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An indirect electrochemical process for the production of naphthaquinone

I. M. DALRYMPLE, J. P. MILLINGTON

Electricity Council Research Centre, Capenhurst, Chester CH1 6ES, UK

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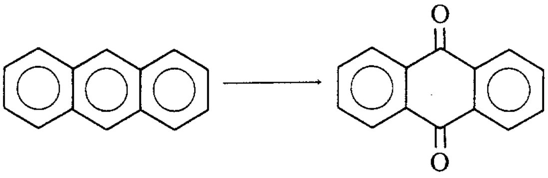
A process for the synthesis of naphthaquinone from naphthalene by use of an electrochemically regenerated oxidizing agent is described. The results obtained in small scale laboratory electrochemical reactors have been reproduced in scaled-up reactors during extended pilot plant trials. Current densities of 1600 A m^{-2} have been sustained, with an overall power requirement of 6000 kW h per tonne of product.

1. Introduction

The use of oxidizing agents such as chromic acid and manganese dioxide has been known by the chemical industry for many decades. In more plentiful times the spent oxidizing solution was discarded on completion of the reaction and only the desired product isolated. Today, as materials become more valuable and the cost of discarding waste increases, the recovery of spent materials such as oxidizing agents becomes more attractive. A process in which the reagent, in this case an oxidizing agent, is regenerated offers other advantages. For example, a range of oxidizing agents may be regenerated electrochemically at high efficiency using essentially the same equipment. As the oxidizing agent is recycled it follows that there is no effluent and the process is environmentally clean. Finally, reagents which would normally be considered as expensive may be used; hence, new and novel synthesis may be carried out.

An example which illustrates these points is the oxidation of naphthalene with electrochemically regenerated ceric sulphate to produce naphthaquinone for subsequent conversion to the important intermediate anthraquinone. Anthraquinone(II) is traditionally prepared by the oxidation [1] of anthracene(I), itself derived from coal tar residues. An alternative route is by a Diels–Alder addition reaction [2] between naphthaquinone(III) and butadiene(IV). Naphthaquinone may be prepared by the oxidation of relatively inexpensive and plentiful naphthalene(V).



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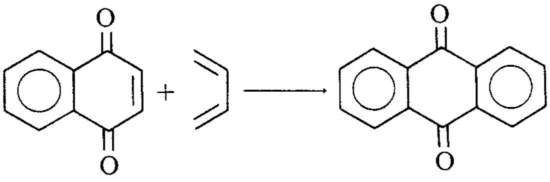

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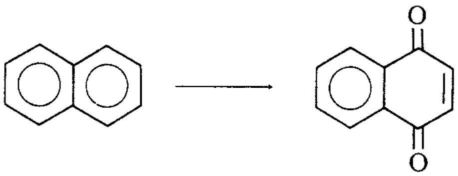

V III

This paper describes a process and a pilot plant for the oxidation of naphthalene using electrochemically generated ceric ion. The process may be considered in two parts. First, a chemical oxidation step (Equation 1) where naphthalene is oxidized to naphthaquinone using a solution of ceric sulphate in sulphuric acid.

$$\mathrm{N} + 6\mathrm{Ce(SO_4)_2} + 2\mathrm{H_2O} \longrightarrow \mathrm{NQ} + 3\mathrm{Ce_2(SO_4)_3} + 3\mathrm{H_2SO_4} \quad (1)$$

Secondly, an electrochemical regeneration step where the spent oxidizing solution from the chemical oxidation step is regenerated (Equation 2).

$$\mathrm{Ce_2(SO_4)_3} + \mathrm{H_2SO_4} \longrightarrow 2\mathrm{Ce(SO_4)_2} + 2\mathrm{H^+} + 2e \quad (2)$$

The relationship between these two processes is most easily described by reference to a block diagram of the pilot plant (Fig. 1).

The oxidizing solution, after preparation in the multipass cell (see 1, 2, 3 in Fig. 1) system is reacted with solid naphthalene in a simple stirred vessel (see 6 in Fig. 1). On completion of the reaction, the naphthaquinone, which is also insoluble in the reaction mixture, is removed by filtration. The spent oxidizing solution is then returned to the cell for regeneration.

