

1/88

CMCRCZ 17 (1), 1-66 (1988)

ISSN 0366-693X

ΧΗΜΙΚΑ ΧΡΟΝΙΚΑ

ΝΕΑ ΣΕΙΡΑ

CHIMIKA CHRONIKA

NEW SERIES

**AN INTERNATIONAL EDITION
OF THE ASSOCIATION OF GREEK CHEMISTS**

CHIMIKA CHRONIKA, NEW SERIES Volume 17, No 1, p.p. 1-66 March (1988)

CHIMIKA CHRONIKA / NEW SERIES

Published by the Association of Greek Chemists

27, Kaningos Street, Athens 106 82, Greece

MANAGING CGMMITEE

Dimitrios KESSISOGLOU, Georgia MARGOMENOU-LEONIDOPOULOU, Angeliki PAPATHANASOPOULOU, Theodora VAKIRJI, Roula SCOULICA

Ex. officio Members: X. PAPAIOANNOU (Repr. Gen. Secretary of G.C.A.)

J. KARABASSIS (Treasurer of G.C.A.)

EDITORS - IN - CHIEF

I. DILARIS, G. MARGOMENOU-LEONIDOPOULOU

EDITORIAL ADVISORY BOARD

N. ALEXANDROU

Org. Chem., Univ. Salonica

A. ANAGNOSTOPOULOS

Inorg. Chem. Tech. Univ. Salonica

D. BOSKOU

Food Chem., Univ. Salonica

P. CATSOULACOS

Pharm. Chem., Univ. Patras

C.A. DEMOPOULOS

Biochemistry, Univ. Athens

C.E. EFSTATHIOU

Anal. Chem., Univ. Athens

A.E. EVANGELOPOULOS

Biochemistry, N.H.R.F., Athens

S. FILIANOS

Pharmacognosy, Univ. Athens

D.S. GALANOS

Food Chem., Univ. Athens

P. GEORGAKOPOULOS

Pharm. Techn., Univ. Salonica

I. GEORGATSO

Biochemistry, Univ. Salonica

M.P. GEORGIADIS

Org./Med. Chem., Agr. Univ. Athens

N. HADJICHRISTIDIS

Polymer Chem., Univ. Athens

T.P. HADJIOANNOU

Anal. Chem., Univ. Athens

N. HADJILIADIS

Gen. Inorg. Chem., Univ. Ioannina

E. HADJOURDIS

Photochem., N.R.C. -D-, Athens

P.V. IOANNOU

Depart. Chem. Univ. Patras

D. JANNAKOUDAKIS

Phys. Chem., Univ. Salonica

V. KAPOULAS

Biochemistry, Univ. Ioannina

M.I. KARAYANNIS

Anal. Chem., Univ. Ioannina

N. KATSANOS

Phys. Chem., Univ. Patras

A. KEHAYOGLOU

Org. Chem. Tech. Univ. Salonica

A. KOSMATOS

Org. Chem., Univ. Ioannina

S.B. LITSAS

Biorg. Chem., Arch. Museum, Athens

G. MANOUSSAKIS

Inorg. Chem., Univ. Salonica

S. MYLONAS

Org. Chem., Univ. Athens

I. NIKOKAVOURAS

Photochem., N.R.C. -D-, Athens

D.N. NICOLAIDES

Org. Chem., Univ. Salonica

C.M. PALEOS

N.R.C. -Democritos-, Athens

V. PAPADOPOULOS

N.R.C. -Democritos- Athens

G. PAPAGEORGIOU

Biophysics, N.R.C. -D-, Athens

V.P. PAPAGEORGIOU

Nat. Products, Tech. Univ. Salonica

S. PARASKEVAS

Org. Chem., Univ. Athens

G. PHOKAS

Pharmacognosy, Univ. Salonica

S. PHILIPAKIS

N.R.C. -Democritos-, Athens

G. PNEUMATIKAKIS

Inorg. Chem., Univ. Athens

K. SANDRIS

Organic Chem. Tech. Univ. Athens

M.J. SCULLOS

Env./Mar. Chem., Univ. Athens

C.E. SEKERIS

Mol. Biology, N.H.R.F., Athens

G. SKALCOS

Microanalysis Tech. Univ. Athens

G.A. STALIDIS

Phys. Chem., Univ. Salonica

Ch. STASSINOPOULOU

N.R.C. -Democritos-, Athens

A. STASSINOPOULOS

Argo AEBE Athens

A. STAVROPOULOS

Ind. Technol., G.S.I.S., Piraeus

C. THOMOPOULOS

Food Techn., Tech. Univ. Athens

I.M. TSANGARIS

Inorg. Chem., Univ. Ioannina

G.A. TSATSAS

Pharm. Chem., Univ. Athens

A.K. TSOLIS

Chem. Technol., Univ. Patras

A. VALAVANIDIS

Org. Chem., Univ. Athens

G. VALCANAS

Org. Chem., Tech. Univ. Athens

A.G. VARVOGLIS

Org. Chem., Univ. Salonica

G.S. VASSILIKIOTIS

Anal. Chem., Univ. Salonica

S. VOLIOTIS

Instrum. Analysis, Univ. Patras

E.K. VOUDOURIS

Food Chem., Univ. Ioannina

D. VRANTI

Tech. Univ. Athens

Correspondence, submission of papers, subscriptions, renewals and changes of address should be sent to Chimika Chronika, New Series, 27 Kaningos street, Athens, Greece. The Guide to Authors is published in the first issue of each volume, or sent by request. Subscriptions are taken by volume at 1000 drachmas for members and 2000 drachmas for Corporations in Greece and 28 U.S. dollars to all other countries except Cyprus, where subscriptions are made on request.

Phototypesetted and Printed in Greece by EPTALOFOS S.A.

ARDITTOU STR. 12-16, 116 36 ATHENS

Υπεύθυνος σύμφωνα με το νόμο: Βασίλειος Μπούλιας, Κάνιγγος 27, Αθήνα 106 82.

CONTENTS

Synthesis of 4-O-p-Nitrobenzoyl-3-N-Trifluoroacetyl-4-Demethoxydaunomycin (<i>in English</i>) by F. Sakellariadou.....	1
Calculation of the electrochemical double-layer capacity C_d and of the uncompensated resistance R_u in the system Fe^{2+}/Fe^{3+} into artificial sea water (<i>in Greek</i>) by Y. Chryssoulakis, S. Markantonatou.....	9
Applicability of electrolytic flotation for the recovery of carbonate fines (<i>in English</i>) by K.A. Matis, G.P. Gallios, G.A. Stalidis.....	29
Optimization of a multiproduct batch process (<i>in English</i>) by P.A. Pilavachi.....	53

ΣΗΜΕΙΩΣΗ: Την επιμέλεια του τεύχους είχε η Επιτροπή Εκδόσεων (Απόφαση της 438/30/8.11.89 Δ.Ε. της Ε.Ε.Χ.)

Θ.Βακιρτζή	Ε.Βουδούρης	Π.Δημοτάκης
Μ.Καζάνης	Α.Κοσμάτος	Μ.Πετροπούλου
Χ.Νούμπας	Ε.Σακκή	Π.Σίσκος
Ρ.Σκούλικα	Δ.Χατζηγεωργίου-Γιαννακάκη	

SYNTHESIS OF 4-*o*-*p*-NITROBENZOYL-3-N-TRIFLUOROACETYL-4-DEMETHOXY- -DAUNOMYCIN

F. SAKELLARIADOU

Applied Geochemistry Research Group, Department of Geology, Royal School of Mines, Imperial College, Prince Consort Road, London SW7 2BP, U.K. (Present address: 4 Ipsilantou st., 16673-Voula, Greece).

(Received March 20, 1985. Revised February 6, 1987)

SUMMARY

A procedure for the preparation of 4-*o*-*p*-nitrobenzoyl-3-N-trifluoroacetyl-4-demethoxy-daunomycin is described. It includes a 17-step synthesis of 4-demethoxy-daunomycinone, following a modified version of the Pappo and Garland technique; a 5-step synthesis of the bromo derivative of 3-trifluoro-acetamido-1,4-bis-*o*-*p*-nitrobenzoyl-L-daunosaminide and the coupling of the aglycone part with the protected form of the sugar in a one step procedure.

Key words: daunomycin, daunomycinone, daunosamine, anthraquinone, Diels-Alder reaction.

INTRODUCTION

Daunomycin is an anthracycline antibiotic which is used clinically for the treatment of various species¹ of human cancer. Its biological activity involves an inhibition of the cellular DNA dependent replication and transcription processes.

Daunomycin was first isolated from the cultures of *Streptomyces peucetius* and *Streptomyces coeruleorubidus* in the Farmitalia^{2,3,4,5} and Rhône Poulenc^{6,7} laboratories, respectively. Its mild acid hydrolysis affords the aglycone daunomycinone and the amino sugar daunosamine.

Various procedures were developed for the synthesis of the aglycone part. In most of them the key constructive step involves a Diels-Alder reaction while the synthetical route is mainly based on the use of quinizarin quinone. Thus, Kende et al⁸ described a synthetical approach of (+)-4-demethoxy-daunomycinone on the basis of the chemistry of quinone-isobenzofuran adducts; Kelly et al⁹ reported a synthetical procedure which is mainly consisted of a Diels-Alder reaction between quinizarin quinone and an appropriate chlorodiene; Garland and Pappo^{10,11} suggested an effective route for the (+)-4-demethoxy-daunomycinone synthesis based on a Diels-Alder addition of the trans-4-(trimethyl-silyl)-

F. SAKELLARIADOU

-2-acetoxy-1,3-butadiene with quinizarin quinone, while Broadhurst et al¹² proposed a 11-step procedure based on a Diels-Alder reaction and using trans-1,2-diacetoxy-1,2-dihydro-benzocyclobutene to give the appropriate diene *in situ*.

Daunosamine, the amino sugar residue of daunomycin, is a 3-amino-2,3,6-trideoxy-L-lyxo-hexose. Daunosamine hydrochloride was synthesized from L-rhamnal by March et al¹³. Conversely, N-acetyl-D-daunosamine and its arabino isomer can be obtained from methyl-3-acetamido-2,3-dideoxy-D-arabinohexopyranoside or its 6-D-lyxo-isomer, as Baer et al¹⁴ suggested. In addition, an interesting synthetical procedure of N-trifluoroacetyl-L-daunosamine was proposed by Fronza et al¹⁵, starting from cinnamaldehyde, formaldehyde and commercial bakers' yeast.

In order to obtain the desired anthracycline, the connection of the aglycone part with the amino sugar is desired. Coupling the (+)-demethoxy-daunomycinone with the 1-chloro-3-N,4-O-bistrifluoroacetyl-daunosamine, following the Koenigs-Knorr method, mixtures of α - and β -glycosides were obtained. On the other hand, under similar conditions, using the 4-O-p-nitro-benzoyl-derivative, the α -glycoside was exclusively produced¹⁶.

MATERIALS AND METHODS

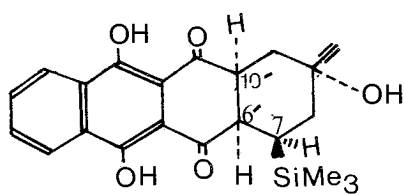
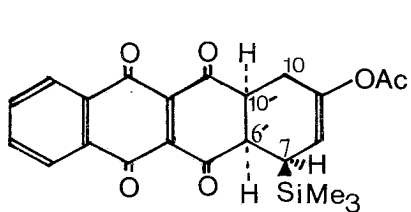
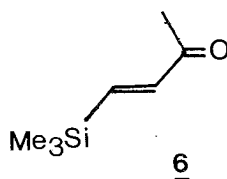
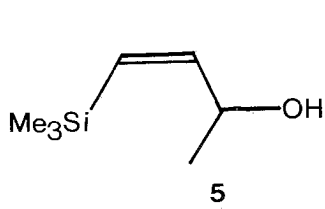
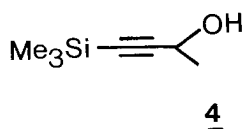
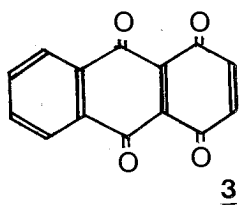
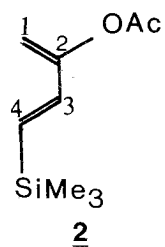
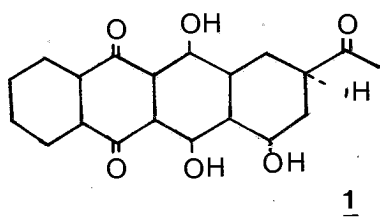
The synthesis of 4-demethoxy-daunomycinone, **7**, was achieved following a modified version of the Pappo and Garland technique in 17 steps. The key step involves a Diels-Alder reaction between E-1-trimethyl-silyl-3-acetoxy-1,3-butadiene, **2**, and quinizarin quinone, **3**.

