

ELECTROLYTIC REDUCTION OF FERRIC TO FERROUS IN TITANIC SOLUTION

N S RAGHAVENDRAN and K C NARASIMHAM

Central Electrochemical Research Institute, Karaikudi - 623 006, INDIA

The electrochemical reduction of ferric to ferrous was studied in titanic sulphate solution using lead electrodes in a diaphragm cell. The effect of variation of current density, temperature and diaphragm materials on the current efficiency and energy consumption was studied. Based on the results obtained on the laboratory scale, studies on a 200A scale were made. A current efficiency of 86-95% could be achieved.

Key words: Electroreduction, ferric iron, titanic solution

INTRODUCTION

During the manufacture of titanium dioxide pigment from titanium ores, two routes are possible, viz. sulphate route and chloride route. In the sulphate route, the iron present in the ore is present partly as ferric sulphate and partly as ferrous sulphate when the ore is leached with sulphuric acid. The ferric iron has to be reduced to ferrous sulphate before TiO_2 is precipitated and ferrous solution is filtered off. The reduction of ferric iron in titanic sulphate solution is now being carried out chemically by the addition of scrap iron. This process has many disadvantages viz. (i) more acid requirement (ii) wastage of more ferrous sulphate (iii) longer retention time.

The electrochemical method for the reduction of ferric to ferrous in titanic solution was investigated [1-3] but the available experimental details are scanty.

The present paper describes the studies made on the electrolytic reduction of ferric iron to ferrous in titanic solution. Based on the results obtained in laboratory scale investigations, a 200A cell was designed and operated successfully.

EXPERIMENTAL**Cell assembly**

The cell assembly consisted of a 250 ml tall-form beaker, fitted with a PVC cover having suitable slots for introducing the electrodes, thermometer and gas vent. The anode was a lead sheet (2.5 cm wide x 12 cm ht.) and blue asbestos rope was wound on the same (9 cm ht.) to act as a diaphragm. The cathode was perforated lead sheet (2.7cm wide x 10cm ht). The interelectrode distance was 2 cm. The cell set-up was kept in an outer glass dish to maintain the temperature by taking water in the same. However the experiments on variation of temperature were done using a thermostat into which the cell set up was placed.

Electrolysis

200 ml of titanic sulphate solution ($\sim 10.5\%$ $TiO_2 + 20.5\%$ acid) containing about 0.56 N ferrous iron (31.3 g/l) and 0.7 - 0.72N (39.5 to 40.2 g/l) ferric iron was used as electrolyte. Direct current was passed from a rectifier (0 - 20V, 25A). The electrolysis was carried out by passing theoretical quantity of electricity and the efficiency was calculated after estimating ferric iron and ferrous iron.

Analysis

Ferrous iron was estimated by dichrometry with ferroin or N-phenylanthranilic acid as indicator. The ferric iron was estimated by iodometry [4].

RESULTS AND DISCUSSION

The results of experiments for the study of different parameters are given in Tables I to III.

Effect of cathode current density

Table I gives the results on the effect of cathode current density on current efficiency.

The results indicate that the reduction of ferric iron in titanic sulphate solution is quantitative upto $4A.dm^{-2}$. There is only a small decrease of 1-3% in current efficiency from quantitative conversion for current densities upto $10A.dm^{-2}$. However, at $20 A.dm^{-2}$ the current efficiency decreases considerably, obviously due to hydrogen evolution, which is normally expected at high current densities. Although quantitative conversion is possible up to $4A dm^{-2}$, for large scale operations, higher current densities will have the advantage of smaller cell capacity and less floor area. Hence for further experiments, current densities of 6 and $10A dm^{-2}$ have been chosen even at the expense of small reduction in the current efficiency, which can be obviated by passing an excess of required current.

Effect of temperature on current efficiency

The current efficiency for the reduction of ferric iron to titanic sulphate solution is quantitative at higher temperatures ($>40^\circ C$) even when cathode current density of 6 or $10A.dm^{-2}$ is employed as indicated in Table II confirming the observations of earlier studies [1]. Increase in temperature also results in lowering of cell voltage and higher temperature ($\sim 60^\circ C$) is also advantageous in the TiO_2 - producing industry.

Effect of diaphragm material

Blue asbestos, terylene cloth and microporous PVC were tried as diaphragm materials. It can be seen from Table III that although the efficiency for asbestos diaphragm is high, the energy consumption is also high. With microporous PVC, anolyte ($4N H_2SO_4$)

TABLE - I. Effect of cathode current density on current efficiency

Volume of electrolyte = 200ml, ferric iron = 0.715N (39.9 g/l); ferrous iron = 0.56N (31.3 g/l); temperature = 30°C; quantity of electricity = 3.83 A.hr.