The experimental work was carried out using two electrochemical cells: a laboratory cell (single anode area, $500\,\mathrm{cm^2}$) and a larger pilot plant cell of identical design (single anode area, $0.185\,\mathrm{m^2}$). Initial measurements of current efficiency and chemical yields, etc., were made using the laboratory cell prior to production of significant quantities of naphthaquinone in the pilot plant.

2. Experimental details

2.1. *Materials*

The source of cerium was a grade of ceric sulphate described as 'low in other rare earths' (cerium content, 98%) (Rare Earth Products Limited). Sulphuric acid was reagent grade (low in iron). The naphthalene was a commercially available grade (99%), but when used as a standard for calibration it was purified by sublimation. Similarly the naphthaquinone used as an analytical standard was purified by recrystallization from ethanol. The oxidizing solution was an almost saturated solution of ceric sulphate (0.125 M) in aqueous sulphuric acid ($184\,\mathrm{g\,l^{-1}}$). The solid naphthalene was ground prior to reaction with the oxidizing solution. In the laboratory experiments this was by means of a ball mill and for the pilot plant experiments a colloid mill was used. In both cases particle size was monitored by means of photomicrography.

2.2. *Analysis*

Ceric ion was determined by titration with ferrous ammonium sulphate using 1, 10 phenanthroline-ferrous sulphate complex as the indicator [5].

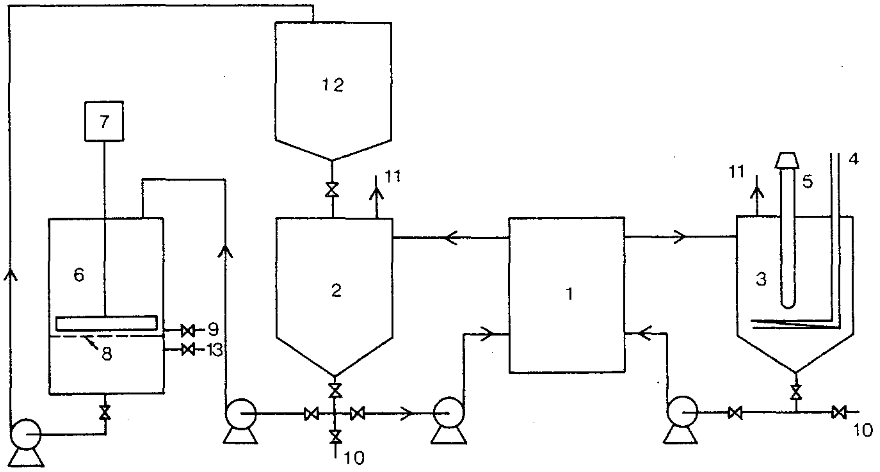

Fig. 1. Block diagram of pilot plant unit. 1, Electrochemical cell; 2, anolyte tank; 3, catholyte tank; 4, cooling coil; 5, silica sheathed heater; 6, chemical reactor; 7, reactor paddle; 8, filter cloth support grill; 9, product take off valve; 10, drain points; 11, gas vents; 12, hold tank; 13, vacuum connection.

Initial analysis of the organic product was made using mass spectrometry and the determination of phthalic acid by-product was later performed by this technique. It was more convenient, however, to estimate both the naphthalene and naphthaquinone content of the product by UV spectroscopy. A purified sample of naphthaquinone showed a convenient absorption (λ max, 247; $\log \varepsilon$, 4.37) in methanol solution, which compares well with the literature value [6, 7] (λ max, 246; $\log \varepsilon$, 4.3) measured in ethanol solution. Similarly, naphthalene in methanol solution gave a peak (λ max, 221; $\log \varepsilon$, 5.10) which is reported in the literature [4] (λ max, 220; $\log \varepsilon$, 5.0) for ethanol solution. Calibration curves were therefore prepared using solutions of known concentration.

2.3. *Chemical experiments*

The chemical reaction of the oxidizing solution of ceric sulphate with naphthalene was investigated in the laboratory prior to the electrochemical study. Clearly this rather complex reaction between a solid in suspension and an oxidizing solution is difficult to study. Consequently no attempt was made to carry out rigorous kinetic studies. In a typical experiment a known amount of naphthalene was shaken (using a mechanical shaker) in a themostatically controlled water bath with a known volume of oxidizing solution. Aliquots were removed from the mixture at known time intervals and the organic and inorganic content determined. To determine the effect of particle size on the rate of reaction, samples of naphthalene of different particle size were prepared by grinding a naphthalene sulphuric acid slurry in a ball mill, using ceramic balls, for differing lengths of time.

