Behavior of Some Impurities in the Electro-refining of Iron

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Knowledge concerning the behavior of trace impurities during electrolysis is important in preparing high purity electrolytic iron. The production of electrolytic iron has a long history[1,2], but very few investigations have been reported on the behavior of trace impurities[3].

Selecting the sulfate bath as an example, the authors studied the behavior of orthophosphate, sulfate and zinc ions in the electrolyte as well as the behavior of silver plated on anodes. The difficulty of trace analysis was avoided by using phosphorus-32, sulfur-35, zinc-65 and silver-110 as radioactive tracers.

Experimental

Experiments were carried out separately with phosphate, sulfate and zinc ions in a bath and also with silver plated on anodes. Phosphate, sulfate and zinc ions were added to the electrolyte with corresponding radioisotopes. Silver was plated anodes without applying electricity in the cyanide bath containing silver-110.

After 48 hours' electrolysis, the distribution of the added radioisotope was determined by a suitable radiation counter. The contents of each element in the deposited iron were calculated from the concentration of the carrier.

Electrolysis.—An assembly having a high enough scale and the stability to discuss the behavior of impurities during the electrolysis has been constructed. The main features of the equipment are the special cathode frame designed to improve the current distribution on the cathode, liquid suppliers which feed the solution to electrolytic cell, and water bath to make up for the loss due to the evaporation of water. The supply solution for the electrolytic cell contains a sufficient amount of sulfuric acid to keep proper pH-values during long operations. The details of the assembly were reported elsewhere[4] with the results of re-electrolysis of electrolytic iron. In the following experiments the electrolytic iron was also used as an anode material.

The conditions of electrolysis are: temperature 60°C, current density 2 amp./dm^2, pH 5~6, 1 M/l. Mohr's salt solution and the period of deposition, 48 hrs. According to Mukai's work[5], sodium *n*-butylsulfonate was added to the bath at the concentration of 1 g./l. in order to protect the deposited metal from dendrite formation and to attain a high current efficiency.

Measurements of Radioactivity.—Phosphorus-32 emits a β-ray of maximum energy 1.71 MeV., which is strong enough to be measured by a liquid immersion type counter. Measurements were carried out by using 20 ml. of the sample solution containing 2 N hydrochloric acid and the correction was made for the absorption due to iron in the solution.

Autoradiography was applied to obtain some information on the distribution of phosphorus in the deposited iron. As the activity of the sample was very weak, X-ray emulsion was selected as a sensitive material. The specimen was moulded in

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[2] W. M. Shafer and C. R. Harr, *J. Electrochem. Soc.*, **105**, 413 (1958).

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synthetic resin and an X-ray film was contacted on the polished plane which was coated with thin collodion film. Exposure was continued for three months.

Sulfur-35 emits a β-ray of maximum energy 0.167 MeV. and a gas flow counter was used for the measurements of its radioactivity. The samples were prepared in the form of barium sulfate precipitates and the self-absorption was corrected. The activity of sulfur-35 in the surface layer of the deposited iron was measured directly by the gas flow counter without separating the iron, because the β-ray of sulfur-35 has the maximum range of about 0.05 mm. in iron.

Silver-110 and zinc-65 emit γ-rays and were measured by a well type scintillation counter using liquid samples without the elimination of co-existing iron.

Results

Phosphate Ion. — Electrolysis was repeated several times at different concentrations of the carrier in the electrolyte. Results are illustrated in Table I.

TABLE I. DISTRIBUTION OF PHOSPHORUS AFTER ELECTROLYSIS

Concentration of phosphate ion*	0.00	0.66	3.30	4.96	6.60
Distribution (%)					
Electrolyte	1.0	1.0	1.0	0.7	0.1
Precipitate	61.9	62.0	36.8	32.4	25.8
Deposited iron	8.0	24.3	55.3	62.2	73.1
Recovery	70.9	87.3	93.1	95.3	98.9
Phosphorus in deposited iron**	+	0.038	0.86	1.9	2.3

* Concentration of the carrier added is expressed in P g./l.

