

Electrochemical production of cuprous oxide using the anode-support system

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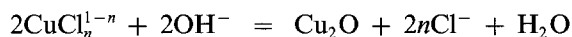
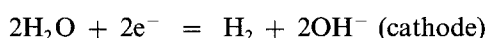
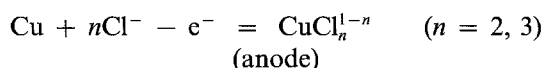
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The preferred process for the production of cuprous oxide powder is by the anodic dissolution of copper in an alkaline solution of sodium chloride. The purpose of the present investigation was to develop a cuprous oxide process suitable for use on an industrial scale using the anode-support system, i.e. an anode comprising a titanium mesh basket loaded with small pieces of high-grade copper scrap. Laboratory investigations with this type of anode together with a titanium mesh cathode were conducted using cells having capacities up to 400 dm³. The recommended operating conditions based on 120 h runs using the 400 dm³ cell are as follows: NaCl: 250 g dm⁻³; c.d.: 6 A dm⁻²; CI: 0.37 A dm⁻³; temperature: 80 °C; pH 10. Of particular importance, especially as regards the quality of the product and cell scale-up, is the relationship between the current and the volume of the electrolyte, denoted as CI and expressed as A dm⁻³. The use of anode and cathode diaphragms of polypropylene obviated the need for additives to counteract copper redox reactions in the cell. The power yield was 0.8–0.9 kWh kg⁻¹. The product was well within ASTM specification D912-65 for Cu₂O for use in antifouling paints.

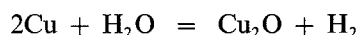
1. Introduction

The production of cuprous oxide powder can be achieved by a number of methods including hydrothermal, electrochemical, chemical and displacement processes [1] with the properties of the final product being related to the particular procedure employed. The electrochemical method is best suited to the production of cuprous oxide on an industrial scale yielding a product which meets the requirements for purity and colour.

The principal reactions in the electrochemical process are the following:



Thus the net reaction is:



The differences in the recommended operating ranges for the different variables in the electrochemical process led Ji and Cooper to study the basic electrochemistry of the process [2]. This work was followed by a detailed study of the process conditions necessary to give a product having in excess of 97% cuprous oxide in a cell with and without a diaphragm [3].

It would be advantageous if the copper sheet anode could be replaced by a titanium mesh basket filled with small pieces of high-grade copper scrap. This type of anode would overcome the problems associated with the melting and casting of anodes and the handling of anode scrap. Consequently the use of this so-called anode-support system which has been developed and used successfully by Gana and co-workers [4–6] in the electrorefining of scrap copper in the La Florida Refinery (Santiago, Chile), was investigated to obtain a new approach to the electrochemical production of cuprous oxide on an industrial scale. The results of the study are reported in this paper.

2. Experimental details

Cells having capacities of 7, 10, 15, 40 and 400 dm³ were employed for the synthesis using a titanium mesh basket filled with pieces of no. 1 copper scrap. The scrap was in the form of chopped 2–5 mm diameter copper wire, 2–4 cm in length for the 400 dm³ cell and 1–1.5 cm in length for the smaller cells. Details of the 15 dm³ cell are shown in Figs 1–5 and of the 400 dm³ cell in Fig. 6.

Syntheses were carried out in the smaller cells using as electrolyte solutions of reagent-grade sodium chloride containing 50–300 g dm⁻³ with a pH range of

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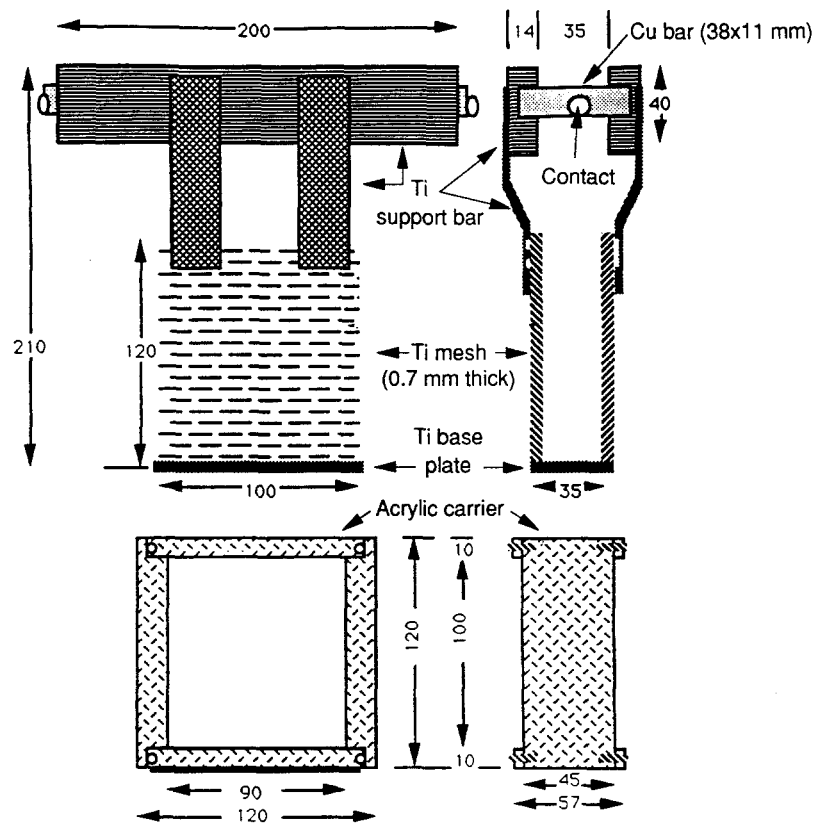