2.4. *Laboratory cell*

The divided bipolar cell was of plate and frame construction employing dished electrodes to reduce the interelectrode gap. The cell separator was an ion conducting membrane (Nafion 415) and the electrodes, both anode and cathode, were constructed from lead alloy sheet (6% antimony). The whole unit was clamped together using a small press. The flow circuit used to feed the cell consisted of separate anolyte and catholyte circuits each with its own pump and reservoir. In addition the anolyte was equipped with a flow meter. The power supply was a variable d.c.

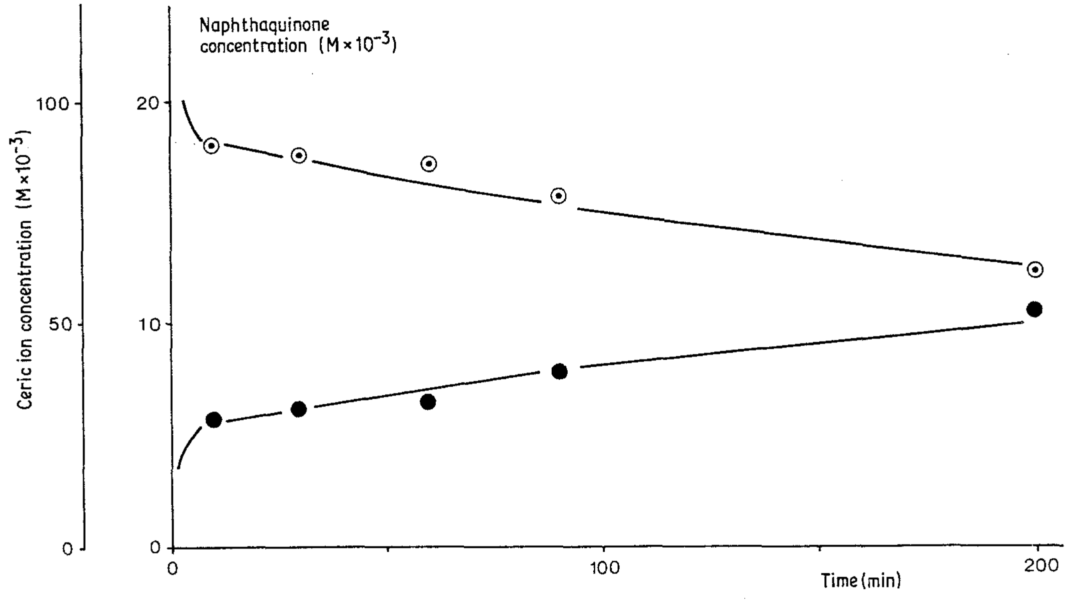

Fig. 2. Typical plot of concentration versus time for the reaction of an excess of solid naphthalene with an acidic solution (185 g l^{-1} H_2SO_4) of ceric sulphate (0.124 M). ○—○, concentration of Ce(IV); ●—●, concentration of naphthaquinone. [Ce(IV)]/[naphthaquinone] = 6.0 ± 0.08.

rectifier (maximum current of 500 A at 10 V). The cell potential was measured using a high input impedance digital voltmeter and the current measured using a calibrated shunt and ammeter. To enable the cell to be operated over a range of electrolyte temperatures a silica sheathed immersion heater was fitted into the anolyte hold vessel. Using this unit, relatively large volumes (20 litres) of electrolyte were used and laboratory runs of significant length could be made. As this unit did not incorporate an organic oxidation stage this was simulated by using the cathode compartment of the cell to reduce the oxidizing solution.

In a typical run the catholyte hold vessel was charged with a solution of ceric sulphate in aqueous sulphuric acid (0.125 M, $Ce_2(SO_4)_3$ in $184\,g\,l^{-1}$ H_2SO_4), which had been the anolyte in the previous experiment. Similarly the anolyte hold vessel was charged with a solution of cerous sulphate derived from the cathodic side of the cell in the previous experiment. The pumps were then started, and when the electrolyte had reached the required temperature the reactifier was switched on and the current adjusted to the desired values. The cell current and voltage and the electrolyte flow rate were then monitored continuously and the ceric ion concentration of the electrolyte measured at predetermined time intervals.