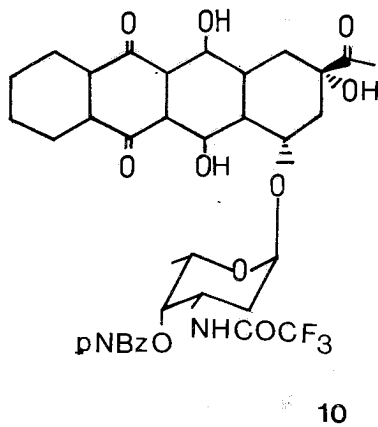
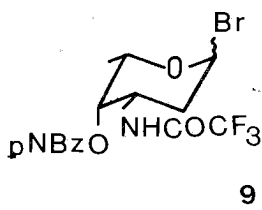
Briefly, the preparation of the butadiene comprises the following stages:

- (a) reaction of pure butyn-3-ol with freshly prepared ethyl magnesium bromide in THF;
- (b) addition of chlorotrimethylsilane;
- (c) removal of the trimethylsilyl substituent by aqueous HCl, that provides the colourless stable oil, **4**;
- (d) partial hydrogenation that affords the *cis*-olefin, **5**;
- (e) oxidation of compound, **5**;
- (f) isomerization of the double bond by acidic acid methanol;
- (g) addition of water followed by extraction with diethyl ether that provides the enone, **6**, and
- (h) addition of anhydrous isopropenyl acetate resulting to the butadiene, **2**.

On the other hand, quinizarin quinone was obtained by oxidizing commercial quinizarin with lead tetraacetate in acetic acid, method of Dimroth and Hilcken¹⁷. Diels-Alder addition

4-DEMETHOXY-DAUNOMYCIN





of the butadiene to the quinizarin quinone gave the cycloadduct, *7*. Catalytical hydrogenation and ethyl acetate treatment were applied to, *7*, leading to the tetracyclic leucoquinizarin. Further methanolysis of the vinyl acetate moiety in the latter compound gave an acetal which was hydrolysed to a ketone. The ketone was ethynylated at its C-9 position providing an isomeric mixture, which mainly consisted of the carbinol, *8*. The carbinol was acetylated using isopropenyl acetate and the resulting 3-acetoxy derivative was subsequently oxidized with lead tetraacetate. The quinone diketone produced was treated with a saturated solution of potassium acetate in acetic acid and then dry KF was added, followed by reduction with sodium metabisulphite. The resulting acetate was hydrolysed with mercuric chloride, aniline and water in refluxing benzene, using the Stanley method. Further acid hydrolysis in aqueous isopropanol produced finally (+)-4-demethoxy-daunomycinone, *1*.

The amino sugar was prepared from the commercially available methyl-L-daunosamine hydrochloride following hydrolysis with dilute HCl, treatment with an excess of trifluoroacetic anhydride and addition of aqueous THF. The obtained sugar was protected by adding two equivalents of *p*-nitrobenzyl chloride. The desired bromo derivative, *9*, of the protected sugar was prepared by using hydrogen bromide gas.

The final coupling of the aglycone part with the sugar, was carried out by adding a solution of, *9*, in CH₂Cl₂ to a mixture of 4-demethoxy-daunomycinone, water, mercuric bromide and dichloromethane.

EXPERIMENTAL

Preparation of (+)-3-acetoxy-1,4,4 α ,8,12 α ,a-tetrahydro-16-trimethyl-silyl-5,6,11,12-

4-DEMETHOXY-DAUNOMYCIN

-naphthacenetetrone

1,4,9,10-Anthracenetetrone (8.97g, 37.7mmol) was added to dry benzene (250ml) under an argon atmosphere. Freshly prepared E-1-trimethyl-silyl-3-acetoxy-1,3-butadiene (5.4g, 24.4mmol) was added and the mixture was stirred for 4 days at 55°C. After stirring overnight cyclohexane (25ml) was added, and the mixture was chilled at 10°C to give (+)-3-acetoxy-1,4 α ,a,12 α ,a-tetrahydro-1 β -trimethylsilyl-5,6,11,12-naphthacenetetrone, 7, as golden tan crystals (9.8g, 79%); m.p. 196°-199°C; δ (CDCl₃) 8.05-8.15 (2H,m), 7.80-7.90 (2H,m), 5.48 (1H,br s), 3.75 (1H,dd,J₅ and 5Hz), 3.44-3.57 (1H,m), 2.19-2.53 (2H,m), 2.10 (3H,s), 1.86-1.94 (1H,m), and 0.2 (9H,s); ν_{\max} 2950, 2920, 2850, 1740, 1720, 1705, 1655, 1590, 1460, 1370, 1270, 1245, 1210, 1110 and 840cm⁻¹.

Preparation of 4-o-p-nitrobenzoyl-3-N-trifluoroacetyl-4-demethoxy-daunomycin

4-Demethoxy-daunomycinone (22.5mg), water (0.01ml), mercuric bromide (4.70mg), molecular sieves 3A (94.11mg) and dichloromethane (0.94ml) were stirred at room temperature. The protected sugar was dissolved in CH₂Cl₂ (0.47ml) and hydrogen bromide was bubbled through the solution for 4min. The mixture was stirred for 20min., at r.t., it was filtered under N₂ funnel and the solid produced was washed with methylene chloride. The solid was dried in a desicator over potassium or sodium hydroxide in a pump for 30min. The residue was dissolved in methylene chloride (0.47ml) and dried molecular sieves 3A (918.82mg) were added. The mixture was added dropwise to the stirring mixture of daunomycinone, at r.t., within 45min., and with external bath cooling. The ice bath was removed and the stirring was continued for 1 hour at r.t. The mixture was washed with water and dried over magnesium sulphate. The drying agent was removed by filtration while the solvent was removed under vacuum to give 4-o-p-nitrobenzoyl-3-N-trifluoroacetyl-4-demethoxy-daunomycin, 10, in a mixture with other compounds, which was separated by chromatography (8.82mg, 21%); m.p. 171°C-175°C; ν_{\max} 3950, 3860, 2050 and 1920cm⁻¹.

RESULTS AND DISCUSSION

Of the initial stages of the overall procedure, the formation of the *cis*-olefin, 5, by a partial hydrogenation of the compound, 4, was the reaction that required more attention. The hydrogenation was carried out in benzene using Pd on BaSO₄. Further reduction of the resulting double bond to a single one was avoided by using a small amount of quinone as a

F. SAKELLARIADOU

poisoning agent. Conversely, the freshly prepared *cis*-olefin was immediately separated from the catalyst, in order to avoid a probable isomerization of the double bond that would produce a ketone.

Characterizing the *cis*-olefin by n.m.r. studies it was found that the two hydrogen atoms of the double bond showed their signals at δ 5.60 and 6.25, the hydrogen of the hydroxyl group at δ 2.2, while the methyl group gave a doublet at δ 1.25. The nine protons singlet at δ 0.15 corresponded to the trimethyl-silyl group.

The Diels-Alder reaction was based on a freshly prepared diene. This was necessary as the diene, **2**, was not especially stable even in the presence of radical inhibitors. Studying this diene by n.m.r., it was shown that the two protons at C-1 gave their signals at δ 4.8-5.0, the two olefinic protons at C-3 and C-4 appeared at δ 6.3 and 5.8 and were coupled with a coupling constant of 20Hz, the three protons of the acetyl group appeared to be a singlet at δ 2.2 and the nine protons of the trimethylsilyl group a singlet at δ 0.1. The Diels-Alder reaction was mild. Thus, it was carried out in dry benzene, at 50°C, under a dry argon atmosphere, over 5 days.

The cycloadduct, **7**, was obtained as pale golden tan crystals in a yield directly dependent upon the quality of the diene. In general, yields of 84% were achieved. The n.m.r. spectrum of the cycloadduct showed that the two protons at C-6' and C-10' occurred at δ 3.75 and δ 3.44-3.57, the two protons at C-10 appeared at δ 2.29-2.53, the three protons of the acetyl group gave a singlet at δ 2.10, the three protons of the trimethylsilyl group a singlet at δ 0.2 and the proton at C-7 gave a singlet at δ 1.86-1.94.

During the preparation of the amino sugar, the thermal lability of the various derivatives of the sugar required removal of the solvents at temperatures as low as possible.

On the other hand, ^1H n.m.r. studies of the sugar derivatives were obtained in d-DMSO solution, due to their insolubility in other commonly used solvents. The final coupling of the protected sugar with the aglycone part was successfully completed, through a comparatively easily achieved reaction, giving 4-*o*-*p*-nitrobenzoyl-3-N-trifluoroacetyl-4-demethoxy-daunomycin, **10**, in a mixture with other minor compounds.

ΠΕΡΙΛΗΨΗ

Σύνθεση της 4-*o*-*p*-νιτροβενζοΐλο-3-N-τριφθοροακετυλο-4-διμεθοξυ-δαουνομικίνης

Περιγράφεται μία μέθοδος παρασκευής της ένωσης 4-*o*-*p*-νιτροβενζοΐλο-3-N-τριφθοροακετυλο-4-διμεθοξυ-δαουνομικίνη. Η μέθοδος αυτή περιλαμβάνει τρία μέρη: (α) σύνθεση της ένωσης 4-διμεθοξυ-δαουνομικινόνη σε 17 στάδια ακολουθώντας μία τεχνική που αποτελεί τροποποίηση της τεχνικής των Parro και Garland, (β) παρασκευή

4-DEME THOXY-DAUNOMYCIN

του βρωμιούχου παραγώγου του 3-τριφθορο-ακεταμιδο-1,4-δι-ο-*p*-νιτροβενζούλιο-L-δαουνοσαμινιδίου σε 5 στάδια και (γ) σύζευξη του άθικτου μέρους με το προστατευμένο παράγωγο του σακχάρου με μέθοδο ενός σταδίου.

ACKNOWLEDGMENTS

I would like to thank Prof. S.V. Ley for his assistance, guidance and interest through the course of this research.

REFERENCES

1. Sakellariadou, F., D.I.C. Thesis, Imperial College, University of London, *Synthesis of (+)-Daunomycin*, p.118, London (1983).
2. Di Marco, A., Gaetani, M., Oregii, P., Scarpinato, B.M., Silverstrini, P., Soldati, M., Dasdia, T. and Valentini, L., *Nature*, 201, 706 (1964).
3. Di Marco, A., Gaetani, M., Dorigotti, L., Soldati, M. and Bellini, O., *Tumori*, 49, 203 (1963).
4. Di Marco, A., Soldati, M., Fioretti, A. and Dasdia, T., *Tumori*, 49, 235 (1963).
5. Dorigotti, L., *Tumori*, 50, 117 (1964).
6. Dubost, H., Ganter, P., Maral, R., Ninet, L., Pinnert, S., Preud'Homme, J. and Werner, G.H., *G.R.Herb. Acad. Sci.*, 257, 1813 (1963).
7. Di Marco, A., Gaetani, M., Oregii, P., Scarpinato, B.M., Silverstrini, P., Soldati, M., Dasdia, T. and Valentini, L., *Nature*, 202, 707 (1964).
8. Kende, A.S., Curran, D.P., Tsay, Y.-G. and Mills, J.E., *Tetrahedron Lett.*, 40, 3537 (1977).
9. Kelly, T.R. and Tsang, W.-G., *Tetrahedron Lett.*, 46, 4457 (1978).
10. Garland, R.B., Palmer, J.R., Schultz, J.A., Sollmann, P.B. and Pappo, R., *Tetrahedron Lett.*, 39, 3669 (1978).
11. Garland, R.B. and Pappo, R., *J.K. Patent Application GB 2022114A* (1979).
12. Broadhurst, M.H., Hassall, C.H. and Thomas, G.J., *J. Chem. Soc. Perkin Trans. 1*, 9, 2239 (1982).
13. Marsh, J.P. Jr, Mosher, C.W., Acton, E.M., Goodman, L., *J. Chem. Soc., Chem. Commun.*, 973 (1967).
14. Baer, H.H., Capek, K., Cook, M.C., *Can. J. Chem.*, 47(1), 89 (1969).
15. Fronga, G., Fuganti, C. and Grasseli, P., *J. Chem. Soc., Chem. Commun.*, 1, 442 (1980).
16. Smith, T.H., Fuziwara, A.N., Lee, W.W., Wu, H.Y. and Henry, D.W., *J. Org. Chem.*, 42, 3653 (1977).
17. Dimroth, O. and Hilcken, V., *Ber.*, 54, 3050 (1921).