Fig. 1. Components of titanium anode-support system and acrylic container. (All measures are in millimetres).

7 to 11, temperatures of 25 to 90 °C, and an anodic current density of 2–10 A dm⁻². The cuprous oxide was removed from the cells, filtered batchwise under a nitrogen atmosphere and dried in a vacuum oven.

The optimum pH for a cuprous oxide for use in antifouling paints was established as 10 ± 0.5. At pH values 7–8, the product had a yellowish colour. The optimum temperature was found to be in the range 70–80 °C. At lower temperatures the yield of cuprous oxide decreased significantly.

In the 40 dm³ cell the following process conditions were employed: NaCl: 150–300 g dm⁻³; temperature: 70 and 90 °C; current density: 2–10 A dm⁻²; and pH 10 ± 0.5. Duration of the electrolysis was 4–48 h without or with agitation mechanically, by circulation of the electrolyte or by bubbling nitrogen.

The chemical stability of the cuprous oxide product was followed over a four-month period with and without protective reagents.

In the experiments with the different cells the use of

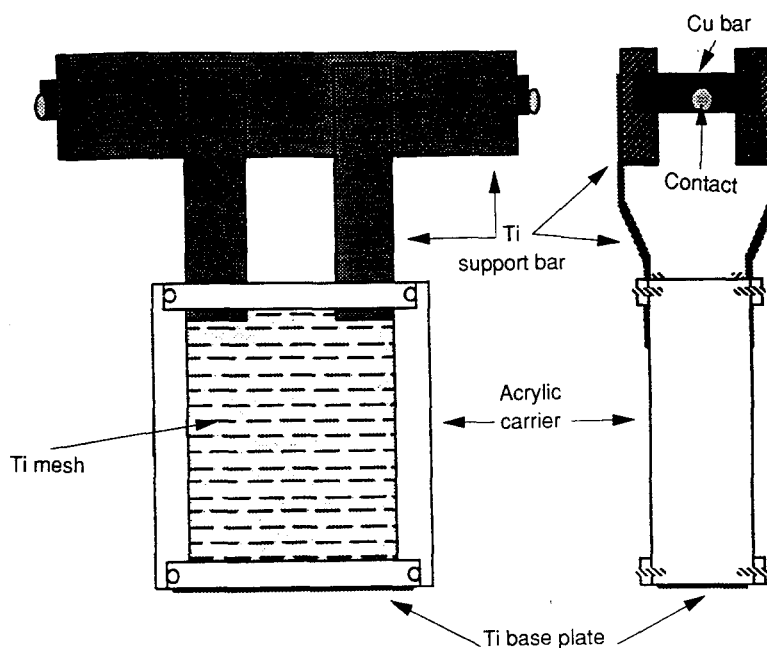


Fig. 2. Mounting of the anode system (without diaphragm).