2.5. *Pilot plant*

The pilot plant is most easily described with reference to the block diagram in Fig. 1: numbers in brackets refer to the numbered sections in the figure. Central to the process is the electrochemical cell (1). This was fed, by means of two pumps, by an anolyte stream (2) and a catholyte stream (3). The catholyte hold vessel had a facility for either heating (5) or cooling (4) the electrolyte; the former by means of a silica sheathed heater and the latter by means of a cold water cooling coil. The hold vessel (12) was of the same volume as the anolyte vessel. The chemical reaction between the freshly prepared oxidizing solution and naphthalene was carried out in a circular vessel (6) equipped with a slow speed paddle (7). The naphthalene was contained on a polypropylene filter cloth supported by a plastic grill (8). The oxidizing solution was allowed to percolate through the solid naphthalene and returned to the hold vessel (12) by means of a pump. A divided bipolar cell of plate and frame construction was used. The cell was large enough to take 10 anode–cathode pairs (each anode being $0.185\,m^2$ giving a total area of $1.85\,m^2$). Both anodes and cathodes were constructed from antimonyl lead (6%), and a commercially available ion conducting membrane (Nafion 415) was used as the cell divider. The electrolyte feed was by means of flexible tubes from both common anolyte manifolds positioned below the cell. A similar manifold collected the electrolyte after passage through the cell. The inlet and exit ports were an integral part of the electrode frames.

The unit was operated continuously to produce batches of naphthaquinone. A typical run took between 12 and 24 h depending on current density and involved approximately 16 cycles. A single cycle was as follows. Freshly ground naphthalene (10 kg) was placed in the reaction vessel (6) and stirred with freshly regenerated ceric sulphate (250 litres, 0.125 M $Ce(SO_4)_2$ in $184\,g\,l^{-1}$ H_2SO_4) for approximately 40 min. At the same time, the same volume of a spent oxidizing solution was regenerated in the electrochemical cell. At the end of the cycle the now spent oxidizing solution was drawn off the naphthalene by means of a vacuum pump (valve 13) and transferred to the hold vessel (12). Freshly prepared oxidizing solution was then transferred from the anolyte vessel (2) to the reactor (6) and spent oxidizing solution fed from the hold vessel (12) to the anolyte vessel (2), and the whole cycle repeated. At the end of the reaction (approximately 15 cycles) the wet cake of naphthaquinone was fed through the large valve (9) by operating the paddle at a low speed.

At the start of the pilot plant work a solution of sulphuric acid (250 litres of 5% v/v H_2SO_4) was used as the catholyte. After several days of operation it was noted that significant quantities of cerium had migrated from the anolyte to the catholyte. The problem was solved by using a catholyte of the same volume and concentration as the anolyte. It was then a simple procedure to prevent the depletion of the anolyte at the

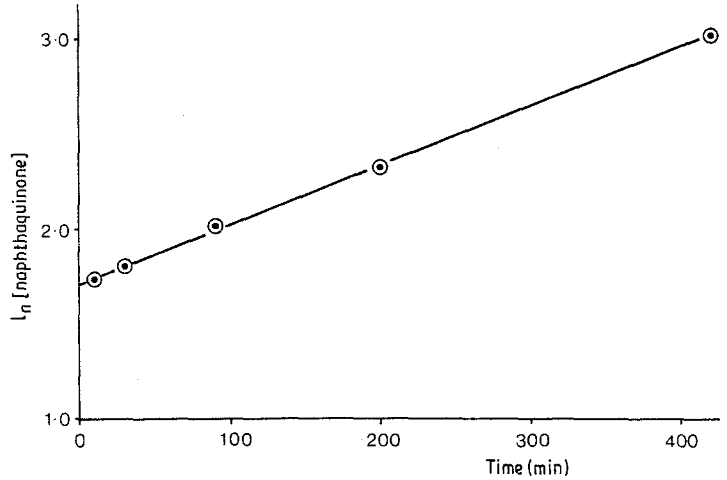

Fig. 3. Typical first order kinetic plot for the reaction of solid naphthalene with an acidic solution ($150\,g\,l^{-1}$) of ceric sulphate (0.125 M).

expense of the catholyte by exchanging the solutions every five runs.

