

ELECTROWINNING OF NICKEL—PERFORMANCE OF CATALYTIC ANODES AND EFFECT OF COBALT AS SOLUTION SPECIES

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Electrowinning of nickel from the sulphate electrolyte has been studied on a laboratory scale. Two types of catalytic anodes viz, activated lead electrode (ALE) and catalytically activated titanium electrode (CATE) have been studied mainly from the point of view of energy saving. The influence of cobalt as solution species on the purity of the cathode nickel as well as the performance of ALE are also reported.

Key words: Electrowinning, nickel, catalytic anodes, influence of cobalt

INTRODUCTION

Electrowinning is one of the important unit operations employed in the different approaches of nickel extraction. Nickel matte produced by smelting sulphides of nickel and cobalt produced from the concentrate and the laterite type ore bodies subjected to prior reduction roasting and leaching are some conventional starting materials used to produce nickel bearing electrolytes for electrowinning purposes. The electrolyte can be either chloride or sulphate solution.

Successful deposition of nickel with respect to quality and quantity depends on factors like pH and level of impurities present in the electrolyte. Cobalt is associated in most of nickel bearing ore bodies and it gets extracted along with nickel during leaching operations. Various solution purification steps are incorporated in the nickel flow sheet, and cobalt level in the final electrowinning electrolyte is maintained below 10 ppm. Nevertheless, cobalt is reported [1] as one of the major contaminants of the cathode nickel. Further, substantial amount of electrical energy is consumed in the electrowinning operation with sulphate electrolyte due to high overpotential of the conventional lead anodes employed, with the attendant oxygen evolution as the main anode reaction. Use of catalytic anodes, which involve oxides of noble metals, with or without non-noble metal oxides, provide good scope for vast reduction in electrical energy consumption, in this context.

Studies relating to energy reduction with employment of new types of catalytic anodes viz. Activated lead Electrode (ALE) or Catalytically Activated Titanium Electrode (CATE) and the influence of various concentrations of cobalt present in the electrolyte on the quality of the deposit are presented in this paper.

EXPERIMENTAL

Electrowinning of nickel was carried out in a three compartment PVC cell where "mytex" separator was used as the diaphragm material. The two end chambers were used as anode compartments and the middle one as cathode compartment. Stainless steel was used as cathode and ALE and CATE were used as anode materials. Nickel sulphate solution of 60 g l⁻¹ nickel with suitable additions of boric acid and sodium sulphate was used as catholyte. The feed solution of the same composition is fed to the cathode compartment and

withdrawn from the anode compartment at the rate of 180 ml h⁻¹. A constant hydrostatic head of 10–15 mm was maintained in the cathode compartment.

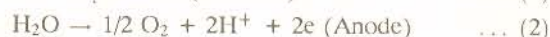
ALE was prepared [2] by activating titanium sponge particles with IrO₂ and embedding the activated particles onto lead substrate by pressing. The catalyst loading employed was 10 g.m⁻² of Ir. In case of CATE, the activation was carried out by coating mixed crystal oxides of Co-Ir by the conventional thermal deposition of chlorides [3]. The load of catalyst was 3 g m⁻² of Ir. The anode potential and cell voltage for lead, ALE and CATE were measured in the current density range of 200–500 A.m⁻². A saturated calomel electrode (SCE) was used as the reference electrode in the anode potential measurements. The potentials quoted are with respect to Normal Hydrogen Electrode (NHE).

Cobalt was added to the electrolyte as cobalt sulphate solution in the range of 1 to 1000 ppm. The electrodeposit of nickel thus obtained was analysed for its cobalt content by Atomic Absorption Spectroscopy.

All chemicals used were of A.R. grade.

RESULTS AND DISCUSSION

When electrowinning is carried out from sulphate electrolyte, the electrode reactions are:



Thus, anode reaction develops acidity in the electrolyte and consequently evolution of hydrogen is promoted as a competing cathode reaction.



Hence, the acidic anolyte is kept separate from the catholyte by using a "mytex" separator as the diaphragm material. However, terylene or polyester cloth has been reported as the diaphragm material in the plant practice [4]. The successful operation of the process mainly depends on maintenance of pH, which in the present study is controlled by maintaining a constant hydrostatic head in the cathode compartment. The conditions of electrowinning arrived at are given in Table I.

TABLE-I: Operating conditions employed in the electrowinning of nickel

Catholyte	Ni ²⁺ 60 g.l ⁻¹ Boric acid 25 g.l ⁻¹ Na ₂ SO ₄ 30 g.l ⁻¹
Feed flow rate	180 ml/h ⁻¹
pH of catholyte	2.5
Current density	200 A.m ⁻²
Diaphragm	Mytex separator
Anode	ALE or CATE
Hydrostatic head of Catholyte	1–1.5 cm
Cell voltage	3.64 V
Duration of electrolysis	4 hrs.
Current efficiency	97%

Lead or its alloy is the anode material customarily used in the electrowinning of nickel from sulphate electrolyte. Oxygen evolution on lead is always associated with high overpotential leading to increased cell voltage. The main advantage sought with the substitution of catalytic anodes is energy saving arising out of reduced cell voltage. Among various types of dimensionally stable anodes proposed for metal electrowinning, ALE generally scores over in the aspects mainly like high surface area provided by sponge/powder support particles, whereas activated titanium anodes pose less engineering problems during fabrication.