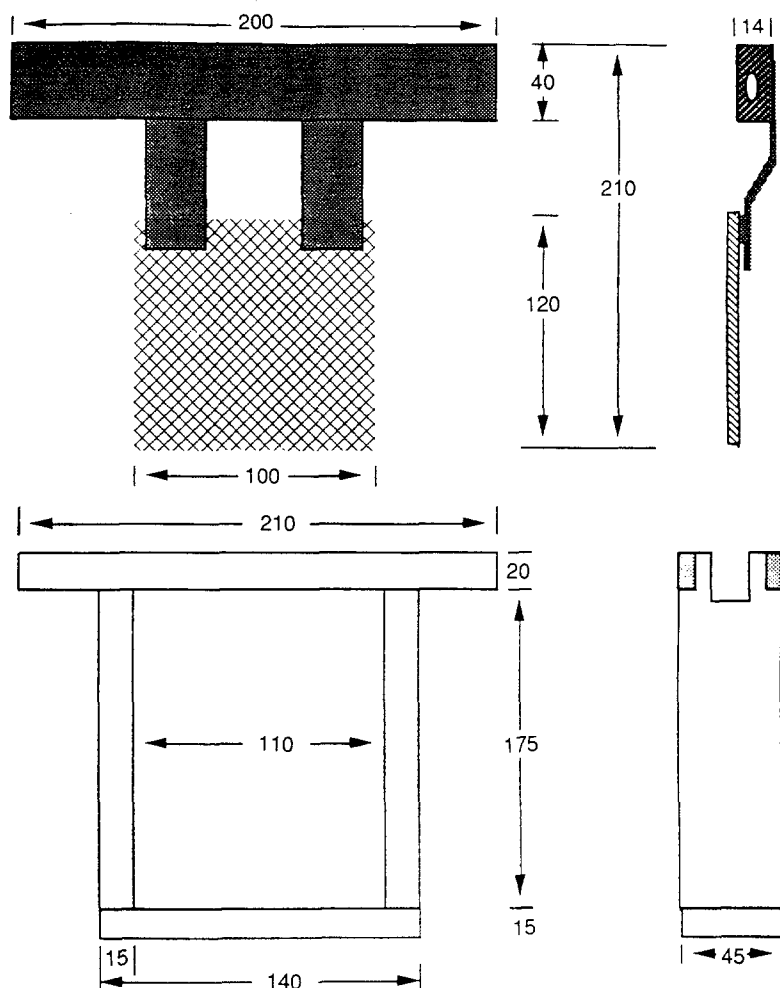


Fig. 3. Components of titanium mesh and acrylic cathode carrier. (All measures are in millimetres).

additives was avoided by employing anodic and cathodic diaphragms supplied by REICOTEX, Casilla 6085, Santiago, Chile. The diaphragms had the characteristics specified in Table 1.

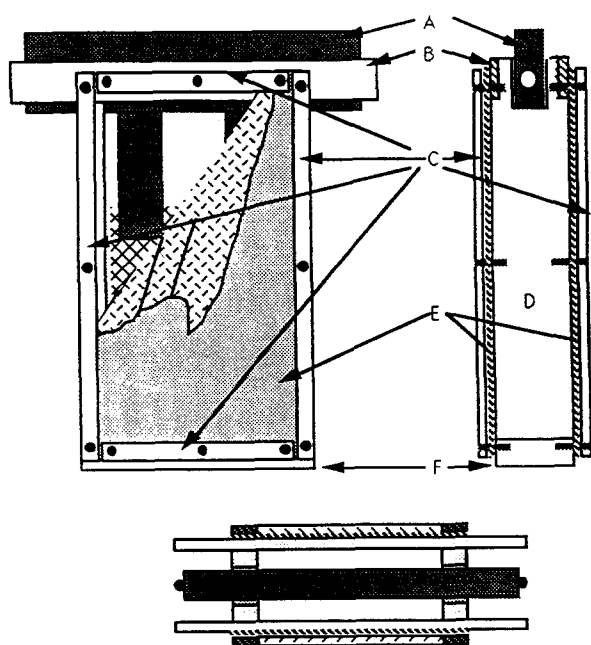


Fig. 4. Mounting of the cathode system. (A) Titanium carrier; (B) cathode carrier lug; (C) acrylic carrier; (D) end section acrylic carrier; (E) polypropylene/polyethylene diaphragm.

In the 400 dm³ cell (operating capacity 344 dm³), two electrode configurations were used, viz.:

- (i) One anode-support of titanium (10.7 dm²) and one copper cathode (9.5 dm²)
- (ii) One central titanium anode-support (21.4 dm²) and two copper cathodes (19 dm²)

The titanium anode-support basket was filled with 10 kg of no. 1 copper scrap in the form of pieces of chopped copper wire (2–5 mm diameter). The electrolyte was agitated by nitrogen bubbling at the mid-point of the cell and circulated in the bottom-top mode at a rate of 10 dm³ min⁻¹ or 3% of the total volume min⁻¹. The electrolyte was maintained at 80 ± 2 °C and kept at a constant level by the dropwise addition of distilled water and the use of hollow polyethylene spheres (2 cm diam.) to reduce evaporation loss. The current flowing through the cell was varied to study the effect of increasing the current per unit volume.