3. Results and discussion

3.1. *Laboratory experiments*

The first area of study was the reaction of naphthalene with ceric sulphate. It can be seen (Fig. 2) that the rate of formation of naphthaquinone follows almost exactly the rate of depletion of ceric ion. From the same data it can be calculated that 6 mol of ceric sulphate are required to produce 1 mol of naphthaquinone. Although these experiments were not designed to collect kinetic data, the rate of production of naphthaquinone gives a linear first order rate plot (Fig. 3), as a large excess of naphthalene was used.

This technique of measuring relative rates was therefore used to assess the effect of naphthalene particle size on the rate of oxidation with cerium (Table 1). It can be seen that the optimum particle size is in the middle of the range studied (0.1–0.05 mm). The slightly lower rates observed at particle sizes higher and lower than the optimum are due to low overall surface area of the particles; in the former case because the particles are relatively large and in the latter case because particle agglomeration takes place.

Table 1. Effect of naphthalene particle size on the rate of reaction with ceric sulphate

Mean particle size (mm)	$t_{1/2}$ *(min)*	k *(min⁻¹) 25° C*
1.0	0.55	1.26
0.15	0.47	1.47
0.05	0.46	1.51
0.02	0.48	1.45
0.005	0.50	1.39

The electrochemical oxidation of cerous to ceric sulphate was studied extensively in the laboratory using the small ($500\,cm^2$) plate and frame cell. A typical current–voltage relationship for this cell and for the larger $0.185\,m^2$ pilot plant unit (see Table 2) is shown (Table 3).

Predictably, for an anodic process in competition with oxygen evolution in a dilute electrolyte, the current efficiency falls with increasing current density (Table 4). The optimum current density, i.e. the minimum overall operating cost, is the resultant of two factors: the capital

Table 2. Experimental details for laboratory and pilot plant cells

	Anode/ membrane gap (mm)	*Anode area* (m^2)	*Cathode/ membrane gap (mm)*
Laboratory cell	3	0.05	4
Pilot plant cell	6	0.185	6

Anode, antimonyl lead (6%); cathode, antimonyl lead (6%); cell membrane, 'Nafion 415'; electrolyte, cerous sulphate (0.125 M in aqueous sulphuric acid, $184\,g\,l^{-1}$); flow rate, $40\,cm\,s^{-1}$.

Table 3. Current–voltage relationship for both laboratory and pilot plant cells

Current density ($A\,m^{-2}$)	*Cell voltage*		
	Laboratory cell ($500\,cm^2$) (50° C)	*Pilot plant cell ($0.185\,m^2$)*	
		(50° C)	*(60° C)*
200	2.2	–	–
500	2.7	3.2	2.9
1000	3.2	3.75	3.0
1500	3.75	4.3	3.95
2000	4.5	4.8	4.7

cost of the plant and the power consumption. Some values for the latter are as shown in the table, but as capital costs change rapidly no attempt was made to estimate these. However, a related parameter, the anode area needed to produce naphthaquinone at a rate of 1 $kg\,h^{-1}$, is shown in Table 4.

Having established the range of operating conditions in terms of current density and temperature, attention was then turned towards improving the mass transfer characteristics of the cell. A range of mesh type turbulence promotors was investigated. All the turbulence promotors gave an improved current efficiency at a given flow rate, the difference between the mesh sizes being slight. The optimum size, however (mesh 20 × 20 × 5 mm), was in good agreement with values published in the literature [8, 9]. A typical result is shown (Fig. 4). For channel flow, i.e. in the absence of turbulence promoter, high current efficiencies are achieved at high flow rates. In contrast, using a mesh turbulence promoter, high current efficiencies are achieved at relatively low flow rates.

A rigorous treatment of the data is not possible as the membrane is not fixed but free to move, with the result that the channel, bounded by the electrode and the membrane, is not of fixed dimensions. However, it is worth noting that in the absence of a turbulence promotor the sharp rise in current efficiency (Fig. 4) corresponds to the critical Reynolds Number (Re = 2500) [10], which is the transition between laminar and turbulent flow.

