6-3-1932

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Recommended Citation

MacFarland, Roy, "The Effect of the Fe^2: Fe^3 Ratio upon the Current Efficiency in the Electrolysis of a Copper Sulfate Solution Containing Iron Sulfate" (1932). *Bachelors Theses and Reports, 1928 - 1970*. 20.
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IN THE ELECTROLYSIS OF A COPPER SULFATE SOLUTION CONTAINING
IRON SULFATE

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Inaugural Thesis

submitted
as a partial fulfillment of the requirements
for the degree of

Bachellor of Science

in

Metallurgical Engineering

from the

Montana State School of Mines
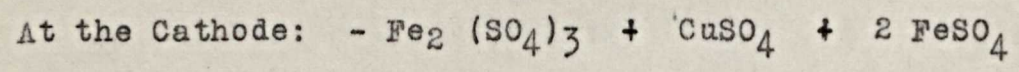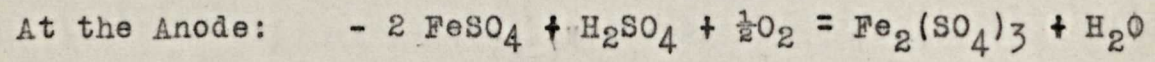
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THE EFFECT OF THE Fe'':Fe''' RATIO UPON THE CURRENT EFFICIENCY IN THE ELECTROLYSIS OF A COPPER SULFATE SOLUTION CONTAINING IRON SULFATE

In the treatment of copper ores by hydro-electro-metallurgical methods, not only is copper deposited, but other metals are also dissolved. In practice it has been found* that iron, under certain conditions, causes the copper to deposit on the cathode as a nonadherent precipitate and also that the iron in solution causes a great decrease in current efficiency, especially when the electrolysis is conducted by operating with a higher current density at the cathode than at the anode.

The present investigation deals with the effects of the two valences of iron on the current efficiency and endeavors to determine whether or not there is a ratio of the two at which point the efficiency becomes zero or approaches it.

The theory of the experiment is that iron present in the ferrous condition is oxidized to the ferric condition at the anode of an electrolytic cell by the oxygen liberated. The resulting ferric iron diffuses to the cathode, where it attacks the copper which has been deposited and is reduced to the ferrous condition again. Since all salts in the electrolyte are present as sulfates the equations may be considered as being:

At the Anode: $- 2\ FeSO_4 + H_2SO_4 + \tfrac{1}{2}O_2 = Fe_2(SO_4)_3 + H_2O$

At the Cathode: $- Fe_2(SO_4)_3 + CuSO_4 + 2\ FeSO_4$

This regeneration of the ferrous sulphate and its diffusing to the anode where it is again oxidized to the ferric condition gives rise to a cycle which goes on as long as the electrolysis continues.

* Kern. Trans. of American Electrochemical Soc. 33, 131 (1918)

Previous investigators do not seem to have attempted a similar experiment. They seemed satisfied to believe that it was the ferric iron which caused the decrease in current efficiency and some have stated that ferrous iron must be present before any copper will remain deposited on the cathode.*

The statements above are not wholly in accord with conclusions based on the present work. In this investigation when solutions of copper sulfate containing ferrous sulfate were electrolyzed it was found that the ferrous iron was converted to ferric iron as the electrolysis proceeded. As the ferric iron content increased, the current efficiency decreased, and when the ratio of the amount of ferrous iron to the amount of ferric iron was approximately 3 to 2 the current efficiency was very low, although no actual zero efficiencies were found. This was found to be the case in two concentrations of iron in electrolytes of equal copper content.

EXPERIMENTATION

For the electrolytic work a glass battery cell was used holding over 2 liters. A wooden block was used as a support for both anode and cathode. (See Fig. 2). The anode was of sheet lead and was fastened by screws to the block. The cathode was held in place by two clips on the block since it was necessary to weigh it after each run. A voltmeter, ammeter, electric stirrer, switch, rheostat, thermometer and battery completed the apparatus. Fig. 1 shows the electrical connections.

* E. L. Larison - E. & M. J. Vol. No. 84, Sept. 7, 1907, 442.