The product was recovered in batches of 40 dm³ without interrupting the current but stopping the agitation and circulation of the electrolyte. After the pulp had stood for 15 min, the supernatant solution was returned to the cell and the slurry (15–20 dm³) was filtered in an enclosed porcelain filter under nitrogen pressure.

Following filtration the washed solid was suspended in distilled water (rendered alkaline to pH 10 with NaOH) and agitated vigorously for 10 min. Decantation

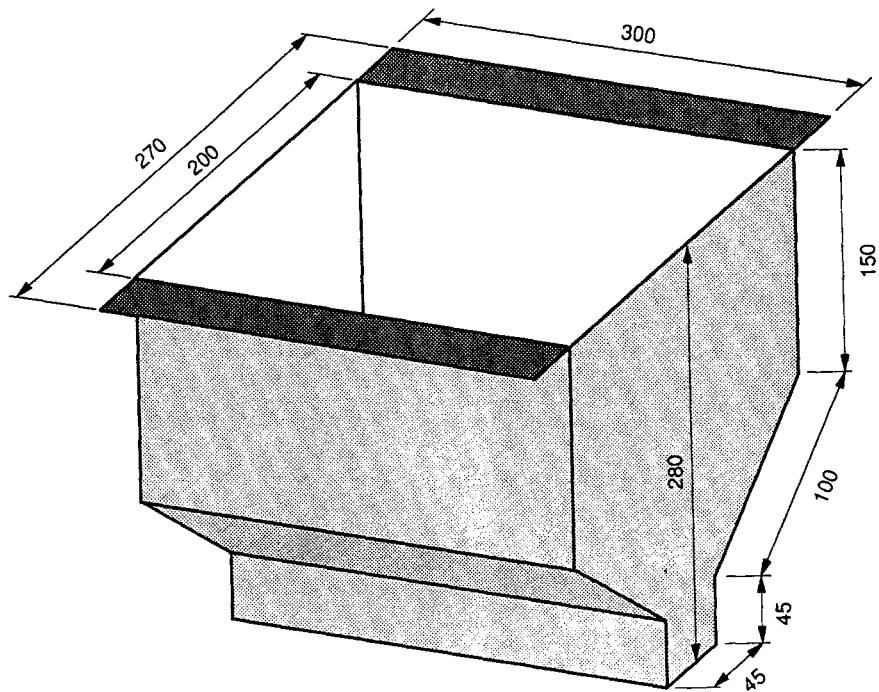


Fig. 5. 15 dm³ coated 316 stainless steel tank for Cu₂O productions. (All measures in millimetres).

and further washing took place until the filtrate was free of chloride ions.

The solid was then agitated for 30 min in a solution containing an appropriate additive* to stabilize the cuprous oxide. After a standing period of 12 h, the supernatant liquor was decanted, the slurry filtered as before and the product dried in a vacuum oven at 60–80 °C and –25 cm Hg. The dried solid was screened through a 325 mesh screen and placed in containers under a nitrogen atmosphere.

3. Results and discussion

3.1. Sodium chloride concentration

To establish the optimum sodium chloride concentration, electrolyses were conducted in a 7 dm³ cell at pH 10 ± 0.5 and 80 °C. Taking the ASTM specification D912-65 (Cu₂O > 97%, Cu_{total} > 86%), the results presented in Table 2 indicate that a good quality product was obtained at sodium chloride concentrations of 250 and 300 g dm⁻³. This finding is in

* 0.2% alcoholic solution of stearic acid, or 0.2% alcoholic solution of benzotriazole, or 0.3% 1:1 aqueous solution of glucose–fructose.