ΥΠΟΛΟΓΙΣΜΟΣ ΤΗΣ ΧΩΡΗΤΙΚΟΤΗΤΑΣ C_d ΤΗΣ ΗΛΕΚΤΡΟΛΥΤΙΚΗΣ ΔΙΠΛΟΣΤΟΙΒΑΔΑΣ ΚΑΙ ΤΗΣ "ΜΗ ΑΝΤΙΣΤΑΘΜΙΖΟΜΕΝΗΣ" ΑΝΤΙΣΤΑΣΗΣ R_u ΣΤΟ ΣΥΣΤΗΜΑ Fe^{2+}/Fe^{3+} , ΣΕ ΤΕΧΝΗΤΟ ΘΑΛΑΣΣΙΝΟ ΝΕΡΟ.

ΓΙΑΝΝΗΣ ΧΡΥΣΟΥΛΑΚΗΣ, ΣΤΕΛΛΑ ΜΑΡΚΑΝΤΩΝΑΤΟΥ

Τομέας ΙΙΙ Επιστήμης και Τεχνικής των Υλικών, Τμήμα Χημικών Μηχανικών, Ε.Μ.Π.,
 Ηρώων Πολυτεχνείου 9, Πολυτεχνειούπολη Ζωγράφου, Αθήνα 15773

(Ελήφθη στις 30 Μαΐου 1986)

ΠΕΡΙΛΗΨΗ

Στην εργασία αυτή επιχειρείται μία διόρθωση των καμπυλών, $E=f(I)$, της τριγωνικής βολταμπερομετρίας στο σύστημα Fe^{2+}/Fe^{3+} σε τεχνητό θαλασσινό νερό, χρησιμοποιώντας ηλεκτροδία από γραφίτη και πλατίνα στους 25°C. Υπολογίσθηκε συγχρόνως η χωρητικότητα C_d της ηλεκτροχημικής διπλοστοιβάδας των ηλεκτροδίων αυτών, καθώς και η τιμή της "μη αντισταθμιζόμενης" αντίστασης R_u .

Βρέθηκαν οι τιμές $C_d=111,9 \cdot 10^{-6} \text{ F/cm}^2$ και $R_u=14,1\Omega$ στην περίπτωση του ηλεκτροδίου από γραφίτη, και οι τιμές $C_d=15,0 \cdot 10^{-6} \text{ F/cm}^2$ και $R_u=10,2\Omega$ σε ηλεκτρόδιο από πλατίνα. Οι τιμές αυτές βρίσκονται μέσα στα όρια των βιβλιογραφικών αναφορών.

Τέλος ο αριθμός των ανταλλασσόμενων ηλεκτρονίων, n , βρέθηκε να πλησιάζει περισσότερο προς την μονάδα ($n=0,91$) μετά από κατάλληλη διόρθωση των βολταμπερομετρικών καμπυλών $E=f(I)$.

Λέξεις κλειδιά: διόρθωση της πτώσης τάσης, σύστημα Fe^{2+}/Fe^{3+} σε τεχνητό θαλασσινό νερό, υπολογισμός της χωρητικότητας της ηλεκτροχημικής διπλοστοιβάδας C_d και της αντισταθμιζόμενης αντίστασης R_u .

I. ΕΙΣΑΓΩΓΗ

Η τριγωνική και η κυκλική βολταμπερομετρία αποτελούν μεθόδους ποιοτικής κυρίως ανάλυσης της κινητικής των ηλεκτροχημικών αντιδράσεων και συστημάτων με τεράστια σημασία. Ωστόσο, οι ποσοτικές μετρήσεις διαφόρων ηλεκτροχημικών μεγεθών που πραγματοποιούνται με τη βοήθεια των μεθόδων αυτών, όπως ο αριθμός των ανταλλασσόμενων

ηλεκτρονίων n , ο συντελεστής διάχυσης D_{ox} και D_{Red} , οι συντελεστές μεταφοράς α και $\beta=1-\alpha$, θεωρούνται μειωμένης ακρίβειας, δεδομένου ότι τα μεγέθη αυτά προκύπτουν ως αποτέλεσμα μελέτης κλασικών ηλεκτροχημικών συναρτήσεων, που επηρεάζονται άμεσα από την μορφή της βολταμετρομετρικής καμπύλης $E=f(I)$ η οποία παραμορφώνεται ανάλογα με το ύψος της τιμής της πτώσης τάσης.

Η μέθοδος της τριγωνικής βολταμετρομετρίας αποτελεί πολύτιμο ερευνητικό εργαλείο για τη μελέτη μεμονωμένων, ή συγχρόνως εξελισσόμενων, ή διαδοχικών αντιστρεπτών ή αναντίστρεπτων ηλεκτροχημικών δράσεων, που είναι δυνατόν να προηγούνται ή να έπονται χημικών αντιστρεπτών ή αναντίστρεπτων δράσεων^{1,2}.

Για τον σκοπό αυτό έχουν γίνει μέχρι τώρα πολλές προσπάθειες διόρθωσης ή αντιστάθμισης της πτώσης τάσης²⁻¹¹. Ξεχωρίζουν οι ερευνητικές εργασίες των J. DÉVAV, B. LENGYEL, L. MÉSZÁROS⁵ και των D. BRITZ, W.A. BROCKE⁸.

Οι πρώτοι επιβάλλουν ένα εναλλασσόμενο ρεύμα υψηλής συχνότητας, έτσι ώστε η ηλεκτροχημική δράση να παραμείνει ανεπηρέαστη, με ένταση ανάλογη εκείνης του ηλεκτροχημικού συστήματος που μελετάται.

Έτσι, το δυναμικό του εναλλασσόμενου ρεύματος, που μετρείται ανάμεσα στο ηλεκτρόδιο εργασίας και το ηλεκτρόδιο αναφοράς, είναι ανάλογο του δυναμικού του συνεχούς ρεύματος που συνδέεται άμεσα με την αντίσταση του διαλύματος.

Το δυναμικό του εναλλασσόμενου ρεύματος στη συνέχεια ενισχύεται και προστίθεται -έπειτα από κατάλληλη επεξεργασία- στο δυναμικό του συνεχούς ρεύματος που επιβάλλει και ελέγχει ο ποτενσιοστάτης, έτσι ώστε η τιμή της σάρωσης του δυναμικού του ηλεκτροδίου εργασίας να διατηρείται αναλλοίωτη και να παραμένει ανεξάρτητη της αντίστασης του διαλύματος.

Οι δεύτεροι εφαρμόζουν την μέθοδο της απότομης διακοπής του ηλεκτρικού ρεύματος του ποτενσιοστάτη με σκοπό τη μέτρηση της πραγματικής τιμής του δυναμικού ανάμεσα στα ηλεκτρόδια εργασίας και αναφοράς, καθώς και της αντίστασης του ηλεκτροχημικού συστήματος, έτσι ώστε να γίνεται στη συνέχεια πραγματοποιήσιμη μία συνεχής αντιστάθμιση της πτώσης τάσης.

~~ΥΠΟΛΟΓΙΣΜΟΣ C_d, R_u ΣΤΟ ΣΥΣΤΗΜΑ Fe^{2+}/Fe^{3+} ΣΕ ΤΕΧΝΗΤΟ ΘΑΛΑΣΣΙΝΟ ΝΕΡΟ~~

Στην προκειμένη μελέτη επιχειρείται για πρώτη φορά, μιά κατά προσέγγιση μέτρηση της "μη αντισταθμιζόμενης" αντίστασης R_u του συστήματος Fe^{2+}/Fe^{3+} σε τεχνητό θαλασσινό νερό ανάμεσα στο ηλεκτρόδιο εργασίας από γραφίτη ή από πλατίνα, και στο ηλεκτρόδιο αναφοράς επιβάλλοντας κάποια επιλεγμένη τιμή δυναμικού συνεχούς ρεύματος σε περιοχή στην οποία δεν εξελίσσεται η ηλεκτροχημική δράση που μελετάται, (το ρεύμα που ρέει διά μέσου των ηλεκτροδίων στην περίπτωση αυτή έχει πολύ μικρή τιμή.) Η προσεγγιστική αυτή "εφ' άπαξ" καταγραφή της αντίστασης κρίνεται στην παρούσα φάση απαραίτητη, δεδομένου ότι η τιμή της R_u μεταβάλλεται χρονικά κατά την διάρκεια της πραγματοποίησης μιάς ηλεκτροχημικής δράσης με αποτέλεσμα η συνεχής μέτρησή της να γίνεται ουσιαστικά προβληματική και εξαιρετικά δύσκολη.

Εφ' όσον η τιμή της αντίστασης R_u γίνει γνωστή, η πτώση τάσης είναι δυνατόν να διορθώνεται σε κάθε χρονική στιγμή με κατάλληλη θετική αντιστάθμιση IR_u στην τιμή της επιβαλλόμενης σάρωσης του δυναμικού. Η τιμή της χωρητικότητας C_d της ηλεκτροχημικής διπλοστοιβάδας υπολογίζεται συγχρόνως στο ίδιο σύστημα.

II. ΒΑΣΙΚΕΣ ΘΕΩΡΗΤΙΚΕΣ ΑΡΧΕΣ

Η πτώση τάσης IR επηρεάζει τα ποσοτικά αποτελέσματα της μεθόδου της τριγωνικής βολταμπερομετρίας τόσο περισσότερο όσο μεγαλύτερη είναι η απόλυτη τιμή της πυκνότητας του ρεύματος κορυφής i_p άρα και της ταχύτητας σάρωσης του δυναμικού v δεδομένου ότι $i_p = f(v^{1/2})$.

Η πυκνότητα του ρεύματος κορυφής i_p που μετρείται πειραματικά είναι μικρότερη σε απόλυτη τιμή της θεωρητικά υπολογιζόμενης και η τάση E που μετρείται πειραματικά είναι μικρότερη της επιβαλλόμενης σε μιά αναγωγική διαδικασία ενώ είναι μεγαλύτερη σε μιά οξειδωτική διαδικασία. Ετσι, για μιά θεωρητικά επιβαλλόμενη ταχύτητα σάρωσης v , η ταχύτητα που επιτυγχάνεται τελικά λόγω της επίδρασης της πτώσης τάσης, είναι μικρότερη εκείνης που θα είχαμε χωρίς την πτώση τάσης στην ανερχόμενη πλευρά της κορυφής ενώ αντίθετα είναι μεγαλύτερη στην κατερχόμενη πλευρά^{1,2}.

Οι βολταμπερομετρικές μετρήσεις κρίνονται αποδεκτές όταν η πτώση τάσης δεν υπερβαίνει τα 0,01V για μία πειραματικά παρατηρούμενη διαφορά τάσης μεταξύ της τιμής της αρχής της καμπύλης της κορυφής E_f και εκείνης της κορυφής της E_p , ίση με $0,1V^{1,2}$.

Χρησιμοποιώντας την πειραματική διάταξη των τριών ηλεκτροδίων (εργασίας-αναφοράς-βοηθητικού) η αντίσταση R_R ανάμεσα στο ηλεκτρόδιο αναφοράς και στο βοηθητικό ηλεκτρόδιο δεν αποτελεί πηγή σφαλμάτων.

Ωστόσο, η αντίσταση ανάμεσα στο ηλεκτρόδιο αναφοράς και στο ηλεκτρόδιο εργασίας R_u , παραμένει πάντα χωρίς αντιστάθμιση ακόμα και αν δεν πραγματοποιείται ηλεκτροχημική δράση με ανταλλαγή ηλεκτρικών φορτίων (Σχήμα 1).

Η προτεινόμενη αντισταθμιστική μέθοδος διόρθωσης¹³ βασίζεται στην επιβολή τετραγωνικού παλμού δυναμικού 10-300mV με συχνότητα 1KHz στο ηλεκτρόδιο εργασίας και σύγχρονη παρακολούθηση της απόκρισης της μεταβολής του ρεύματος I σε συνάρτηση με το χρόνο t .