Diagrams of Apparatus and Electrical Connections

Fig. 1

— Battery +

Knife Switch

Rheostat

Voltmeter

Ammeter

To Anode   ToCathode

Details of Cell

Fig. 2

$2\frac{1}{2}$"

5"

Anode

Cathode

5"

6"

$3\frac{1}{2}$"

$7\frac{1}{2}$"
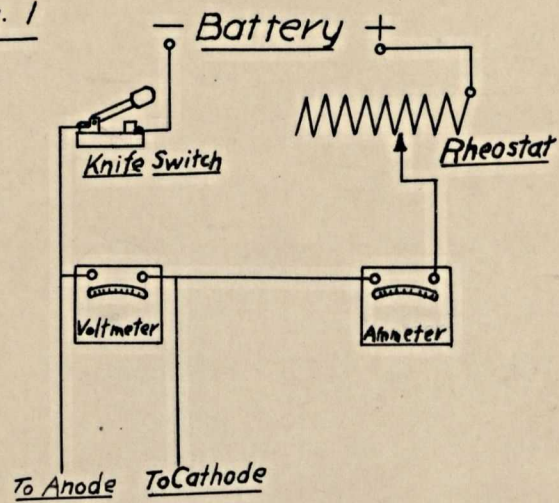
$4\frac{1}{2}$"

Solutions of approximately 2% iron and 5% copper were used in the first tests, and of 5% iron and 5% copper in the second tests. These solutions consisted of sulfate salts made up in the concentrations listed. Some sulfuric acid was added to increase the conductivity of the electrolyte.

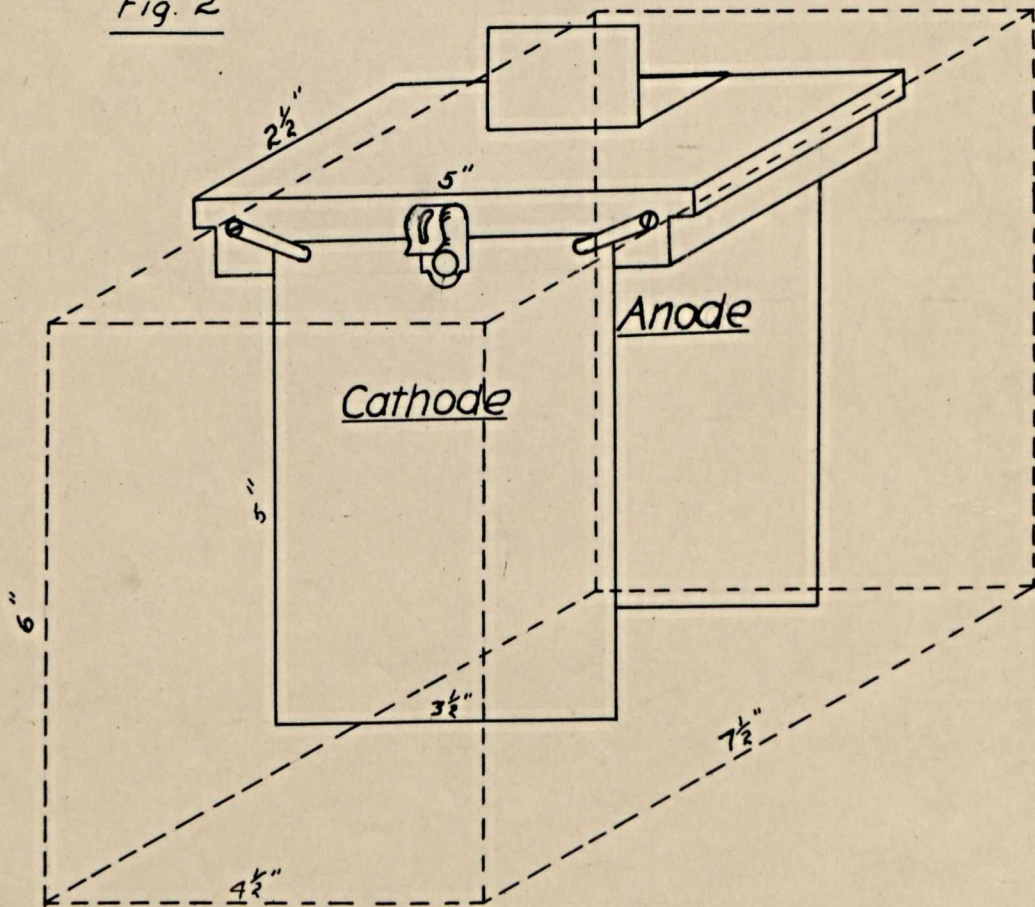The electrolysis was run in the following manner: at the end of a definite period of time, usually 30 min., the cathode was removed, washed with distilled water, dried with 96% grain alcohal, and weighed. From the increase in weight of copper and the amount of current used the current efficiency was calculated. At the same time a 5 cc sample of the electrolyte was analysed for the ferrous and total iron, determining the ferrous iron immediately by the permanganate method, and then determining the total iron by a standard dichromate method.*