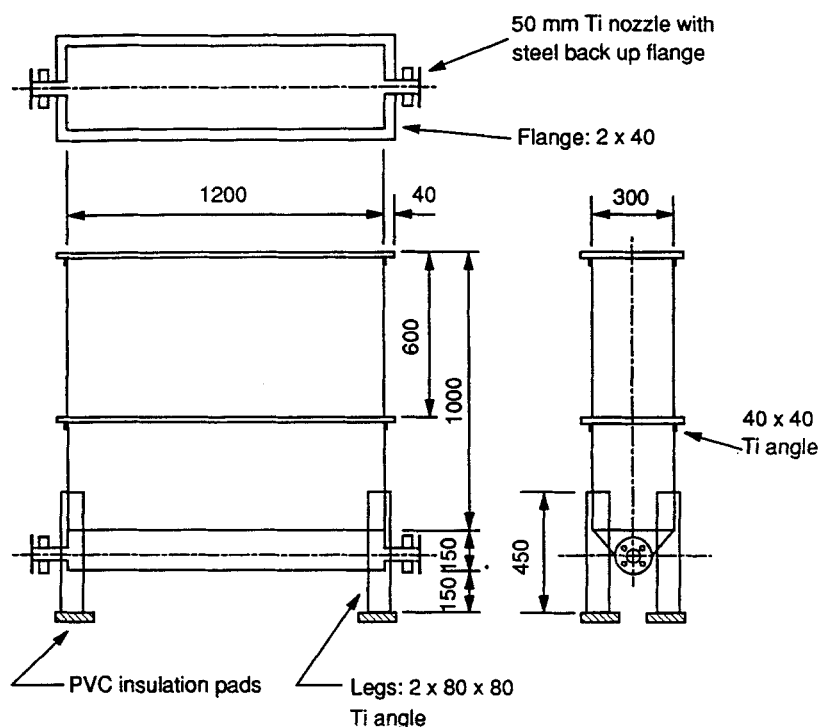


Fig. 6. 400 dm³ titanium cell tank for Cu₂O production. (All measures in millimetres).

Table 1.

Material	Anodic diaphragm: monofilament polypropylene cloth (article 3006)	Cathodic diaphragm: non-woven cloth of polypropylene/polyethylene (article 3010)
Thickness/mm	1.1	approx. 3
Weight/g m ⁻²	290	400
Water absorption/%	0.05	0.05
Max. working temp./°C	90	90
Resistance to alkaline soln.	excellent	excellent
Air permeability/(dm ³ dm ⁻² min ⁻¹)	600	312

agreement with Ji and Cooper's electrochemical data [2]. Their results showed the presence of maxima in the anodic peak and limiting current densities at a sodium chloride concentration of 260 g dm⁻³. A concentration of 250 g dm⁻³ was selected as the optimum value for the experimental work in the laboratory cells. This concentration avoided the crystallization problems associated with high sodium chloride levels.

3.2. Influence of pH on colour of cuprous oxide

Experiments carried out in the 7 dm³ cell demonstrated that the colour of the cuprous oxide is dependent on the pH change occurring during the electrolysis. The results given in Table 3 show that a negative ΔpH ($\text{pH}_{\text{final}} - \text{pH}_{\text{initial}}$) led to a product having a yellow or orange-yellow colour. On the other hand, a positive pH change gave a red or more commonly a dark red cuprous oxide.

In the pH range 7–9 the cuprous oxide is very fine having a yellow-orange colour. At pH 10 ± 0.5 the cuprous oxide has a red-violet colour and a composition well suited to its use in antifouling paints. A colour progressing from red to dark red is indicative of an increasing percentage of cupric oxide.

The net chemical reaction, $2\text{Cu} + \text{H}_2\text{O} \longrightarrow \text{Cu}_2\text{O} + \text{H}_2$, indicates that there should be no change in pH in the process. Changes in pH are an indication of the occurrence of other reactions in the cell which may affect the composition and state of subdivision of

Table 2. Contents of Cu₂O and total Cu in product from a 7 dm³ cell at different NaCl concentrations (pH 10 ± 0.5 and $80 \pm 5^\circ\text{C}$)

Exp.	c.d.* /A dm ⁻²	NaCl /g dm ⁻³	Cu ₂ O /%	Cu _{Total} /%
A	10	250	97.27	86.24
B	10	250	97.45	86.74
C	10	150	91.39	86.14
D	4	300	98.21	86.45
E	4	300	98.96	86.05
F	4	300	98.18	86.27
G	4	250	98.17	86.27
H	4	250	98.37	86.33
I	4	150	97.76	87.00
J	2	250	94.80	86.01
K	2	150	95.26	87.07

* Nominal c.d. based on the geometrical area of the titanium basket anode

the product. This matter is discussed further later in this paper.

3.3. Electrolyses in cells up to 40 dm³ in capacity

Representative results for the preparation of cuprous oxide in cells having capacities of 7, 10, and 40 dm³ are shown in Table 4. Taking the ASTM specification, the best results were obtained in experiments R7-9 where there was very little change in pH and no elemental copper in the product.

As expected, the filtration system has a definite effect on the quality of the product especially as regards the cupric oxide content. The superiority of pressure filtration under nitrogen as compared with suction filtration is illustrated by the data in Table 5.

In selecting the optimum operating conditions leading to a high quality cuprous oxide, it became apparent that a key consideration is the 'concentration of current' factor ($CI/A \text{ dm}^{-3}$). This is underlined by the data in Table 6 for electrolyses using 15 and 40 dm³ cells. According to these results the best quality cuprous oxide was obtained using a concentration of current in the range 0.35 to 0.42 A dm⁻³.