Όπως αναφέρθηκε (§I), η τιμή του δυναμικού του ηλεκτροδίου εργασίας εκλέγεται κατάλληλα, έτσι ώστε στην τιμή αυτή να μην πραγματοποιούνται ανταλλαγές ηλεκτρικών φορτίων (δράσεις Faraday).

Η απόκριση του ηλεκτροδίου εργασίας χαρακτηρίζεται από την ικανότητά του να ακολουθήσει τον επιβαλλόμενο τετραγωνικό παλμό και είναι συνάρτηση της αντίστασης R_u και της χωρητικότητας C_d της ηλεκτροχημικής διπλοστοιβάδας του ηλεκτροδίου εργασίας. Το γινόμενο $R_u \cdot C_d$ χαρακτηρίζει την ταχύτητα απόκρισης του ηλεκτροδίου εργασίας και εκφράζεται σε μονάδες χρόνου (t). Αποτελεί την σταθερά χρόνου του ηλεκτρολυτικού κελλιού και υποδεικνύει την μικρότερη δυνατή τιμή χρόνου πάνω από την οποία το ηλεκτροχημικό σύστημα είναι δυνατόν να δεχθεί κάποια υπολογίσιμη μεταβολή (Σχήμα 2).

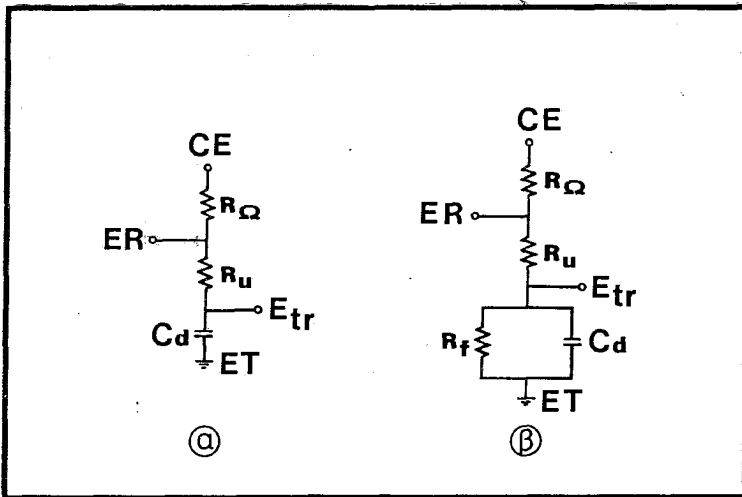
Εχει αποδειχθεί πειραματικά ότι η διεπιφάνεια ηλεκτροδίου εργασίας/ηλεκτρολύτη συμπεριφέρεται ως ένας πυκνωτής χωρητικότητας C_d .

Το επιβαλλόμενο δυναμικό E σε κάθε χρονική στιγμή ισούται με το άθροισμα του δυναμικού στα άκρα του πυκνωτή E_c και του δυναμικού στα άκρα της αντίστασης R_u , E_R (Σχήμα 1(a)).

$$E = E_R + E_c \quad (1)$$

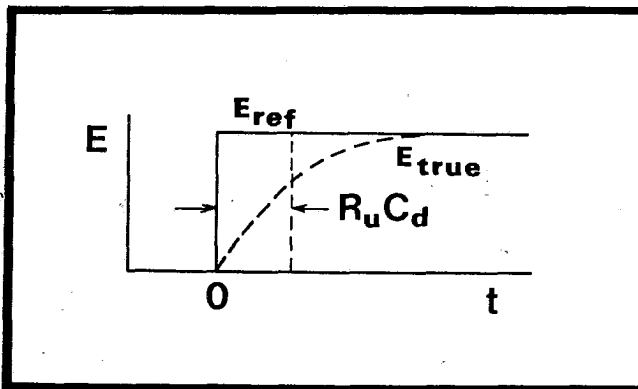
$$E_c = q / C_d \quad (2)$$

ΑΠΟΛΟΓΙΣΜΟΣ C_d, R_u ΣΤΟ ΣΥΣΤΗΜΑ Fe^{2+}/Fe^{3+} ΣΕ ΤΕΧΝΗΤΟ ΘΑΛΑΣΣΙΝΟ ΝΕΡΟ



ΣΧΗΜΑ 1. Απλή σχηματική παράσταση (α) : ενός συστήματος τριών ηλεκτροδίων χωρίς να πραγματοποιείται ηλεκτροχημική δράση. Συνολική αντίσταση του συστήματος: $R_{\Omega} + R_u$ και (β) : ενός συστήματος όπου εξελίσσεται ηλεκτροχημική δράση. Ρεύματα "Faraday" διέρχονται διά μέσου της αντίστασης R_f και άλλα ρεύματα (όχι "Faraday") διά μέσου της ηλεκτροχημικής διπλοστοιβάδας χωρητικότητας C_d . Συνολική αντίσταση του συστήματος $R_{\Omega} + R_u + R_f$.

R_f : συμβολική αντίσταση της πραγματοποιούμενης ηλεκτροχημικής δράσης, ET : ηλεκτρόδιο εργασίας, ER : ηλεκτρόδιο αναφοράς, CE : βοηθητικό ηλεκτρόδιο, E_{tr} : δυναμικό.



ΣΧΗΜΑ 2. Σχηματική παράσταση της επίδρασης της σταθεράς χρόνου του κελλιού στην πραγματικά επιβαλλόμενη τιμή του δυναμικού στο ηλεκτρόδιο εργασίας. $E_{true} = E_{ref}(1 - \exp(-t/R_u C_d))$ (ίδια Σχήμα 1).

Δεδομένου ότι ισχύει η σχέση (2), αντικαθιστώντας την τιμή των E_c και $E_R = IR_u$ έχουμε ότι:

$$E = IR_u + q/C_d \quad (3)$$

Δεδομένου επίσης ότι $dq = Idt$, η εξίσωση (3) μετασχηματίζεται στην παρακάτω εξίσωση (4), η οποία έχει σαν λύση τη σχέση (5):

$$\frac{dq}{dt} = \frac{q}{R_u C_d} + \frac{E}{R_u} \quad (4)$$

$$q = EC_d [1 - \exp(-t/R_u C_d)] \quad (5)$$

Διαφορίζοντας στη συνέχεια τη σχέση (5), αποκτούμε τη σχέση (6), που εκφράζει την απόκριση του ηλεκτροδίου εργασίας, στον επιβαλλόμενο παλμό του δυναμικού (Σχήμα 3):

$$I = \frac{E}{R_u} \exp\left(\frac{-t}{R_u C_d}\right) \quad (6)$$

Κάθε φορά που επιβάλλεται κάποιος παλμός δυναμικού στο ηλεκτρόδιο εργασίας η ύπαρξη της αντίστασης R_u προκαλεί κάποια μείωση του θεωρητικά επιβαλλόμενου παλμού κατά το μέγεθος IR_u .

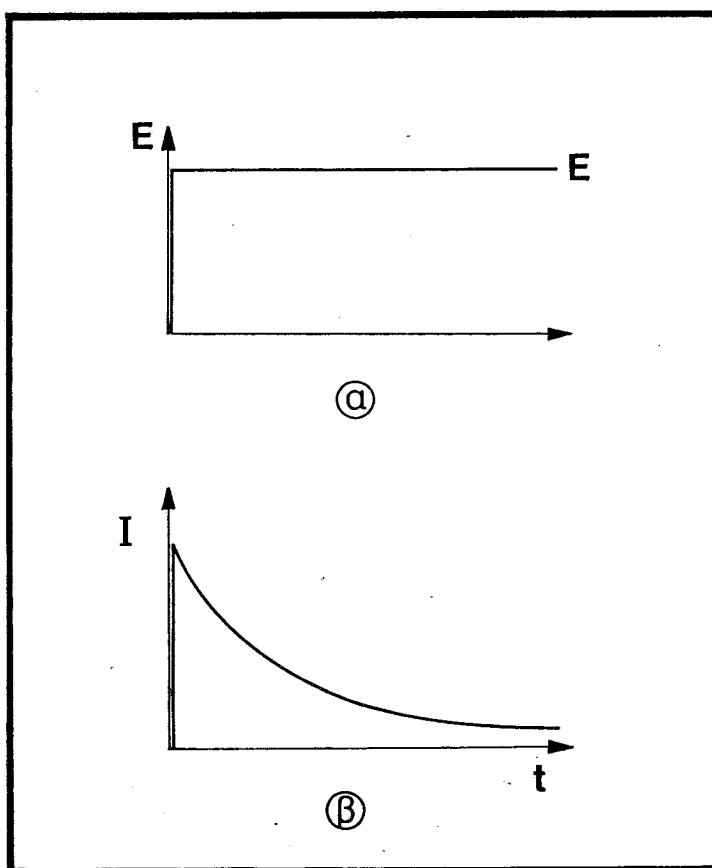
Στην πραγματικότητα με τη βοήθεια ειδικού ποτενσιόμετρου του ποτενσιοστάτη επιλέγουμε, αυξάνοντας συνεχώς το ποσοστό f της αντισταθμιστικής αντίστασης R_f , fR_f , κατάλληλη τιμή του δυναμικού αντιστάθμισης ifR_f έτσι ώστε αυτό να γίνει θεωρητικά ίσο σε απόλυτη τιμή με το μέγεθος iR_u . Με τη μέθοδο αυτή είναι δυνατόν να επιτύχουμε άλλοτε "υπερ-αντιστάθμιση" άλλοτε "υπό-αντιστάθμιση" δεδομένου ότι είναι εξαιρετικά δύσκολο -αν όχι αδύνατο- να επιτύχουμε πλήρη αντιστάθμιση.

Η αντισταθμιστική αυτή τάση προστίθεται με τη βοήθεια κατάλληλα κατασκευασμένου ηλεκτρονικού κυκλώματος του ποτενσιοστάτη και φέρνει το ηλεκτρόδιο εργασίας σε δυναμικό μεγαλύτερο του θεωρητικά

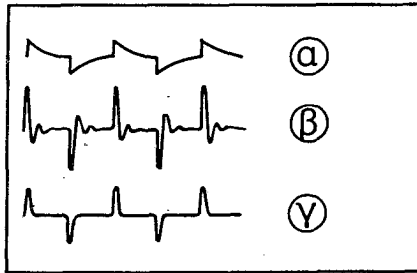
~~ΠΟΛΩΣΙΜΟΣ C_d, R_u ΣΤΟ ΣΥΣΤΗΜΑ Fe^{2+}/Fe^{3+} ΣΕ ΤΕΧΝΗΤΟ ΘΑΛΑΣΣΙΝΟ ΝΕΡΟ~~

επιβαλλόμενου, έτσι ώστε η φόρτιση της ηλεκτροχημικής διπλοστοιβάδας χωρητικότητας C_d να γίνεται γρήγορα.

Όσο η επιβαλλόμενη αντισταθμιστική τάση αυξάνεται η απόκριση του ηλεκτροδίου εργασίας γίνεται ταχύτερη και το πλάτος της έντασης I μεγαλύτερο για τον ίδιο χρόνο, όπως φαίνεται και από την μαθηματική έκφραση της απόκρισης $I-t$ της σχέσης (6) (Σχήμα 4).



ΣΧΗΜΑ 3. Σχηματική παράσταση της χρονικής μεταβολής της έντασης του ρεύματος πυκνωτή $I-t$ (β) όταν επιβάλλομε μία σταθερή τιμή δυναμικού E για χρόνο t (α).



ΣΧΗΜΑ 4. Μορφή της απόκρισης I-t του ηλεκτρόδιου εργασίας κατά τη διάρκεια της αντισταθμιστικής διαδικασίας για την διόρθωση της πτώσης τάσης IR_u . (α): αργή απόκριση, (β): "υπεραντιστάθμιση", υπερβολικά γρήγορη απόκριση, ταλαντώσεις, (γ): σωστή αντιστάθμιση, γρήγορη απόκριση.

Υπερβολική αντισταθμιστική τάση προκαλεί ταλαντώσεις του συστήματος. Κρίνεται λοιπόν σκόπιμο να ελαττώνεται η τιμή της επιβαλλόμενης αντισταθμιστικής τάσης κατά 10-20% της τιμής για την οποία παρατηρούνται οι ταλαντώσεις^{2,8}. Η σωστή μορφή της απόκρισης φαίνεται στην περίπτωση (γ) του Σχήματος 4.