Calculations were made as the runs were completed, and were checked again before being entered in the tables. The results obtained are tabulated in table I and are shown graphically in Fig. 3.

Table I in the accompanying results sheets shows the results obtained on a run containing 19.15 grams of iron per liter and approximately 50 grams of copper.

Table II shows the results obtained with the iron amounting to 48.5 grams per liter and the copper 50 grams per liter.

Table III shows the results obtained by Roy and Moran in their thesis work at the Montana School of Mines for 1929.✝

* Keffer - "Methods in Non-Ferrous Metallurgical Analysis."

✝ Roy and Moran Thesis Work-MSM-1929.

Volume of Electrolyte - 2100 cc
Cu conc   - 50   g/liter
Fe'' at start   - 19.15 g/liter
Fe''' at start   - None

TABLE I

Temp.	Amps.	Volts	Time in Minutes	Cathode Weight Before	After	Diff.	Current Eff.	Iron Ferrous	Ferric	Fe''/Fe'''
17.2	2.0	2.9	15	21.918	22.508	.590	99.4	1.906	.009	212.
18.75	2.0	2.87	15	22.507	23.072	.564	95.0	1.781	.134	13.3
19.5	2.	2.83	20	23.072	23.7952	.7232	91.5	1.729	.186	9.3
12.4	2.	3.02	30	23.7948	24.8678	1.0730	90.5	1.656	.259	6.4
11.7	2.	3.07	30	24.867	25.8974	1.0304	87.0	1.512	.403	3.75
18.	2.	2.85	30	25.897	26.8936	.9966	84.	1.425	.490	2.91
18.5	2.	2.91	15	26.8936	27.3588	.4652	78.5	1.385	.530	2.61
18.8	2.	2.93	15	27.3584	27.8168	.4584	77.2	1.359	.556	2.44
19.2	2.	2.92	15	27.8168	28.2796	.4628	78.2	1.322	.593	2.23
20.	2.	2.84	15	28.2796	28.7248	.4452	75.2	1.291	.624	2.07
	2.	2.91	31	28.7232	29.5728	.8496	69.2	1.178	.737	1.6
	1.		31	29.5728	29.7584	.1856	29.3	1.145	.770	1.48

Volume $= 2100$ cc
Copper Conc $= 50$ g/liter
Total Iron $= 48\frac{1}{2}$ g/liter