Table 3. Influence of pH on the colour of Cu₂O (7 dm³ cell, NaCl 250 g dm⁻³, 80°C)*

Exp.	pH _i	pH _f	ΔpH	Colour	Exp.	pH _i	pH _f	ΔpH	Colour
29	9.0	7.9	-1.1	yellow	25	10.1	10.8	0.7	red
36	8.9	7.9	-1.0	yellow	31	10.2	10.8	0.6	red
19	9.2	8.0	-1.2	yellow	37	9.8	11.1	1.3	red
2	8.5	8.0	-0.5	yellow	38	10.0	11.2	1.2	red
11	9.0	8.2	-0.8	yellow	7	10.1	10.8	0.7	dark red
1	10.4	8.7	-1.7	yellow	26	10.5	10.9	0.4	dark red
3	10.1	8.9	-1.2	yellow	20	10.1	11.0	0.9	dark red
4	10.2	9.4	-0.8	orange	32	10.5	11.0	0.5	dark red
13	10.1	9.4	-0.7	orange	6	10.5	11.1	0.6	dark red
5	10.1	9.5	-0.6	orange	12	10.1	11.3	1.2	dark red
21	10.2	10.2	0.0	orange-red	16	10.1	11.3	1.2	dark red
30	10.1	10.3	0.2	orange-red	27	10.4	11.3	0.9	dark red
8	10.2	10.2	0.0	red	18	10.3	11.5	1.2	dark red
9	10.1	10.2	0.1	red	28	10.5	11.6	1.1	dark red
22	10.1	10.3	0.2	red	24	10.0	11.7	1.7	dark red
14	10.1	10.4	0.3	red	10	10.1	11.8	1.7	dark red
17	10.1	10.4	0.3	red	35	10.0	11.9	1.9	dark red
15	10.0	10.5	0.5	red	33	10.1	12.0	1.9	dark red
23	10.3	10.5	0.2	red	34	10.1	12.0	1.9	dark red

* pH measured on solution taken between electrodes

Table 4. Representative results obtained using 7, 10 and 40 dm³ cells (NaCl 250 g dm⁻³, 80 °C)

Exp.	c.d. /A dm ⁻²	I /A	Vol /dm ³	t /h	pH		Cu ₂ O /%	Cu ⁰ /%	Cu _r /%	TRP* /%	V _i [†] /V
					initial	final					
R-1	4	2.4	7	4	10.8	9.4	95.77	0.04	86.59	95.86	1.42
R-2	4	2.4	7	4	10.0	9.8	96.60	0.05	86.86	96.70	1.44
R-3	6	3.6	7	4	10.3	10.0	96.88	0.02	85.74	96.93	1.67
R-4	10	6	7	4	10.3	10.7	96.82	0.01	86.90	96.88	1.93
R-5	10	6	7	4	10.4	9.7	97.08	0.04	86.93	97.17	1.92
R-6	10	6	7	4	10.4	9.8	97.13	0.03	86.31	97.20	1.92
R-7	10	6	10	4	10.4	10.2	99.50	0.00	86.81	99.50	1.95
R-8	8	4.8	10	4	10.2	10.0	99.40	0.00	86.46	99.40	1.80
R-9	6	3.6	10	4	10.1	10.0	99.14	0.00	86.63	99.14	1.59
‡R-10	6	10	40	18	10.1	10.1	97.80	0.19	87.15	98.23	1.90

* TRP = total reducing power

† V_i = anode-cathode voltage

‡ For R-10, the results of the chemical analysis are the average of those obtained in four experiments carried out under the same conditions

3.4. Electrolysis with 400 dm³ cell

Table 7 gives the results for 10 runs with the semi-industrial cell of 400 dm³ (working volume 344 dm³). An examination of these data substantiates further the importance of the concentration of current factor (CI) especially in maintaining the pH of the solution. With low CI values (0.10–0.24 A dm⁻³), the pH decreases and the cuprous oxide does not meet the ASTM standards. At high CI values (0.62–1.87 A dm⁻³), the pH increases and the cuprous oxide is of poor quality. Under such conditions it appears that there is a different reaction stoichiometry with a greater or lesser consumption of hydroxyl ions in the process and the generation of products other than cuprous oxide, such

 Table 5. Influence of filtration system for Cu₂O on the content of CuO in product (7 dm³ cell, NaCl 250 g dm⁻³, pH 10, 80 °C)