III. ΠΕΙΡΑΜΑΤΙΚΕΣ ΣΥΝΘΗΚΕΣ

Οι πειραματικές συνθήκες της εργαστηριακής αυτής μελέτης έχουν ήδη περιγραφεί αναλυτικά σε προηγούμενη εργασία¹⁴.

Στην προκείμενη περίπτωση χρησιμοποιήθηκαν ηλεκτρόδια εργασίας από καθαρό λευκόχρυσο, Pt, ($\phi:0,5\text{mm}$, $S_{Pt}=0,143\text{cm}^2$) και καθαρό γραφίτη TFA ($\phi:1\text{mm}$, $S_{\text{γραφίτη}}=0,259\text{cm}^2$).

Η απόκριση του ηλεκτρόδιου εργασίας, I-t, πάρθηκε σε παλμογράφο TEKTRONIX 5223 με ψηφιακή μνήμη και φωτογραφήθηκε κατ' ευθείαν από την οθόνη του.

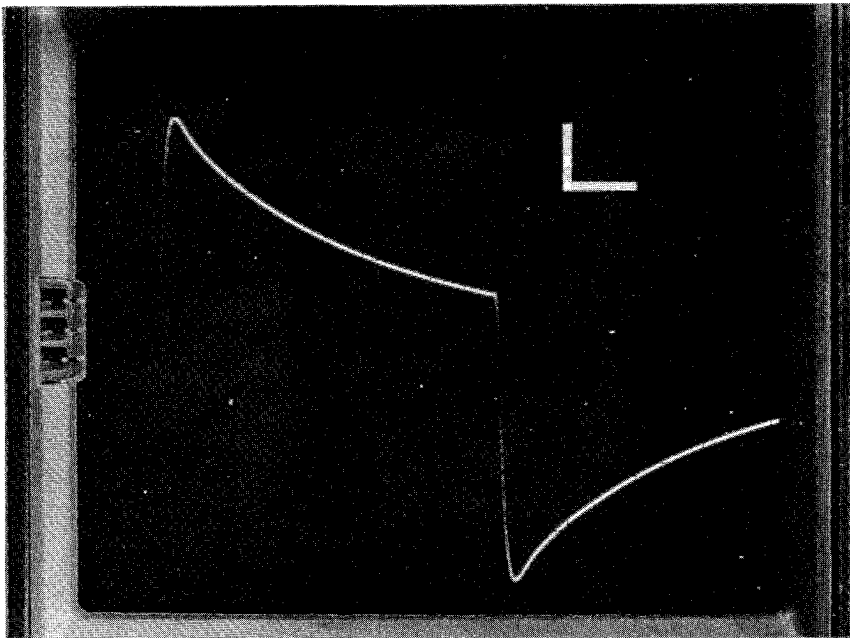
Η αντισταθμιστική τάση IR_u επιβλήθηκε με τη βοήθεια ειδικής ηλεκτρονικής διάταξης του "Model 376, Logarithmic Current Converter της PAR.

IV. ΑΠΟΤΕΛΕΣΜΑΤΑ - ΣΥΖΗΤΗΣΗ

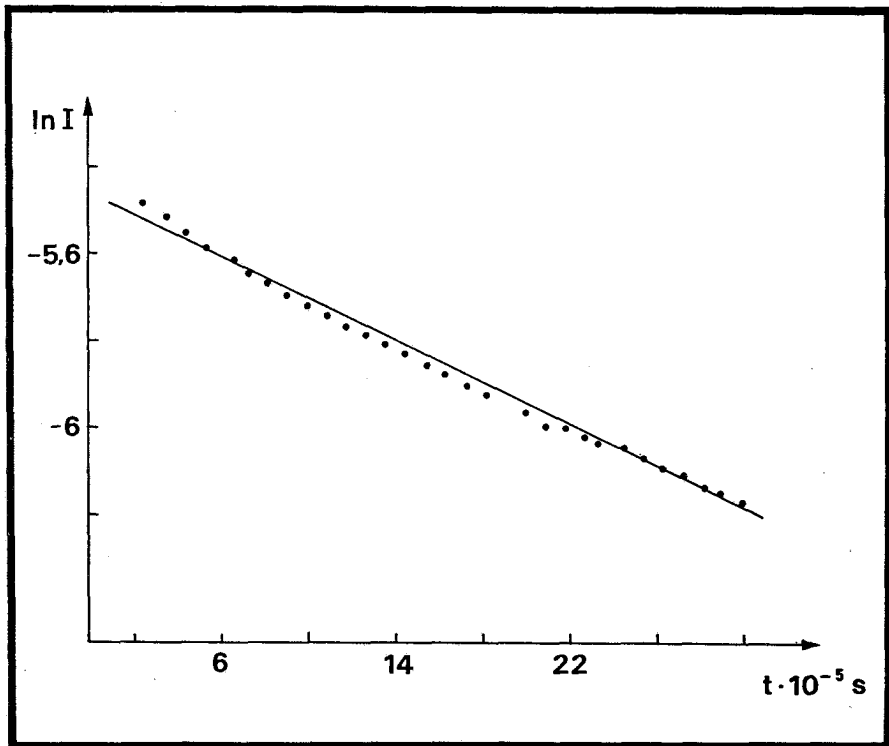
Στο Σχήμα 5 παρουσιάζεται η απόκριση ενός ηλεκτρόδιου εργασίας από γραφίτη TFA, όταν επιβάλλεται σε αυτό ένας τετραγωνικός παλμός δυναμικού πλάτους 60mV και συχνότητας 1KHz.

Μετασχηματίζοντας τη σχέση (6) έχουμε:

$$\ln I = \ln \frac{E}{R_u} - \frac{t}{R_u C_d} \quad (7)$$



ΣΧΗΜΑ 5. Απόκριση $I-t$ ενός ηλεκτρόδιου εργασίας από γραφίτη ($S_{\text{γραφίτη}}: 0,259 \text{ cm}^2$), όταν επιβάλλεται σε αυτό ένας παλμός δυναμικού $E=60 \text{ mV}$ και συχνότητας 1KHz, σε σύστημα τεχνητού θαλασσινού νερού + $FeCl_3 \cdot 6H_2O$ ($C [FeCl_3 \cdot 6H_2O] = 58,9 \cdot 10^{-3} \text{ mole/l}$). Αξονες $X=0,1 \text{ ms/υποδ.}$, $Y=0,001 \text{ A/υποδ.}$



ΣΧΗΜΑ 6. Μελέτη της συνάρτησης $\ln I=f(t)$ που αναφέρεται στις πειραματικές συνθήκες του Σχήματος 5.

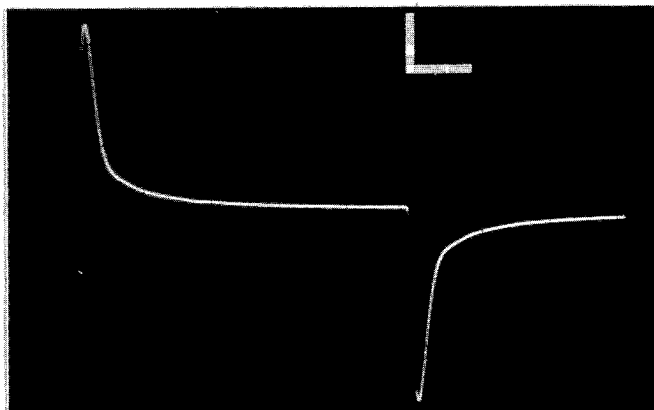
Η μεταβολή $I=f(t)$ είναι γραμμική (Σχήμα 6). Η κλίση της ευθείας αυτής μας δίνει την τιμή $-(1/R_u C_d)$ η δε αποτέμνουσα για $t=0$ την ποσότητα $\ln(E/R_u)$. Με τον τρόπο αυτό υπολογίζονται συγχρόνως η τιμή της αντίστασης R_u και η χωρητικότητα της ηλεκτροχημικής διπλοστοιβάδας C_d .

Έτσι βρέθηκε ότι:

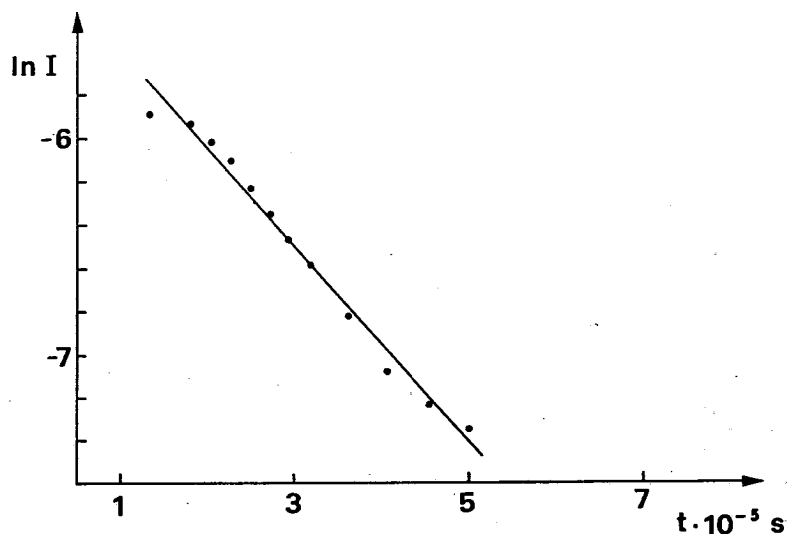
$$R_u = 14,1 \Omega \quad \text{και} \quad C_d = 111,9 \cdot 10^{-6} \text{ F/cm}^2.$$

Εάν χρησιμοποιήσουμε ένα ηλεκτρόδιο εργασίας από πλατίνα, Pt, η απόκριση $I-t$ του ηλεκτροδίου αυτού στον ίδιο παλμό δυναμικού παρουσιάζεται στο Σχήμα 7 και η μελέτη της μεταβολής $\ln I=f(t)$ στο Σχήμα 8.

Στην περίπτωση αυτή $R_u = 10,2 \Omega$ και $C_d = 15,0 \cdot 10^{-6} \text{ F/cm}^2$.



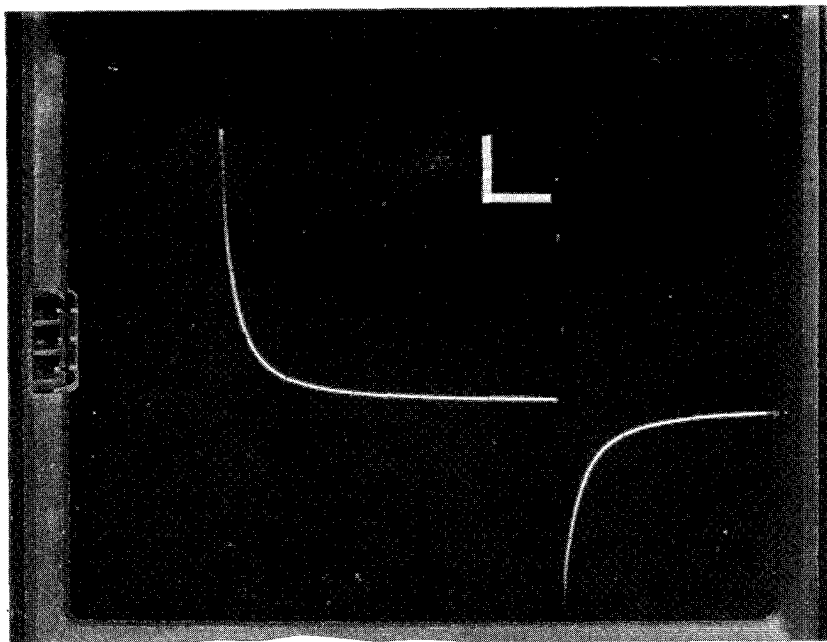
ΣΧΗΜΑ 7. Απόκριση $I-t$ ενός ηλεκτροδίου εργασίας από πλατίνα, Pt, ($S_{Pt}=0,143cm^2$), όταν επιβάλλεται σε αυτό ένας παλμός δυναμικού $E=60mV$ και συχνότητας $1kHz$ σε σύστημα τεχνητού θαλασσινού νερού + $FeCl_3 \cdot 6H_2O$ [$C^{\circ}(FeCl_3 \cdot 6H_2O) = 58,9 \cdot 10^{-3} mole/l$]. Αξονες $\chi=0,1ms/υποδ.$, $\gamma=0,001A/υποδ.$