S. No.	Current (A)	Cathode current density (A.dm ⁻²)	Voltage (V)	Conc. after electrolysis		Current efficiency (%)	Energy consumption (Kwh/kg of Fe ⁺⁺⁺)
				Ferric (N)	Ferrous (N)		
1.	0.15	1	2.5	Nil	1.27	100	1.20
2.	0.30	2	2.6	Nil	1.28	100	1.25
3.	0.60	4	2.8	Nil	1.27	100	1.35
4.	0.90	6	3.0	0.007	1.26	99	1.45
5.	1.50	10	3.4	0.017	1.25	97.6	1.65
6.	3.00	20	4.1	0.10	1.16	86	2.30

TABLE II: Effect of temperature on current efficiency

Cathode current density: (A) 6 A.dm⁻² (B) 10 A.dm⁻², other conditions same as in Table I.

S. No.	Temperature (°C)	Voltage (V)	Concentration after electrolysis		Current efficiency (%)	Energy consumption (KWh/kg of Fe ⁺⁺⁺)	
			Ferric (N)	Ferrous (N)			
1	A	30	3.0	0.007	1.26	99	1.45
	B	30	3.4	0.017	1.25	97.6	1.65
2	A	40	2.9	Nil	1.27	100	1.40
	B	40	3.3	0.014	1.25	98	1.60
3	A	50	2.8	Nil	1.27	100	1.35
	B	50	3.2	Nil	1.27	100	1.55
4	A	60	2.7	Nil	1.27	100	1.30
	B	60	3.1	Nil	1.28	100	1.50

has to be separately used and hence this will create some difficulties in the scale up of the cell. To make sure that the process is efficient, it is better to wrap the anode with blue asbestos diaphragm and over which terylene cloth in the form of a bag can be used.

The reduction of ferric iron can take place either directly at cathode or by the titanous sulphate solution formed by the reduction of titanous sulphate at the cathode and acting as a redox couple or by both reactions taking place simultaneously.

BENCH SCALE EXPERIMENTS

Based on the optimum conditions arrived at in the laboratory scale, a 200A cell was designed and operated.

Description of the cell

The cell assembly consisted of a mild steel cell, 30 (l) x 30 (b) x 45 cm (ht), having rubber lining inside. But this cell was later replaced with a polypropylene cylindrical tank (39cm dia x 39cm ht) as the rubber lining developed bulges in two or three places with solution creeping to the mild steel portion. A PVC cell cover, having slots and holes to introduce the electrodes, thermometer and feed liquor funnel, was used. Two lead (commercial variety) cathodes (20 cm wide x 40 cm ht) and four lead anodes (20 cm wide x 40 cm ht) wrapped with blue asbestos rope/terylene cloth were used. The inter-electrode distance was 2.0 cm.

After assembling the cell, 30 litres of electrolyte containing about 42-43 g of ferric iron and 29-32g of ferrous iron in titanous sulphate

TABLE-III: Effect of diaphragm material on current efficiency

Volume of electrolyte = 200 ml; ferric iron = 0.777 N (43.4 g/l); ferrous iron = 0.413 N (23.1 g/l); quantity of electricity = 4.2 A hr; cathode current density = 10 A.dm⁻²; temperature = 60°C

S. No.	Diaphragm	Av. voltage (V)	Conc. after electrolysis		Current efficiency (%)	Energy consumption (Kwh/Kg of Fe ⁺⁺⁺)
			Ferric (N)	Ferrous (N)		
1.	Blue asbestos	3.35	0.012	1.18	98.3	1.65
2.	Terylene cloth	3.15	0.036	1.15	95.2	1.60
3.	Microporous PVC (160 ml solution as catholyte & 50 ml of 4N H ₂ SO ₄ as anolyte)	2.8	0.054	0.86	91.4	1.47

TABLE-IV: Bench scale experiments

Current: 200A; cathode C.D. 9.6A. dm⁻²; 60 - 70°C

S. No.	Initial composition					Final composition					Average voltage (V)	Duration Hr. Min.	Current efficiency (%)	Energy consumption (kwh/kg of ferric)	Remarks
	Sp.gr.	Fe ³⁺ (g/l)	Fe ²⁺ (g/l)	TiO ₂ (g/l)	Acid (g/l)	Sp.gr.	Fe ²⁺ (g/l)	Ti ₂ O ₃ (g/l)	TiO ₂ (g/l)	Acid (g/l)					
1	1.5 (32°C)	42.7	29.1	157.3	356.4	1.48 (40°C)	71.6	2.8	148.4	299.4	3.5	3 14* 3 29++	96.7	1.73* 1.86++	with fresh cathode
2	1.49 (31°C)	42.5	29.0	-	-	1.49 (33°C)	71.7	1.2	150.2	-	3.9	3 40* 3 57++	84	2.24* 2.39++	cathode was not cleaned
3	1.47 (31°C)	42.3	32.0	145.2	-	1.48 (32°C)	74.3	5.6	154.6	258.8	4.1	3 30* 3 56++	87	2.0* 2.29++	-do-
4	1.47 (31°C)	42.3	32.0	145.2	-	1.49 (33°C)	74.6	4.1	160.4	287.7	3.5	4 45* 5 25++	86	1.90* 2.18++	-do- & Lower C.D. 7.2 A.dm ⁻²
5	1.47 (34°C)	42.3	29.1	146.0	312.2	-	71.4	6.2	152.0	260.2	3.8	3 15* 3 45++	95	1.89* 2.14++	cathode after cleaning the surface