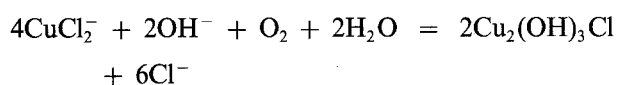
Exp.	CuO /%	Filtration system	pH _f	Colour	c.d. /A dm ⁻²
4	0.00	c	9.4	orange	2
1	0.00	c	8.7	yellow	2
3	0.00	c	8.9	yellow	2
5	0.00	c	9.5	orange	2
8	0.00	c	10.2	red	3
9	0.00	c	10.2	red	3
13	0.00	c	9.4	orange	4
21	0.00	c	10.2	orange-red	6
23	0.00	c	10.5	red	6
29	0.00	c	7.9	yellow	8
19	0.02	b	8.0	yellow	6
2	0.03	b	8.0	yellow	2
15	0.03	b	10.5	red	4
11	0.04	b	8.2	yellow	4
36	0.04	b	7.9	yellow	10
14	0.08	b	10.4	red	4
20	0.25	b	11.0	dark red	6
7	0.28	b	10.8	dark red	3
12	0.21	a	11.3	dark red	4
6	0.34	a	11.1	dark red	3
10	0.45	a	11.8	dark red	4

a = suction filtration without inert atmosphere

b = suction filtration with inert atmosphere

c = pressure filtration under nitrogen

as cupric oxychloride.



The presence of Cu₂(OH)₃Cl or CuCl₂ · 3Cu(OH)₂ in alkaline solution high in chloride ion (e.g. 4 M NaCl) is supported by the E_n-pH diagram for the Cu-Cl⁻-H₂O system [7]. Cyclic voltammetry experiments conducted by Ji and Cooper [8] at 80 °C in an electrolyte containing 250 g dm⁻³ (4.28 M) NaCl and 0.5 g dm⁻³ (0.013 M) NaOH showed that the anodic dissolution of copper was followed by the continuous formation of Cu₂O. In the case of cyclic voltammetry measurements at 25 °C in less concentrated chloride solution (1 M NaCl) and 0.01 M NaOH Drogowska *et al.* [9] found that CuCl was formed at the electrode following copper dissolution. This compound flaked from the electrode surface and reacted with the electrolyte to give a mixture of Cu₂O, CuCl₂ · 3Cu(OH)₂ and CuCl₂ · 3Cu(OH)₂ · 3H₂O.

On the basis of the data reported in Table 7, five additional electrolyses of 120 h duration were carried out using the following conditions:

NaCl	250 g dm ⁻³	Temperature	80 °C
c.d.	6 A dm ⁻²	Time	120 h
Voltage	2.0 ± 0.1 V	pH, initial	10.1
Current	128 A	pH, final	10.1
CI	0.37 A dm ⁻³		

In these experiments, the central anode-support was used with two cathodes, one on each side of the anode. The anode and cathodes were masked with sheets of polypropylene and polypropylene/polyethylene respectively. The electrolyte flow was bottom to top at a rate of 1.6–2.0% of total volume per minute. The final product was stabilized with a 0.2% alcoholic solution of stearic acid and dried at 80 °C in a vacuum oven. The quality of the product obtained in the five runs is shown in Table 8.

The use of diaphragms in the cell in place of additives to the electrolyte to inhibit the redox reactions is important in ensuring a high quality product. This is underlined by the fact that there are a number of

Table 6. Quality of Cu_2O obtained in 15 and 40 dm^3 cells (NaCl 250 g dm^{-3} , pH 10, 80 °C, anodic and cathodic diaphragms, pressure filtration under N_2 , 8 h. electrolysis)

Series	No. of Expts	c.d. / A dm^{-2}	Ranges		Average analyses (dispersion \pm 0.2%)				
			I/A	CI/A dm^3	Cu_2O /%	Cu^0 /%	Cu_T /%	TRP /%	CuO /%
A	7	2-7	2.1-7.3	0.05-0.18	96.72	0.00	87.13	96.73	1.53
B	9	2-10	3.1-12.5	0.21-0.31	97.36	0.10	86.80	97.59	0.29
C	10	3-8	5.2-16.6	0.35-0.42	98.86	0.08	87.89	99.03	0.01
D	8	4-10	7.3-20.8	0.47-1.39	96.97	0.27	86.71	97.58	0.39

electrochemical reactions which are thermodynamically more favourable than the cathode reaction for the reduction of water (Table 9).

Metallic copper in the cuprous oxide product could be generated in the cathode compartment electrochemically or chemically by hydrogen reduction. On the other hand, fine particles of metallic copper resulting during the anodic dissolution of copper in the titanium mesh basket could fall to the bottom of the cell as an anodic slime and contaminate the cuprous oxide. Hence special care must be exercised as regards agitation and the selection of the anodic and cathodic diaphragms.