The temperature of the electrolyte is clearly an important factor (Table 4); higher temperatures result in higher current efficiencies. However, during the early part of the pilot plant work a progressive increase in the anode potential was observed during runs carried out at what was then considered to be the optimum temperature (60° C). This behaviour was not observed during any of the laboratory experiments or during runs on the pilot plant at lower temperatures. Examination of the anode revealed a black tarry deposit which on analysis was shown to be a mixture of product and starting material. An examination of the melting points of a range of naphthalene–naphthaquinone mixtures (Table 5)

Table 4. Current density–current efficiency relationship for both laboratory and pilot plant cells

Current density ($A\,m^{-2}$)	*Temp. (° C)*	*Current efficiency (total for 90% conversion to ceric sulphate*		*Power consumption ($kWh^{-1}\,kg^{-1}$ of naphthaquinone)*	*Electrode area to produce 1 $kg\,h^{-1}$ of naphthaquinone (m^2)*
		Laboratory cell	*Pilot plant cell*		
500	60	80 2			
1000	60	65 2			
1500	60	62 2			
2000	60	56 2			
1000	60		70 3	5.45	1.45
1500	50		67 3	6.17	0.96
2000	50		60 3	8.21	0.85
1000	30	30 3			
1000	40	43 3			
1000	50	62 3			

Experimental conditions as given in Table 2. Turbulence promoter, mesh type (20 × 20 × 5 mm).

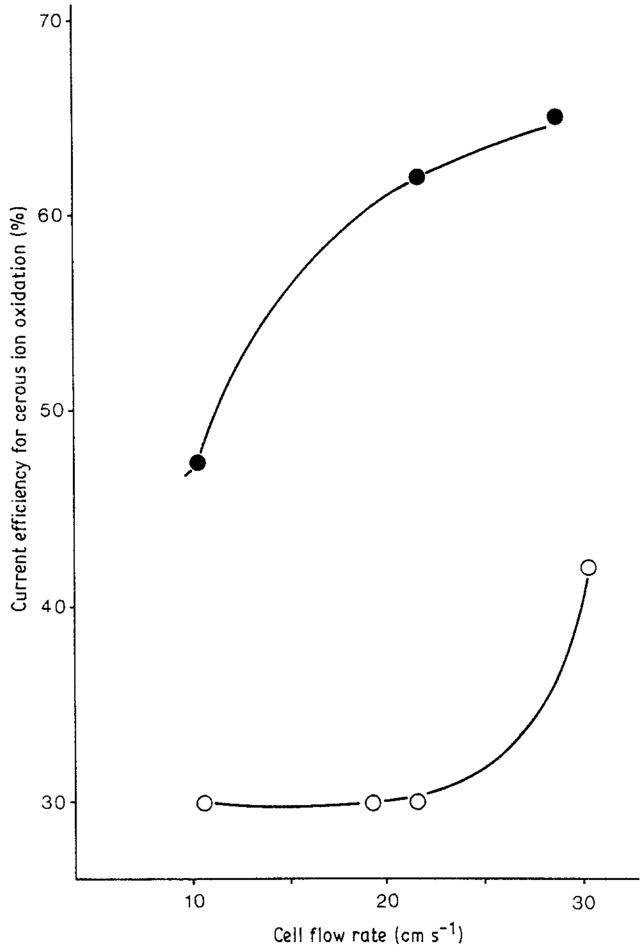

Fig. 4. Variation of current efficiency with flow rate for laboratory cell. Electrodes, both anode and cathode antimonyl lead; cell membrane, 'Nafion 415'; anode/membrane gap, 3 mm; cathode/membrane gap, 4 mm; electrolyte, ceric sulphate (0.125 M) in aqueous sulphuric acid (184 g l^{-1}). ○——○, cell with open channel, i.e. no turbulence promoter; ●——●, cell with plastic (PVC) mesh turbulence promotor (20 × 20 × 3 mm) in the anode compartment.

showed an eutectic mixture with a melting point (61° C) close to the electrolyte temperature. Clearly, the coating of the electrode was due to small amounts of both product and starting material remaining in the electrolyte after filtration in the chemical reactor. Operation of the cell at a lower electrolyte temperature (50° C) completely solved the problem.

Table 5. Melting points for a range of mixtures of naphthalene and naphthaquinone

Naphthalene (wt %)	*Mole fraction*	*Melting point (° C, uncorrected)*
0	0	128
10	0.120	125
20	0.235	119
25	0.291	89–95
30	0.345	71–77
40	0.451	61
50	0.552	62
60	0.649	61
70	0.742	63
80	0.832	63
90	0.918	67
100	1.0	80

Finally, in this section of the work, a range of possible anode materials was examined (Table 6). It can be seen that despite the differences in over-voltage characteristics all the materials are suitable.

