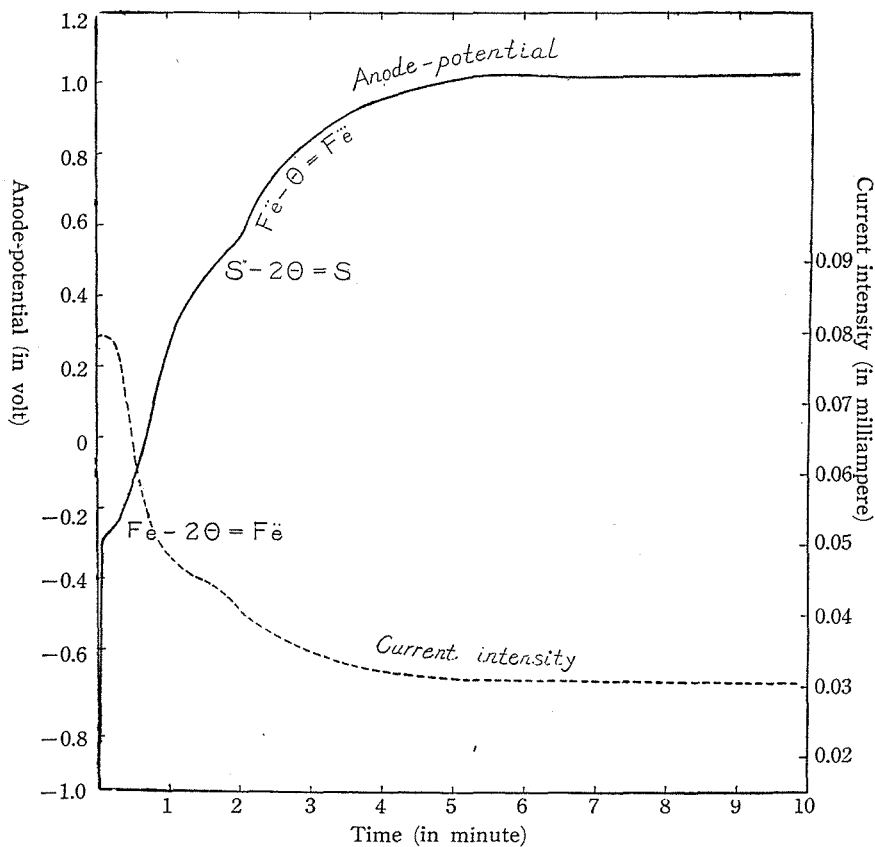
(Continued)

Time		Scale reading of potentiometer	Anode potential in volt	Current intensity in milliampere
minute	second			
4	6	+14.35	+0.957	0.0320
	10	+14.58	+0.964	0.0319
	20	+15.19	+0.980	0.0317
	30	+15.25	+0.982	0.0315
	42	+15.80	+0.997	0.0313
	50	+15.85	+0.998	0.0311
5	0	+16.22	+1.008	0.0310
	10	+16.29	+1.010	0.0309
	18	+16.60	+1.018	0.0308
	25	+16.60	"	"
	32	"	"	"
	40	+16.62	+1.019	0.0307
	50	"	"	"
6	4	"	"	"
	11	"	"	"
	20	"	"	"
	28	"	"	"
	35	"	"	"
	42	"	"	"
	51	"	"	"
	59	"	"	"
7	9	"	"	0.0306
	20	"	"	"
	30	"	"	"
	44	+16.75	+1.023	0.0305
	54	+16.80	+1.024	"

Remained unchanged until 10' 6".

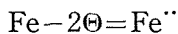
The above results are plotted in two curves in Fig. 14. It may be seen in the figure, that the first step of depolarisation occurred at the potential of ca. -0.28 volt, the second at ca. 0.5 volt, and the third at ca. 1.2 volts. Corresponding to these potential steps, the time-current intensity curve shows also three distinct halting points.

Fig. 14

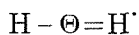


2) Chemical change

The first halting point of the potential curve in Fig. 14 occurred at the same time as that of the current curve. At this time, the reactions



and



should take place, because a metallic iron electrode shows usually a long marked halting point at this potential when it is anodically polarised in 0.01 n H_2SO_4 under the similar current density. Even when the current density is much larger and consequently the iron is passivified, this halting of potential is often very distinct.