The structure of the cuprous oxide product was similar to that observed by Ji and Cooper in earlier work [3]. The pores in the cuprous oxide particles explain the difficulty in washing the cuprous oxide free of chloride. However, the chloride content of the product was well within the ASTM specification.

3.5. Stability of cuprous oxide

Regarding the stability of the cuprous oxide, Table 10 gives data on the total reducing power of the product as a function of time when the product was without protection or protected via treatment with a 0.2% alcoholic solution of stearic acid or with a 0.3% 1:1 aqueous solution of glucose-fructose. It is obvious

from these results that stabilization of the cuprous oxide is an important consideration.

4. Conclusions

From the data on the experiments in the 400 dm^3 cell, it can be concluded that it is possible to carry out continuous electrolyses of long duration (120 h) with reproducible results, maintaining a constant pH and obtaining a cuprous oxide product meeting ASTM specification D912-65. The following are the recommended operating parameters:

NaCl	250 g dm^{-3}
c.d.	6 A dm^{-2}
Temperature	80 °C
CI	0.37 A dm^{-3}
pH	10

Especially important as regards scale-up is the parameter *CI*, which expresses the current per unit volume of electrolyte. The use of additives to control redox reactions in the cell can be avoided by the use of polypropylene and polypropylene/polyethylene diaphragms for anode and cathode respectively.

Acknowledgements

The authors would like to express their appreciation

Table 7. Representative results obtained using a 400 dm^3 cell (effective volume 344 dm^3 , NaCl 250 g dm^{-3} , 80 °C, 36 h electrolysis)

Exp.	c.d. / A dm^{-2}	I / A	CI / A dm^{-3}	pH		Cu_2O /%	Cu^0 /%	Cu_T /%	TRP /%	V_i / V	Product quality
				initial	final						
400-1	2	43	0.12	10.1	9.2	95.68	0.03	86.79	95.89	1.60	poor
400-2	4	86	0.24	10.0	9.8	96.71	0.05	86.68	96.69	1.88	poor
400-3	6	128	0.37	10.1	10.1	98.51	0.00	85.79	98.51	2.07	good
400-4	8	172	0.50	10.1	10.1	97.82	0.00	86.90	97.83	2.73	good
400-5	10	215	0.62	10.0	10.9	96.54	0.04	86.93	96.56	3.12	poor
400-6	12	257	0.75	10.1	11.3	96.13	0.03	86.31	96.60	4.72	poor
400-7	15	322	0.94	9.9	12.1	95.50	0.07	87.81	98.50	5.95	poor
400-8	20	429	1.20	10.3	12.0	95.40	0.05	86.64	99.40	6.78	poor
400-9	25	536	1.55	10.1	12.0	95.14	0.07	86.59	99.14	7.67	poor
400-10	30	644	1.87	10.0	11.8	95.80	0.14	87.35	98.00	8.80	poor

TRP = total reducing power; V_i = anode-cathode voltage

Table 8. Quality of Cu₂O obtained in a 400 dm³ cell

Exp.	Cu ₂ O %	Cu ⁰ %	Cu _r %	TRP %	Cl ⁻ %
400-11	98.03	0.00	87.12	98.18	0.21
400-12	97.96	0.15	87.50	97.95	0.19
400-13	97.89	0.18	87.16	98.68	0.22
400-14	98.01	0.01	87.10	98.95	0.23
400-15	97.97	0.10	87.25	98.40	0.20
Average	97.97	0.09	87.22	98.43	0.21

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Table 9. Reduction of Cu(I) species to Cu⁰ at the cathode

Electrode reaction	E ⁰ /V
Cu ⁺ + e ⁻ = Cu ⁰	0.522
CuCl _(aq) + e ⁻ = Cu ⁰ + Cl ⁻	0.124
CuCl ₂ + e ⁻ = Cu ⁰ + 2Cl ⁻	0.190
CuCl ₃ ²⁻ + e ⁻ = Cu ⁰ + 3Cl ⁻	0.178
Cu ₂ O + H ₂ O + 2e ⁻ = 2Cu ⁰ + 2OH ⁻	-0.361
2H ₂ O + 2e ⁻ = H ₂ + 2OH ⁻	-0.828

Table 10. Reducing power (% TRP) of Cu₂O without and with treatment to stabilize the Cu₂O

Days	A	B	C
1	97.78	97.85	98.23
15	96.69	97.56	98.16
60	96.51	97.21	97.97
90	96.44	97.02	97.41
120	94.31	97.04	97.41

A = without protection
 B = protected with 0.2% alcoholic solution of stearic acid
 C = protected with 0.3% aqueous solution of glucose-fructose (1:1)

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