3.2. *Pilot plant experiments*

Prior to the operation of the plant for the production of naphthaquinone the characteristics of the cell were measured and compared with those of the laboratory cell. The current–voltage relationship (Table 3) is predictably similar to the two cells as is the current efficiency–current density relationship

Table 6. Electrode potential and current efficiency for a range of electrode materials

Anode material	*Anode potential vs SCE (V)*		*Current efficiency (total for 90% conversion)*
	$Ce_2(SO_4)_3$ in H_2SO_4 (M)	*H_2SO_4 (M)*	
Lead dioxide-coated titanium	1.94	1.96	29.1
Lead (99.9%)-coated mild steel	1.82	1.86	31.0
Antimonyl lead (6%)	1.74	1.77	31.0
Platinum iridium-coated titanium	1.66	1.48	28.1

Cathode, platinum metal; cell separator, glass frit (No. 4); electrolyte, cerous sulphate (0.125 M) in aqueous sulphuric acid; current density, 1000 A m^{-2}; flow rate, glass paddle (1000 r.p.m.).

(Table 4). The slightly higher current efficiencies observed for the pilot plant cell are almost certainly due to a better control of the cell internal pressure. This was achieved on the pilot plant scale because it was possible to fit pressure gauges to the larger cell. From this data it is clear that the optimum operating conditions for the cell are a current density of 1500 A m^{-2} and electrolyte flow rate and temperature of 40 cm s^{-1} and 50° C, respectively. It is also essential to have a turbulence promotor in the anode compartment in order to achieve high current efficiencies.

To produce naphthaquinone the pilot plant was run on a campaign basis, with the sequence of operations as follows. The chemical reactor was charged with a known weight of freshly ground naphthalene. A freshly regenerated solution of ceric sulphate was added and the resultant slurry stirred gently by the paddle. During this time the second solution of now reduced ceric sulphate was regenerated in the electrochemical cell. The reaction time and the regeneration time were of the same duration (~40 min). For batches of different size the regeneration time was adjusted by means of the cell size and electrolyte volume. At the end of the reaction time the spent ceric sulphate was transferred to the anode compartment of the cell and the regenerated ceric sulphate pumped into the reactor, as described in the experimental section. A log sheet for a typical run is shown (Table 7).

Table 7. Log sheet for a typical pilot plant run

Cycle number	*Total cycle time (min)*	*Total cell potential (V)*	*Current efficiency for 90% conversion to Ce(IV) (%)*	*Total naphthaquinone produced (kg)*	*Current efficiency for naphthaquinone production (%)*
1	40	17.6	61		
2	80	17.6	–		
3	120	17.6	65	1.43	60
4	160	17.6	–		
10	400	17.3	70	5.01	63
11	440	17.2	68		
12	480	17.2	63		
13	520	17.2	65	6.91	62
14	560	17.1			
16	640	17.1	68	8.28	65

Anode, antimonyl lead (6%), membrane gap 6 mm; cathode, antimonyl lead (6%), membrane gap 6 mm; total anode area, 0.74 m^2 (4 anodes); cell membrane, 'Nafion 415'; turbulence promotor, mesh type (20 × 20 × 5 mm); electrolyte, cerous sulphate (0.125 M) in aqueous sulphuric acid (184 g l^{-1}); current density, 1620 A m^{-2}; electrolyte temperature, 50° C; reactor temperature, 50° C; cycle time, 40 min; charge, 10 kg naphthalene (freshly ground).

The naphthalene was only partially converted (80–90%) to naphthaquinone, as the small amount of unchanged naphthalene was conveniently separated during the next stage of the synthesis. High conversions (~98%) to naphthaquinone may be achieved at the expense of slightly longer reaction times.

In conclusion it has been shown that ceric sulphate, an exotic reagent which would normally be considered only for laboratory use, may be used on an industrial scale. With the simple but highly efficient reactors described, scale-up from laboratory to pilot plant size presents no problems and current densities of 1600 A m^{-2} can be sustained over long periods. It has also been shown that a range of anode materials is suitable, but as the electrolyte is not highly corrosive and in view of its low cost, lead, or one of its alloys, is the best choice. The oxidation of naphthalene with cerium is a smooth reaction giving a high chemical yield (98% naphthaquinone) with only a small amount of by-product (2% phthalic acid) even at high conversion. The electrochemical route provides an attractive potential route to naphthaquinone and, via subsequent Diels–Alder addition reaction, to anthraquinone.

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