** Weight percentage.

\+ Far less than 0.0004. The value was estimated by using the specific activity of carrier concentration, 0.66 g./l.

When the concentration of phosphate ion was higher than 3 g./l. in the electrolyte as phosphorus, more than half of the added phosphate ions were deposited on the cathode. On the contrary, at the concentration lower than 3 g./l. co-precipitation of phosphate ions with iron hydroxide was dominant over the deposition on the cathode. The recovery of phosphorus-32 became difficult with the decrease of the concentration of the carrier.

The concentration of phosphate ion in the electrolyte decreased rapidly at the beginning of electrolysis and almost all of the added phosphate ions were eliminated by the end of electrolysis.

Autoradiography was applied to the vertical section of the deposited metal. Fig. 1a shows a typical pattern of the autoradiograph obtained from the section illustrated in Fig. 1b. The high concentration of phosphorus near the mother plate was observed, even when pits or dendrites were formed. The distribution coincides with the observed decrease of the concentration of phosphate ion in the bath at the beginning of electrolysis.

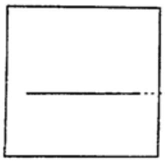

Fig. 1a

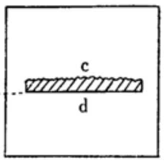

Fig. 1b

Fig. 1a: Autoradiograph.
Fig. 1b: Section of the specimen.
c: Solution side
d: Mother plate side

By applying the same method of autoradiography on the horizontal plane of the deposited metal, the flat distribution of phosphorus was observed.

Sulfate Ion.—The concentration of sulfate ion was about 2 g.-ion/l. in the sulfate bath and sulfur-35 was added to the electrolyte in the form of sulfate ion. The deposited metal from this bath was proved to contain 0.017~0.018 wt. per cent of sulfur by measuring the radioactivity.

Five washing steps were applied to the deposited metal. The effect of washing on the sulfur contents of the surface layer of the metal is illustrated in Fig. 2.

The solution side of the deposited metal had a higher activity than the mother plate side at the beginning of washing. By washing,

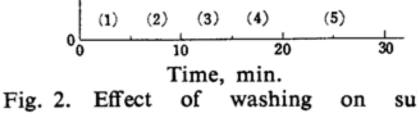

Fig. 2. Effect of washing on sulfur contents.

○ Solution side, △ Mother plate side

Conditions of washing:
(1) Boil in hot water for 5 minutes.
(2) Boil in hot water for 5 minutes.
(3) Immerse in 60°C 0.01 N HCl for 5 minutes.
(4) Immerse in 60°C 0.1 N HCl for 5 minutes.
(5) Boil in hot water for 10 minutes.

the activity of both sides decreased to the same level and the contents of sulfur was reduced from 0.018 to 0.008 wt. per cent.

Autoradiography was tried in vain on the deposited metal. The sulfur seems to have been removed from the surface of the specimen during the wet polishing process.

Zinc Ion.—Experiments were carried out at the concentration of added zinc carrier 0.65 and 1.30 mg./l. in the electrolyte. In both cases, nearly 90% of the added zinc-65 ions were deposited on the cathode. A part of the remaining 10% was co-precipitated with iron hydroxide and the rest remained in the electrolyte.

Silver Plated on Anodes. — After 48 hours' electrolysis, over 90% of the silver ions that were separated from anodes were precipitated with iron hydroxide and only about 2% were deposited on the cathode. The amount of silver plated on anodes was calculated as 0.47 ppm in iron from the amout of silver separated from anodes by electrolysis. About 0.008 ppm of silver against iron were included in the deposited iron.

Summary

Phosphate ions were found to deposit themselves on the cathode like a cation. This phenomenon suggests the formation of a complex ion which has positive charges. The results on sulfur confirms the importance of washing which was pointed out by Schafer and Harr[2] in achieving low values of total sulfur in the deposited metal. Silver was eliminated effectively by electrolysis, but it will be still difficult to remove zinc from iron by electrolysis.

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