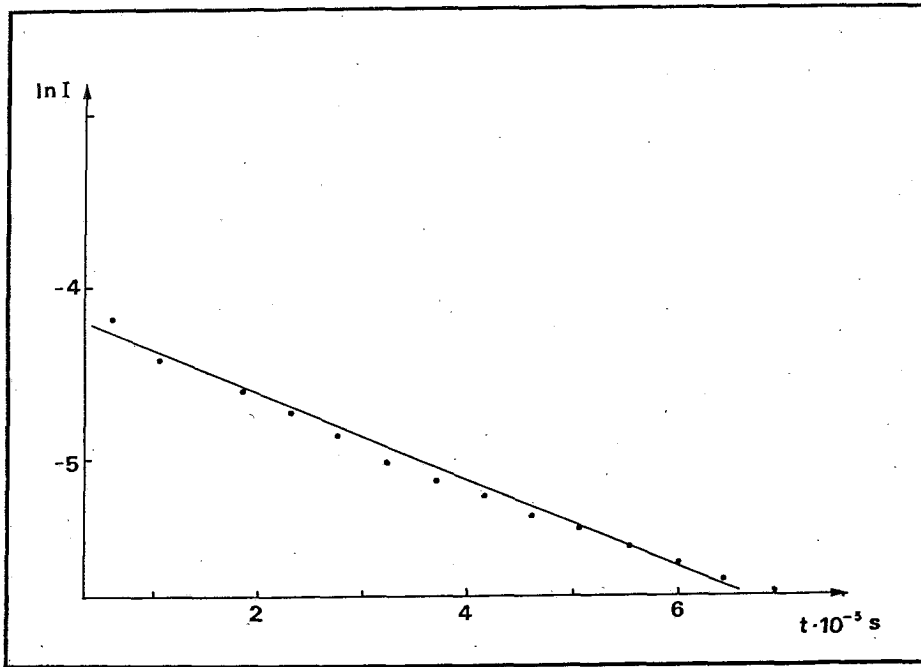
ΣΧΗΜΑ 8. Μελέτη της συνάρτησης $\ln I=f(t)$ που αναφέρεται στις πειραματικές συνθήκες του Σχήματος 7.

Ωστόσο εάν επιβάλλομε στο ίδιο ηλεκτρόδιο εργασίας από πλατίνα ένα παλμό μεγαλύτερου πλάτους $E=300\text{mV}$ της ίδιας όμως συχνότητας 1KHz η απόκριση του ηλεκτροδίου εργασίας $I-t$ παρουσιάζεται στο Σχήμα 9 η δε μελέτη της συνάρτησης $\ln I=f(t)$ στο Σχήμα 10.

Από την κλίση της ευθείας που προέκυψε υπολογίζεται η τιμή της χωρητικότητας $C_d = 15,0 \cdot 10^{-6} \text{ F/cm}^2$. Οι τιμές της χωρητικότητας C_d που υπολογίσθηκαν τόσο σε γραφίτη όσο και σε πλατίνα βρίσκονται μέσα στα όρια των τιμών που δίνονται στη βιβλιογραφία². Ωστόσο η τιμή της χωρητικότητας που υπολογίσθηκε σε γραφίτη πιθανόν να υποδηλώνει κάποιο φαινόμενο προσρόφησης πάνω στο ηλεκτρόδιο αυτό.



ΣΧΗΜΑ 9. Απόκριση $I-t$ ενός ηλεκτροδίου εργασίας από πλατίνα, Pt, ($S_{Pt}=0,143\text{cm}^2$), όταν επιβάλλεται σε αυτό ένας παλμός δυναμικού $E=300\text{mV}$ και συχνότητας 1KHz , σε σύστημα τεχνητού θαλασσινού νερού + $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ [$C^\circ(\text{FeCl}_3 \cdot 6\text{H}_2\text{O})$] = $58,9 \cdot 10^{-3} \text{ mol/l}$). Αξονες $X=0,1\text{ms/υποδ.}$, $Y=0,005\text{A/υποδ.}$



ΣΧΗΜΑ 10. Μελέτη της συνάρτησης $\ln I = f(t)$ που αναφέρεται στις πειραματικές συνθήκες του Σχήματος 9.

Παρατηρούμε επίσης ότι οι τιμές των R_u και C_d που μετρήθηκαν χρησιμοποιώντας ένα ηλεκτρόδιο εργασίας από άνθρακα διαφέρουν από τις αντίστοιχες τιμές που υπολογίσθηκαν σε πλατίνα. Αυτό κρίνεται λογικό δεδομένου ότι η τιμή της αντίστασης R_u περιλαμβάνει το σύνολο των παντοειδών αντιστάσεων ανάμεσα στα ηλεκτρόδια εργασίας της πλατίνας και του άνθρακα -των οποίων η φυσικοχημική συμπεριφορά οπωσδήποτε διαφέρει- και του ηλεκτροδίου αναφοράς.

Αντίθετα η μεταβολή του πλάτους του επιβαλλόμενου δυναμικού αφήνει ανεπηρέαστες τις τιμές των C_d που μετρήθηκαν, στην περίπτωση του ηλεκτροδίου της πλατίνας.

Θα πρέπει ωστόσο να σημειωθεί εδώ, ότι οι τιμές των R_u και C_d που υπολογίσθηκαν σε άνθρακα περιέχουν ένα ποσοστό λάθους που οφείλεται

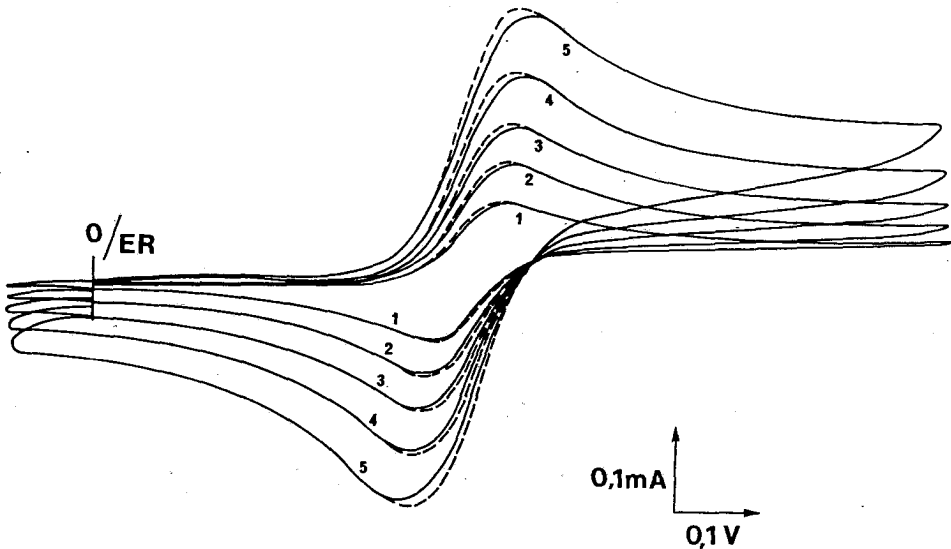
στην διαφορά της φαινόμενης-γεωμετρικής επιφάνειας του ηλεκτροδίου που μετρείται, και της πραγματικής επιφάνειας.

Στο Σχήμα 11 παρουσιάζεται ένα σύνολο βολταμπερομετρικών καμπυλών $E=f(I)$ με ηλεκτρόδιο εργασίας από πλατίνα, σε ηλεκτρολυτικό λουτρό τεχνητού θαλασσινού νερού και αρχικής συγκέντρωσης $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$, $C^\circ \text{FeCl}_2 \cdot 4\text{H}_2\text{O} = 2 \cdot 10^{-2} \text{ mol/l}$ χωρίς διόρθωση και με διόρθωση της πτώσης τάσης. Οι βολταμπερομετρικές αυτές καμπύλες, όπως αυτές μελετήθηκαν σε παλαιότερη εργασία¹⁴ περιγράφουν το αντιστρεπτό οξειδοαναγωγικό σύστημα $\text{Fe}^{2+} - e \rightleftharpoons \text{Fe}^{3+}$ με αριθμό ανταλλασσόμενων ηλεκτρονίων $n=1$.

Η αντιστρεπτότητα του συστήματος αυτού αποδεικνύεται από το γεγονός ότι:

α. η διαφορά $(E_{pa} - E_{pc})_{v=0} = 0,073\text{V}$ πλησιάζει την τιμή $0,0595\text{V}$ (θεωρητικά υπολογισμένη τιμή για $T=25^\circ\text{C}$ και $n=1$)^{1,2,3} και

β. ο λόγος $I_{pa}/I_{pc}=0,95$ (μέση τιμή) πλησιάζει τη μονάδα (θεωρητική τιμή).

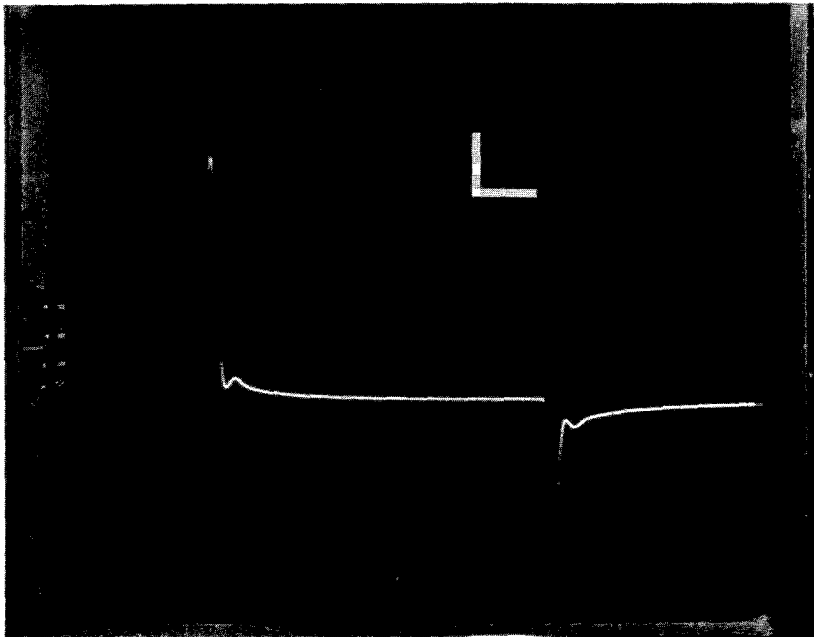


ΣΧΗΜΑ 11. Βολταμπερομετρικές καμπύλες $E=f(I)$ χωρίς διόρθωση (διακεκομμένη γραμμή) και με διόρθωση (συνεχής γραμμή) στο σύστημα: τεχνητό θαλασσινό νερό + $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$, $C^\circ (\text{FeCl}_2 \cdot 4\text{H}_2\text{O}) = 2 \cdot 10^{-2} \text{ mol/l}$. Ηλεκτρόδιο εργασίας: Pt, $T=25^\circ\text{C}$, Ταχύτητα σάρωσης του δυναμικού: (1): $0,02\text{Vs}^{-1}$, (2): $0,05\text{Vs}^{-1}$, (3) $0,1\text{Vs}^{-1}$, (4): $0,2\text{Vs}^{-1}$, (5): $0,4\text{Vs}^{-1}$.

~~ΕΠΙΠΛΟΚΙΣΜΟΣ C_p , R_p ΣΤΟ ΣΥΣΤΗΜΑ Fe^{2+}/Fe^{3+} ΣΕ ΤΕΧΝΗΤΟ ΘΑΛΑΣΣΙΝΟ ΝΕΡΟ~~

Η διόρθωση των βολταμπερομετρικών αυτών καμπυλών επιτεύχθηκε επιβάλλοντας αντισταθμιστική τάση ίση με το 85% της τάσης για την οποία το σύστημα αρχίζει να πάλλεται έτσι ώστε η μορφή της απόκρισης I-t του ηλεκτροδίου εργασίας (Σχήμα 12) να προσεγγίσει εκείνη του Σχήματος 4γ (λιγότερο από την περίπτωση του Σχήματος 7) όπως περιγράφηκε ήδη στην παραγραφο II.

Οι τιμές των E_{pc} , E_{pa} , I_{pc} , I_{pa} καθώς και του λόγου I_{pa}/I_{pc} που προέκυψαν μετά από μέτρηση των μεγεθών αυτών στις διορθωμένες καμπύλες $E=f(I)$, συγκριτικά με εκείνες που προκύπτουν χωρίς διόρθωση, παρουσιάζονται στον Πίνακα I.