Table II presents the data on anode potential obtained for lead, ALE and CATE in the nickel electrowinning operations at different current densities. Voltage saving to the extent of 0.55–0.76V is observed for the ALE, while it is 0.35 to 0.56V for CATE. The energy saving calculated from these data is around 20% at 200 A m⁻² which is normally employed in electrowinning of nickel. Moreover, the reduction in anode potential is maintained at higher current densities also. Further, the rise in anode potential with increase in current density for both ALE and CATE is not to that extent observed for lead electrodes. This could be related to the fact that the Tafel slope of 0.05V for oxygen evolution on IrO₂ is lower when compared to 0.12–0.15V for Pb/PbO₂ [5]. On lead anodes, the presence of thick oxide layer contributes to higher resistivity, leading to enhanced anode potential, whereas in the case of ALE, higher surface area provided by activated titanium sponge particles, facilitates lowering of effective current density resulting in reduced anode potential.

TABLE-II: Data on saving in anode potential

Current density A m ⁻²	Anode potential (V)			Saving in anode potential (mV)	
	Lead	ALE (10 g Ir.m ⁻²)	CATE (3 g Ir.m ⁻²)	ALE	CATE
200	2.10	1.55	1.75	550	350
300	2.20	1.57	1.75	630	450
400	2.28	1.58	1.77	700	510
500	2.35	1.59	1.79	760	560

Durability or life time of active coating depends much upon

the working potential of the anode. A minimum potential rise of 20–40mV in the higher current densities, as seen from table II, for the catalytic anodes is a good indication for the useful life of the IrO₂/mixed oxides of Ir-Co employed.

Table III compares the data on the voltage components for the ALE of the present study and for the lead electrodes employed in the production of the cathode nickel in the Outokumpu process [1]. There is a saving of nearly 450mV when comparison is made on the basis of anode potentials. But this is not reflected in the cell voltage, the reason being that the mytex separator used in the present study offers higher resistance compared with cloth diaphragms employed in the industrial cells of Outokumpu process.

TABLE-III: Voltage components

Electrolyte: NiSO₄ Anode current density: 200–220 A m⁻²

Voltage components	Activated lead electrode (ALE)	Conventional lead electrode— Outokumpu process
Cathode potential (V)	0.66	0.6
Anode potential(V)	1.55	2.0
Cell voltage(V)	3.64	3.6

Table IV shows the content of cobalt in cathode nickel as a function of its concentration in the catholyte. The extent of codeposition of cobalt is found to increase with increase in cobalt level in the electrolyte. It is known that E⁰ of –0.28V for the deposition of cobalt and E⁰ of –0.25V for the deposition of nickel are close to each other. In addition, since the cathode potential is around –0.66V, the chance of codeposition is not ruled out and these aspects throw much light.

TABLE-IV: Influence of cobalt species on the purity of nickel deposit

Cobalt content in catholyte (ppm)	Cobalt content in nickel deposit (%)
Trace	0.024
1	0.026
5	0.027
10	0.040
100	0.350
200	0.600
500	1.200
1000	2.300

Incidentally, the presence of cobalt in the electrolyte is not found to influence the ALE employed for the electrowinning of nickel. But its influence on lead anode has been reported for anode depolarisation and the mechanism proposed [6] in this context is that oxygen evolution on lead takes place through the formation of Co(II)/Co(III) couple and the overpotential for the oxygen evolution is reduced to the extent of 100–150mV depending upon the level of cobalt in the electrolyte. But formation of this kind of electrochemical couple on the sites of the active coating and its influence on anode potential may not be feasible with the catalytic anode where oxygen is already evolved at lower potential. The standard electrode potential of the cobalt couple is 1.82V and it is

not operative at the working anode potential of the ALE.

CONCLUSION

The nature of deposit and current efficiency obtained in the electrowinning of nickel are found to depend on the pH of catholyte which is controlled by the rate of feed solution and by using mytex separator as the diaphragm material. Use of ALE/cobaltite activated Ti anode wherein IrO₂ mixed-crystal oxides of Co-Ir is used as catalyst at a loading level of 3–10 g m⁻², is found to bring about a considerable reduction in anode potential leading to energy saving in this electrowinning process. Cobalt, a likely contaminant in the electrowinning circuit is not found to influence the performance of ALE employed. But its presence in the electrolyte affects the purity of the nickel deposit obtained.

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