* At the time of completion of ferric reduction

++ Total duration (i.e. after passing excess current)

solution (9 to 11% TiO_2 + 18 - 22% sulphuric acid) was taken in the cell for electrolysis. Direct current was supplied from a 3 phase rectifier (0-20V, 250A). The electrolysis was continued beyond the theoretical quantity of electricity so as to have titanous sulphate (3-4% Ti_2O_3) in the solution thereby avoiding any oxidation of ferrous iron. The temperature was allowed to increase. The final solution was subjected to complete analysis. The results are presented in Table IV. The variation of current efficiency as well as concentrations of ferric and ferrous iron with quantity of electricity is shown in Fig.1

It can be seen from the results that the current efficiency for the reduction of ferric iron with fresh or cleaned lead surface is always higher (about 8-10%) than that with the surface of the cathode used for the subsequent electrolysis without cleaning the surface. A slimy black layer was observed on the surface of the cathode in such cases. However, the current efficiency, though decreased for such cathodes, did not vary much even after repeated use. There is a lowering of acid content at the end of electrolysis, although one should expect an increase in acid content for the final liquor. The cause is still under investigation. From Fig. 1, it is observed that the change in the concentration of ferric to ferrous with quantity of electricity is almost a straight line thereby indicating an almost uniform conversion at all the stages of electrolysis.

CONCLUSION

It is possible to reduce the ferric iron in titanic sulphate solution electrolytically, which has the following advantages as against the chemical method:

- (a) Consumption of less acid
- (b) No additional ferrous is added to the electrolyte
- (c) Cheaper even for the present power tariff
- (d) Liquor quality is better

Acknowledgement: The authors wish to express their sincere thanks to the Managing Director and staff of M/s Travancore Titanium Products, Trivandrum for sending solution for laboratory scale experiments and providing facilities to carry out bench scale experiments at the factory site. The authors also thank Shri. C.R. Balaji, J.R.F. for his help in carrying out analysis during the initial stages of the investigation.

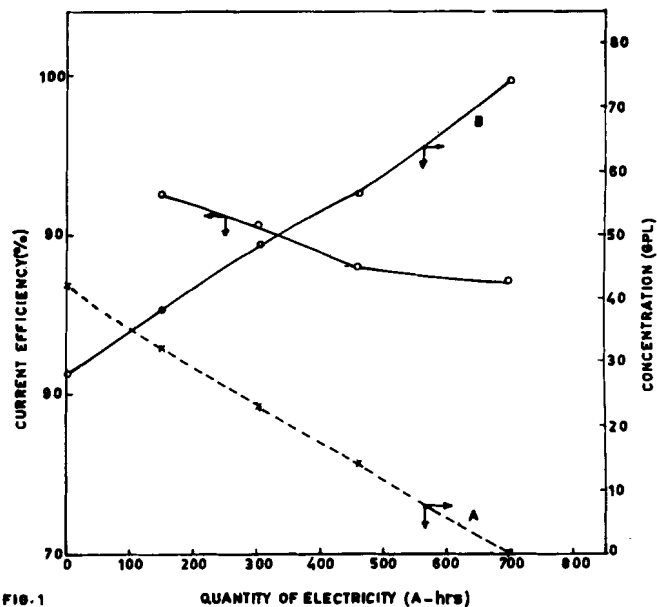


FIG. 1

Fig.1: Current efficiency and concentration of Fe^{+++} and Fe^{++} with quantity of electricity. A = Fe^{+++} ; B = Fe^{++}

REFERENCES

1. K Ya Grachev and S I Rempel, *Trudy Ural Ind Inst im Kirova*, No:6 (1938) 52, 76; *C.A.* 33 (1939) 8505
2. K Ya Grachev and S I Rempel, *J Applied Chem (USSR)*, 10 (1937) 1355; *C.A.* 32 (1938) 1584
3. I G Shcherbakov and K Ya Grachev, *Ibid*, 10 (1937) 607; *C.A.* 31 (1937) 6975
4. A I Vogel, *A text book of quantitative inorganic analysis including elementary instrumental analysis*, III ed. Longmans, (1961) p 309, 372