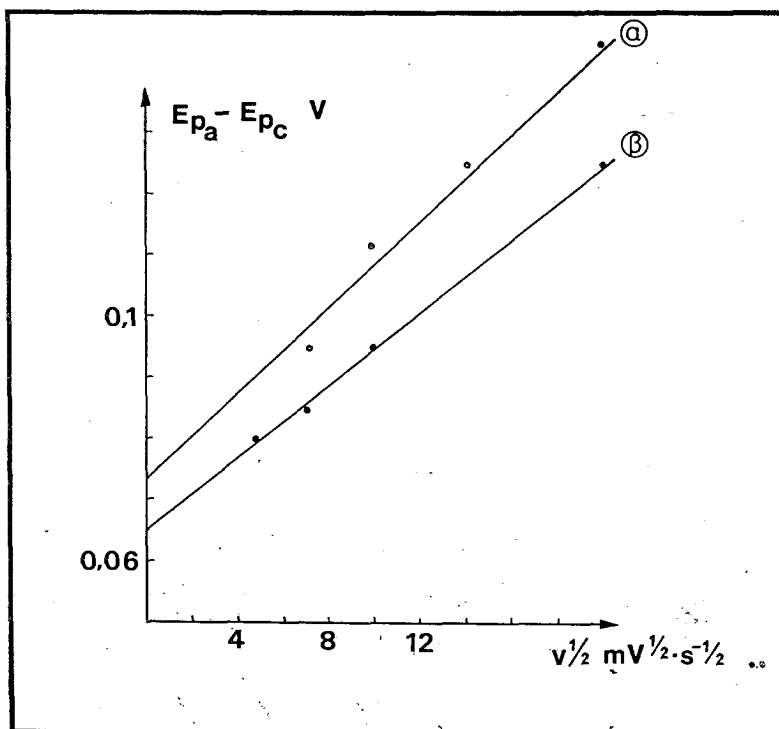


ΣΧΗΜΑ 12. Απόκριση I-t ενός ηλεκτροδίου εργασίας από πλατίνα, Pt, ($S_{Pt}=0,143cm^2$), όταν επιβάλλεται σε αυτό ένας παλμός δυναμικού $E=60mV$ και συχνότητας 1KHz, σε σύστημα τεχνητού θαλασσινού νερού + $FeCl_2 \cdot 4H_2O$ ($C^{\circ}[FeCl_2 \cdot 4H_2O] = 2 \cdot 10^{-2} mole/l$). Με τη βοήθεια της αντισταθμιστικής διάταξης του Model 376 "Logarithmic Current Converter" έχει επιβληθεί η κρίσιμη τιμή ifR_f του σωστού δυναμικού αντιστάθμισης.

ΠΙΝΑΚΑΣ Ι. Τιμές των μεγεθών E_{pa} , E_{pc} , I_{pa} , I_{pc} και του λόγου I_{pa}/I_{pc} που αντιστοιχούν στις καμπύλες $E=f(I)$ του Σχήματος ΙΙ χωρίς διόρθωση και με διόρθωση της πτώσης τάσης.

Χωρίς διόρθωση						Με διόρθωση				
v $mV \cdot s^{-1}$	E_{pc}, V	E_{pa}, V	I_{pc}, mA	I_{pa}, mA	I_{pa}/I_{pc}	E_{pc}, V	E_{pa}, V	I_{pc}, mA	I_{pa}, mA	I_{pa}/I_{pc}
20	0,400	0,480	0,100	0,095	0,930	0,400	0,480	0,1025	0,100	0,975
50	0,390	0,485	0,145	0,140	0,965	0,395	0,480	0,148	0,143	0,966
100	0,380	0,492	0,185	0,175	0,945	0,390	0,485	0,193	0,190	0,984
200	0,375	0,500	0,240	0,220	0,916	0,385	0,490	0,253	0,243	0,960
400	0,365	0,510	0,295	0,290	0,983	0,375	0,500	0,325	0,310	0,960

ΥΠΟΛΟΓΙΣΜΟΣ C_d, R_u ΣΤΟ ΣΥΣΤΗΜΑ Fe^{2+}/Fe^{3+} ΣΕ ΤΕΧΝΗΤΟ ΘΑΛΑΣΣΙΝΟ ΝΕΡΟ



ΣΧΗΜΑ 13. Μελέτη της συνάρτησης $E_{DC} - E_{pa} = f(v^{1/2})$ στο σύστημα τεχνητό θαλασσινό νερό + $FeCl_2 \cdot 4H_2O$ [$C^\circ(FeCl_2 \cdot 4H_2O)$] = $2 \cdot 10^{-2}$ mole/l). Ηλεκτρόδιο εργασίας : Pt, $T = 25^\circ C$.

Καμπύλη (α): χωρίς διόρθωση, $(E_{pa} - E_{DC})_{v=0} = 0,073V$, $n=0,81$

Καμπύλη (β): με διόρθωση, $(E_{pa} - E_{DC})_{v=0} = 0,065V$, $n=0,91$.

Στο Σχήμα 13 παρουσιάζεται επίσης η μελέτη της μεταβολής της συνάρτησης $E_{pa} - E_{pc} = f(v^{1/2})$ για τις διορθωμένες και μη βολταμπερομετρικές καμπύλες του Σχήματος 11. $(E_{pa} - E_{pc})_{v=0} = 0,065V$ στις καμπύλες $E=f(I)$ όταν έχει επιβληθεί η σωστή αντισταθμιστική τάση απ' όπου προκύπτει ότι ο αριθμός των ανταλλασσόμενων ηλεκτρονίων $n=0,91$, (χωρίς αντιστάθμιση $(E_{pa} - E_{pc})_{v=0} = 0,073$ και $n=0,81$). Συγχρόνως η μέση τιμή του λόγου $I_{pa}/I_{pc} = 0,97$ πλησιάζει περισσότερο στη μονάδα στις ίδιες καμπύλες $E=f(I)$.

Από το σύνολο των πειραματικών παρατηρήσεων που παρουσιάστηκαν παραπάνω γίνεται προφανής η σημασία της πειραματικής αντιστάθμισης της πτώσης τάσης των βολταμπερομετρικών καμπυλών $E=f(I)$ δεδομένου ότι επιτρέπει την ποσοτική εκμετάλλευση των αποτελεσμάτων και κατ'

επέκταση τη σωστή ερμηνεία της κινητικής των ηλεκτροχημικών αντιδράσεων ή πολυπλοκώτερων ηλεκτροχημικών συστημάτων.

SUMMARY

CALCULATION OF THE ELECTROCHEMICAL DOUBLE-LAYER CAPACITY C_d AND OF THE UNCOMPENSATED RESISTANCE R_u IN THE SYSTEM Fe^{2+}/Fe^{3+} INTO ARTIFICIAL SEA WATER.

YANNIS CHRYSOULAKIS, STELLA MARKANTONATOU

Section III Material Science, Department of Chemical Engineering, National Technical University of Athens, 9 Iroon Polytechniou str., Zografou Campus, Athens 15773

In the present study the value of the uncompensated resistance R_u on a graphite and platinum electrodes has been calculated by applying a rectangular pulse of 60mV potential E and 1KHz frequency and measuring the response in current I versus time t .

The variation $I=f(t)$ is linear and can be described by the equation:

$$\ln I = \ln \frac{E}{R_u} - \frac{t}{R_u C_d}$$

where C_d is the value of the double-layer capacity.

From the slope and the abscissa at $t=0$ of the graph of the above equation, the values of R_u and C_d were calculated and found to be $R_u=14,1\Omega$ and $C_d=111,9 \cdot 10^{-6} \text{ F/cm}^2$ on the graphite electrode and $R_u=10,2\Omega$ and $C_d=15,0 \cdot 10^{-6} \text{ F/cm}^2$ on the platinum one.

The values of R_u and C_d on a carbon working electrode differ from these on platinum. In contrast the variation of the amplitude of the

ΥΠΟΛΟΓΙΣΜΟΣ C_d, R_u ΣΤΟ ΣΥΣΤΗΜΑ Fe^{2+}/Fe^{3+} ΣΕ ΤΕΧΝΗΤΟ ΘΑΛΑΣΣΙΝΟ ΝΕΡΟ

applied potential has no influence on the C_d values on the platinum electrode.

We have also applied a method for the ohmic drop compensation of the system Fe^{2+}/Fe^{3+} in sea water at ambient temperature using triangular voltamperometry on graphite or platinum working electrodes.

The voltamperometric curves $E(I)$ were corrected and the values of the function $(E_{pc} - E_{pa})_{v=0} = f(v^{1/2})$, $I_{pa}/I_{pc} = f(v^{1/2})$ now approach more the corresponding theoretical ones.

Using a potentiometer we have selected the correct portion iR_f of the compensating resistance R_f , so that the added compensating potential iR_f approaches as close as possible the absolute value of the product iR_u that corresponds to the observed ohmic drop.

Key Words: C_d , R_u measurements, R_u compensation

ΒΙΒΛΙΟΓΡΑΦΙΑ

1. ΧΡΥΣΟΥΛΑΚΗΣ Ι., *Σύγχρονες Μέθοδοι Διερεύνησης των Ηλεκτροχημικών Αντιδράσεων*, Έκδοση Ε.Μ.Π., Αθήνα 1982
2. BARD A.J., FAULKNER L.R., *Electrochemical Methods, Fundamentals and Applications*, John Wiley and Sons 429, 596 (1980)
3. ΜΑΡΚΑΝΤΩΝΑΤΟΥ Σ., Διπλωματική εργασία Ε.Μ.Π., Αθήνα 1983
4. VRIES W.T., VAN DALEN E., *J.Electroanal.Chem* **10**, 183 (1965)
5. DEVAY J., LENGYEL B., MESZAROS L., *Acta Chim.Acad.Sci. Hung.* **66**, 269 (1970)
6. WHINSTON P.E., VANDENBORN H.W., EVANS D.H., *Anal.Chem.* **45**, 8, 1298 (1973)
7. YARNITZKY C., FRIEDMAN Y., *Anal.Chem.*, **47**, 6, 876 (1975)
8. BRITZ D., BRÖCKE W.A., *J.Electroanal.Chem.*, **58**, 301 (1975)
9. SMITH D.E., *Crit.Rev.Anal.Chem.*, **2**, 247 (1971)
10. HARRAR J.E., POMERNAKKI C.L., *Anal.Chem.*, **35**, 47 (1973)
11. BRITZ D., *J.Electroanal.Chem.*, **88**, 309 (1978)
12. DELAHAY P., *New Instrumental Methods in Electrochemistry*, Interscience Pub. Inc., New York (1954)
13. PAR, Model 376 Logarithmic Current Converter, *Operating and Service Manual III*, 2 (1979)
14. CHRYSOULAKIS Y. ALEXOPOULOS I., *Metaux-Corrosion-Industrie*, N°699-700, 3 (Nov-Dec 1983)

APPLICABILITY OF ELECTROLYTIC FLOTATION FOR THE RECOVERY OF CARBONATE FINES

K.A. MATIS, G.P. GALLIOS and G.A. STALIDIS

*Laboratory of General and Inorganic Chemical Technology (114),
Aristotle University of Thessaloniki*

(Received July 9, 1986)

SUMMARY

Electrolytic flotation, which is characterised by the generation of fine gas bubbles, has been applied in this study for the recovery of magnesite and dolomite fine particles. After a brief introduction in the fines problem, the flotation generally of salt-type minerals is reviewed, as it is believed that has attracted rather little attention in comparison with sulphides, oxides and silicate systems. The different physicochemical properties relevant to flotation are covered. The separation of this group of minerals from each other is extremely difficult, due to similar flotation responses, so for obtaining selectivity modifiers were used. Such agents, tried to samples of the individual pure minerals and artificial mixtures of them were carboxymethylcellulose, sodium hexametaphosphate, sodium fluorosilicate and sodium pyrophosphate.

Key Words: Electrolytic flotation, fines, dolomite, magnesite, modifiers, recovery.

INTRODUCTION

The Fines Problem

Mineral processing approaches a crossroads nowadays, as the demand for minerals is continuing, while the grade of ores diminishes. For the recovery of fine mineral particles, in order to avoid losses of values, considerable interest is growing in developing new processes and improving old ones. Any new processing method to treat fine particles has to meet at the same time the present day environmental and economic constraints.

Fines are produced as a result of liberation and also in other cases, as an unavoidable by-product during mining, grinding or classification¹. There are many examples of ores that consist mostly of fines.