TABLE II

Temp.	Amps.	Volts	Time in Minutes	Cathode Weight Before	After	Diff.	Current Eff.	Iron Ferrous	Ferric	Fe''/Fe'''
27.9	2.	2.38	15	29.6868	30.2482	.5614	94.7	4.803	.047	101.7
25.8	2.	2.4	15	30.2470	30.8008	.5538	93.5	4.776	.074	64.6
24.4	2.	2.45	15	30.7886	31.301	.5124	86.4	4.569	.281	15.9
7.2	2.	2.45	15	31.3010	31.8118	.5100	86.2	4.522	.328	13.8
23.7	2.	2.57	30	31.8100	32.7972	.9872	83.2	4.472	.378	11.8
23.	2.	2.42	30	32.7972	33.7370	.9398	79.5	4.362	.488	8.96
23.	2.	2.45	30	33.7370	34.6446	.9076	76.0	4.288	.562	7.65
23.	2.	2.42	30	34.6446	35.5264	.8818	74.6	4.203	.647	6.16
26.4	2.	2.45	20	35.5264	36.0792	.5528	70.2	4.166	.684	6.46
25.8	2.	2.5	30	36.0800	36.8322	.7522	63.4	3.982	.868	4.15
24.4	2.	2.57	30	36.8322	37.5862	.7540	63.6	3.908	.942	3.7
24.4	2.	2.61	30	37.5862	38.3258	.7396	62.6	3.823	1.027	3.5
24.	2.	2.56	30	38.3258	39.0324	.7066	58.0	3.774	1.076	3.21
24.	2.	2.67	30	39.0324	39.7204	.688	58.2	3.715	1.135	
23.	2.	2.76	30	39.7204	40.3866	.6662	56.2	3.59	1.26	2.85
23.	2.	2.76	30	40.463	41.0466	.5836	49.2	3.479	1.371	2.53
23.	2.	2.78	30	41.0466	41.674	.6274	53.5	3.455	1.395	2.40
22.5	2.	2.83	30	41.674	42.261	.587	49.5	3.443	1.407	2.45
22.5	2.	2.85	30	42.261	42.8028	.5518	46.5	3.418	1.418	2.38
22.	2.	2.76	30	42.8028	43.3378	.535	45.5	3.294	1.432	2.12
22.	2.	2.88	31	43.3378	43.8593	.5215	42.5	2.855	1.551	2.11
25.8	2.2	2.76	75	43.8588	44.947	1.0882	36.7	2.280	1.565	2.08
23.	2.1	2.75	60	44.947	45.6612	1.7142	30.1	2.75	1.57	2.08
	2.	2.7	150	45.6612	46.4854	.8242	34.8	2.863	1.587	1.45
24.5	2.	2.76	120	46.4859	46.817	2.3311	18.85	2.809	1.987	1.365
24.5	2.	2.75	90	46.802	48.817	.9368	21.1	2.80	2.041	1.355
	2.	2.7	135	48.7388	49.7388	.7832	6.5	2.79	2.05	1.38
21.5	2.	2.9	180	49.7388	50.522	1.3472	14.1	2.80	2.06	1.355
23.5	2.	2.9	240	50.522	50.8692	1.007	13.2	2.81	2.05	1.38
24.	2.	2.85	156	50.887	51.877	1.2506	3.01	2.805	2.04	1.37
	2.		241	51.874	53.1206	1.1854	1.58		2.045	
				53.1206	53.306	.150				
				53.306	53.454					

Effect of $\frac{\overline{Fe}''}{\overline{Fe}'''}$ Upon Current Efficiency

I - Concentration 20 grams Fe./liter
                   50 grams Cu./liter

II   "   50 grams Fe./liter
                   50 grams Cu./liter

III Roy and Moran, Thesis 1929
     Montana School of Mines

Ratio $\frac{Fe''}{Fe'''}$

Current Efficiency in %

DISCUSSION OF RESULTS

From Fig's. I, II, and III, it is evident that the iron concentration of an electrolyte greatly affects the current efficiency. It is also apparent that different current efficiencies are obtained when different concentration of iron are present. It seems logical to believe that the smaller the amount of iron present, the greater the current efficiency. This is shown especially well by curves I and II where a 2% and a 5% iron concentration were electrolyzed.

Another interesting observation noticeable in runs I and II was the formation in I of a froth on the surface of the electrolyte while none appeared in II. This froth was due to the oxygen liberated at the anode. The lower iron concentration in the first case did not require all the oxygen liberated to be oxidized to the ferric condition, while in the second case the oxygen was probably present in just the right amount to oxidize the iron to the ferric state and leave no froth. The difference in the curves I and II may likewise be due to an insufficient amount of oxygen in the case II. Another difference between I and II was the fact that while the cathode in I near the end of the run became a dark bronze in color except where the copper was being removed by the ferric iron, in II the cathode was a bright copper color throughout. It is possible that the excess oxygen in the first experiment formed a thin film of copper oxide on the cathode surface.

From Fig's. I, II, and III it seems logical to believe that the ferric iron is formed faster than the ferrous iron when the C.E. is high and that as the C.E. decreases, the rate of increase in ferric iron over ferrous iron decreases and finally

an equilibrium is reached in the formation of the two valences.

CONCLUSION

In the electrolysis of a copper sulfate solution containing iron sulfate, using insoluble anodes:

1. The current efficiency decreases as the ferric iron content increases.

2. Iron in the ferrous condition does not materially affect the current efficiency.

3. There exists a ratio of ferrous: ferric iron at which point the current efficiency approaches zero, and even becomes negative. This ratio is limited, however, by the total concentrations of iron present.