At the second halting point of the potential curve, which occurred also at the same time as that of the current curve, hydrogen sulphide

and ferrous sulphide must be oxidised, as the potential agrees exactly with that which we have seen in Fig. 13, viz. ca. 0.5 volt.

The occurrence of the oxidising reaction



at the potential of ca. 0.8 volt is indicated in the time-potential curve of Fig. 14 as the beginning of the oblique portion of the latter. Since the potential rise and accompanying current fall occur gradually in this reaction as has already been shown, neither curve shows a distinct halting point during this reaction.

At the final halting point, the electrode reaches the state of mechanical polarisation. Sulphur atoms, which have been hitherto oxidised to free state, may now be further oxidised to sulphuric acid and consequently the disintegration of crystal proceeds rapidly as was already discussed.

3) Influence of the preliminary cathodic polarisation upon the final anode potential

To examine whether the preliminary cathodic treatment has any effect upon the settled potential, the following experiments were made. Perfectly fresh electrodes were first cathodically polarised in 0.01 n H₂SO₄ for 4 minutes with the current of the density of 3 milliamperes per sq. cm., and then the current was reversed and the electrode was polarised anodically with current of various densities. The result is given in Table 41.

Current density in anodic polarisation in m. a./sq. cm.	Final anode potential in volt
4.978	1.219
0.400	1.120
0.099	1.079
0.012	0.974

This result, coinciding well with that of Table 34 and with the curve in Fig 11, shows that the preliminary cathodic treatment has little influence on the settled anode potential.

Summary

1. The settled potential in a cathodic polarisation of pyrite is higher in concentrated acid than in dilute, but the relation is quite opposite in the case of alkaline electrolyte.

2. The potential change in cathodic polarisation occurs in three steps if the electrolyte is dilute acid and the current density is sufficiently large. At the first halting point, dissolved oxygen in the electrolyte acts as a depolariser, and at the second, the electrode material itself. The potential of the final halting point corresponds to that of iron-hydrogen alloy which evolves hydrogen gas.

3. The final settled potential in cathodic polarisation differs according to the current density, but it coincides with one of the above three halting points.

4. Preliminary anodic polarisation has no influence upon the settled potential in the succeeding cathodic polarisation, but its effect is observable at the beginning of the latter process in a decrease of the velocity of potential fall, which is presumably due to the liberation of Fe^{+++} ions from the oxidised crust.

5. In an anodic polarisation of pyrite in dilute sulphuric acid the potential rise occurs in three stages. The velocity of potential rise in the first stage is very large, that in the second is moderate, while that of the third is extremely small. The occurrence of the second stage is due to the depolarising action of Fe^{++} ions in the diffusion layer.

At the final stage, sulphur is oxidised to sulphuric acid and consequently the disintegration of crystal lattice can proceed rapidly. The constancy of potential at this stage is due to the rapid supply of ferrous sulphate to the diffusion layer.

6. In $0.01\text{ n H}_2\text{SO}_4$, the settled potential rises with increase of current density until the latter becomes ca. 1.21 volt, but the further increase of current density does not raise the anode potential, and the oxygen-evolution does not occur even under considerable current densities. The anode potential required for the oxidation of pyrite is, therefore, ca. 1.2 volts at 30°C . and in $0.01\text{ n H}_2\text{SO}_4$.

7. The anode potential rises with the dilution of both acid and alkali electrolyte. It also rises with the fall of the temperature.

8. The potential-change in an anodic polarisation which is preceded by a moderately strong cathodic polarisation occurs in 4 stages. When the current density in the anodic polarisation is ca.

0.1 milliampere per sq. cm., the first halting point of the time-potential curve occurs at the potential of ca. -0.27 volt, and is due to the depolarising action of active metallic iron. The second halting point, occurring at ca. 0.5 volt, is due to the depolarisation of S'' ions. The third stage, corresponding to the period of oxidation of Fe'' ions, begins at ca. 0.8 volt. The fourth stage of practically constant anode potential is that of the oxidation of pyrite-electrode itself as is described above.

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