Flotation, of course, is one of the important unit operations in mineral processing; but the application of conventional separation methods,

as froth flotation, is generally uneconomical. Many of the effects of particle size on flotation recovery in industrial concentrators of copper, lead and zinc were at first shown by Gaudin².

The observed size ranges of maximum flotation recovery varies a lot; for instance, the following figures were tabulated by Fuerstenau³: at industrial scale, 50-150 μm for fluorite, 20-100 μm for galena 3-20 μm for cassiterite, 15-100 μm for sphalerite and at laboratory scale, 10-30 μm for barite, 40-110 μm for fluorite, 170-240 μm for galena, 50-150 μm for pyrite, 9-50 μm for quartz, 20-50 μm for wolframite, etc.

Examining the role of particle and bubble size, it was suggested that attachment of particles to bubbles depends on the relative dimensions of them⁴. Volkova⁴, examining the floatability of calcite by oleic acid, observed that mineralization occurred for smaller bubbles with finer particles, while larger grains were floated by a group of bubbles. With further addition of collector, flotation of particles of a given size was possible by much smaller bubbles.

Following this study, Eigeles insisted in an optimum relationship between the diameter of the air bubble and particle⁴. Similar conclusions were reached, rather empirically in water, and wastewater engineering, where the particle size is usually of colloidal size. Certainly, there are differences between the fields of wastewater engineering and mineral processing, however, the particle size presents a similarity when processing fines.

So, going to the fine size range, the idea was to reduce the bubble size and expect better flotation behaviour. With the same reasoning, another effort was to increase the size of particles by flocculation and then flotation, a method applied already successfully in practice to taconites (iron-bearing materials)⁵. Nevertheless, flocculation/flotation suffers from the obvious disadvantage that it is difficult to be a selective process, as required in such operations when trying to concentrate the valuable minerals and avoid the gangue.

In practice, it is not easy to reduce bubble size without affecting other variables in the system. Perhaps, it is for this reason that the published studies concerning the effect of bubble size on the industrial flotation of fine ore pulps are rather limited¹. Although fine bubbles will improve certain aspects of flotation, it follows that no general conclusion can be drawn as to whether or not the use of fine bubbles

ELECTROLYTIC FLOTATION OF CARBONATE FINES

will improve the overall results of any flotation system. In a recent publication of flotation kinetics with fine bubbles, it was said that each system should be studied individually⁶.

Electrolytic Flotation

One of the flotation techniques that are known to produce fine bubbles is electrolytic flotation. The technique was previously reviewed^{7,8}. In the latter, the application to effluent treatment was covered and mainly for the industrial oil wastes. Scope of this paper is to examine whether this method is also applicable to recover fines, and the area of carbonate minerals was selected, specifically magnesite and dolomite. The carbonates are considered to belong to the group of salt-type minerals, being of interest to our country. It is noted that the economics of the process at this stage, was not taken into account. Preliminary results were published⁹, while parallel work on dissolved-air flotation has been carried out¹⁰.

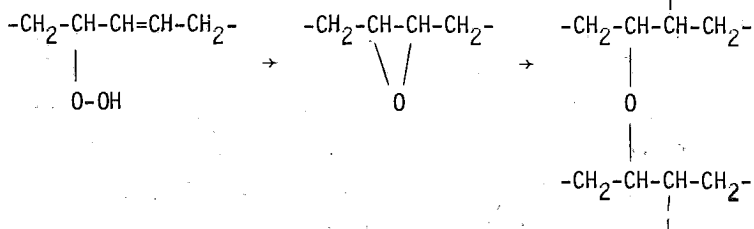
The main work on electrolytic flotation was carried out in the USSR. Little attention was paid in the West, particularly for mineral processing. One of the few exceptions is a study on cassiterite-bearing feed at the Camborne School of Mines¹¹. Glembotskii gave the application to pyrites, manganese and diamond fines, among other¹². It was stated, after comparison with conventional flotation, that the technique brought about additional expenditure for the energy required by electrolysis, but in most cases, this was compensated by:

- a) lowering or complete elimination of collector consumption,
- b) improved flotation rate,
- c) better quality of the concentrate,
- d) utilization of raw materials that could not be beneficiated by any other existing process, and
- e) possibility of complete utilization of raw materials.

A theoretical analysis was presented to describe the deposition of Brownian particles onto hydrogen bubbles under surface interactions¹³. The polystyrene lattices were studied experimentally to examine the effect of the charge on both particles and bubbles on the total collection efficiency. Equations were also derived to describe the kinetics of separation of fine suspensions by electrolytic gases and a procedure was proposed for the calculation of the optimum dimensions of a unit with

ideal displacement and its productivity¹⁴.

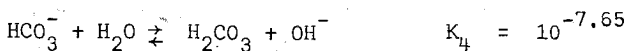
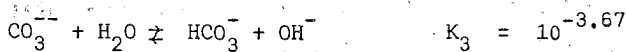
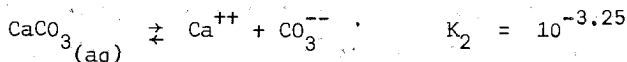
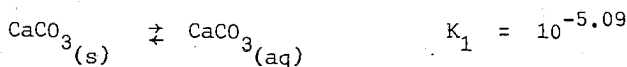
In non-sulphide systems, very often oleic acid is used as the flotation collector, being very effective. The double-bond reactivity of oleate was discussed¹⁵. Some evidence suggested that cross-linking may occur between oleate chains via an epoxide linkage leading to a polymerized layer of collector molecules with greater hydrophobic character, according to the schema¹⁵:



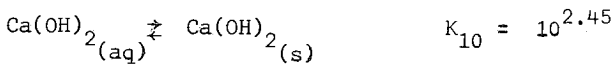
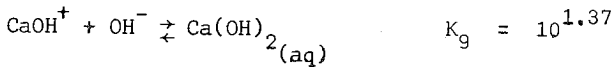
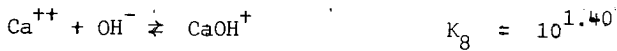
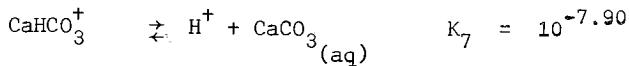
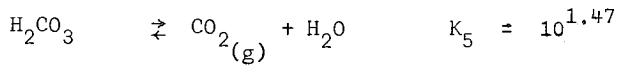
Flotation of Salt-Type Minerals

Salt-type minerals of economic value, like magnesite (also apatite, barite, fluorite, etc.), are associated in nature with silicate minerals, such as quartz and clay, sulphide minerals such as pyrite and other salt-type minerals, such as calcite and dolomite, depending on the origin of the ore deposit. Their separation from other salt-type minerals is extremely complex and often not achieved, particularly if the ores are of microcrystalline type. The minerals in this category are characterised by solubilities, lower than those of simple salt minerals (halite, sulfate), but higher than most oxides and silicates. Certainly, as the particle size is reduced the specific surface becomes larger, which influences their behaviour in many ways, among them, with increased solubility.

For example, calcite dissolves in water with their ions undergoing the following reactions¹⁶:



ELECTROLYTIC FLOTATION OF CARBONATE FINES



Due to the solubility, the mechanisms of surface charge generation for salt-type minerals are basically different from other systems, as it is controlled, in addition to any preferential dissolution of constituent species, by the presence of various complex charged species that result from the hydrolysis reaction that the constituent ion may undergo. By the streaming potential method, it was found a point of zero charge of 6-6.5 for magnesite, and a pH less than 7.0 as isoelectric point for dolomite, given in an excellent review¹⁶.

Adsorption of collectors, their orientation on mineral surfaces and hence the resultant flotation are dependent on a number of factors:

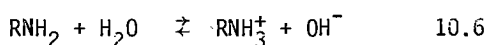
i) surface properties of the mineral, including charge characteristics, chemical composition, and crystal structure; ii) collector characteristics, such as functional groups, chain length and concentration; iii) ionomolecular composition of the aqueous phase, which depends on other relevant solution properties, temperature, pH, ionic strength, and the presence of various dissolved mineral species and their reaction products with each other as well as with collector ions in the solution.

Long chain electrolytes used as collectors for the salt-type minerals possess one or more ionic groups and the role of these polar groups in governing flotation is indeed a major one. The ionic part determines whether the collector is anionic or cationic and whether it is completely or partially ionized. Relevant collectors are fatty acid soaps RCOONa , alkylphosphates RPO_4Na_2 , alkylsulphates RSO_4Na , alkylsulphonates RSO_3Na , amine salts, primary RNH_3Cl , secondary $\text{RNH}_2(\text{CH}_3)\text{Cl}$, tertiary

~~K.A. MATTIS, G.P. GALLIOS, G.A. STALIDIS~~

$\text{RNH}(\text{CH}_3)_2\text{Cl}$ and quaternary ammonium salts $\text{RN}(\text{CH}_3)_3\text{Cl}$; where R is a long chain alkyl group containing eight or more carbon atoms.

In the case of weakly ionizable collectors, which are widely used, it is important to consider their ionomolecular composition and the effect of the composition on the formation of insoluble salts or ionomolecular complexes. Fatty acids and amines undergo dissociation



and the resulting ions form insoluble salts with multivalent metal ions. Solubility data for collector metal salts, even though important for a proper understanding of flotation, are not easily available for all the collector systems¹⁶.

The presence of inorganic species other than the mineral constituents will also affect the flotation properties in a number of ways. In the case of calcite and apatite, H^+ and OH^- as well as all the products of hydrolysis of the constituent ions have been shown to be potential determining. In addition, fluoride in pulp water has been found to alter the zeta potential of apatite significantly.

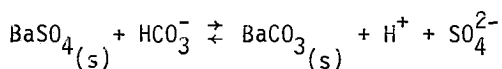
In sparingly-soluble salt-type minerals, we can distinguish three types of behaviour in flotation collector/mineral systems, where covalent bonding occurs: i) Chemisorption. Interaction of the reagent with the surface without movement of metal atoms (ions) from their lattice sites; adsorption is limited to a monolayer. ii) Surface reaction. Interaction of reagent with the surface together with movement of metal atoms from their lattice sites; multilayers of reaction product may form. iii) Bulk precipitation. Interaction of metal ions and reagent away from the surface out in the bulk solution¹⁷.

The existence of electrochemical potential is precisely why surface precipitation can often occur in certain systems, even in the absence of bulk precipitation. It was shown that it is possible to have precipitation in the inter-facial region even before conditions for precipitation are met in the bulk solution¹⁸. The extent of bulk vs. surface precipitation will depend essentially upon the mineral solubility and the dissolution kinetics. High solubility and fast kinetics will promote bulk precipitation. The collector consumed for the latter is unavailable for flota-

ELECTROLYTIC FLOTATION OF CARBONATE MINES

tion and hence bulk precipitation (for instance, calcium oleate) is detrimental to flotation.

The collection process was considered as one of surface reaction than adsorption and as an illustration, the use of soda ash was considered on the surface properties of barite. Equilibrium in solution is controlled by the reaction:



and the surface of barite, as it can be demonstrated, behaves as BaCO_3 than BaSO_4 in the presence of sodium carbonate, used often for pH adjustment.

In the case of carbonate minerals it is extremely important to consider the role of atmospheric CO_2 in determining thermodynamic characteristics. The calculations clearly show that, in this case, the solubility and stability characteristics of various solids can be totally different depending upon whether (or not) the system is open to the atmosphere¹⁹.

Using solution equilibria Ananthapadmanathan and Somasundaran, constructed a diagram showing the amount of Ca^{2+} in solution from apatite, calcite supernatants and also calcium oleate¹⁷. To develop an understanding of the flotation properties of this group of minerals it is usually necessary to examine the relevant physicochemical properties, like crystal structure, solubility, surface charge and adsorption behaviour, as these minerals behave in a complex and different manner from most other groups. Previous work on the floatability of calcite has been published²⁰.

EXPERIMENTAL PART

The electrolytic flotation cell constructed in the Laboratory was a modified Hallimond type with electrodes, in the place of the porous diffuser, shown in Figure 1. The content of the cell was 270 cm³ and the tests were conducted in deionised water, working with 3g of material. A stirring of 150 rpm was applied to keep the particles in suspension.

Pure natural minerals were used as materials in this study. Magnesite coming from Chalkidiki and dolomite from the Kozani area. Chemical analysis of magnesite gave a loss on ignition of 51.40%, MgO 47.80, CaO 0.32, SiO₂ 0.42 and R₂O₃ 0.06%. Dolomite had a l.o.i 46.21%, MgO 21.42,

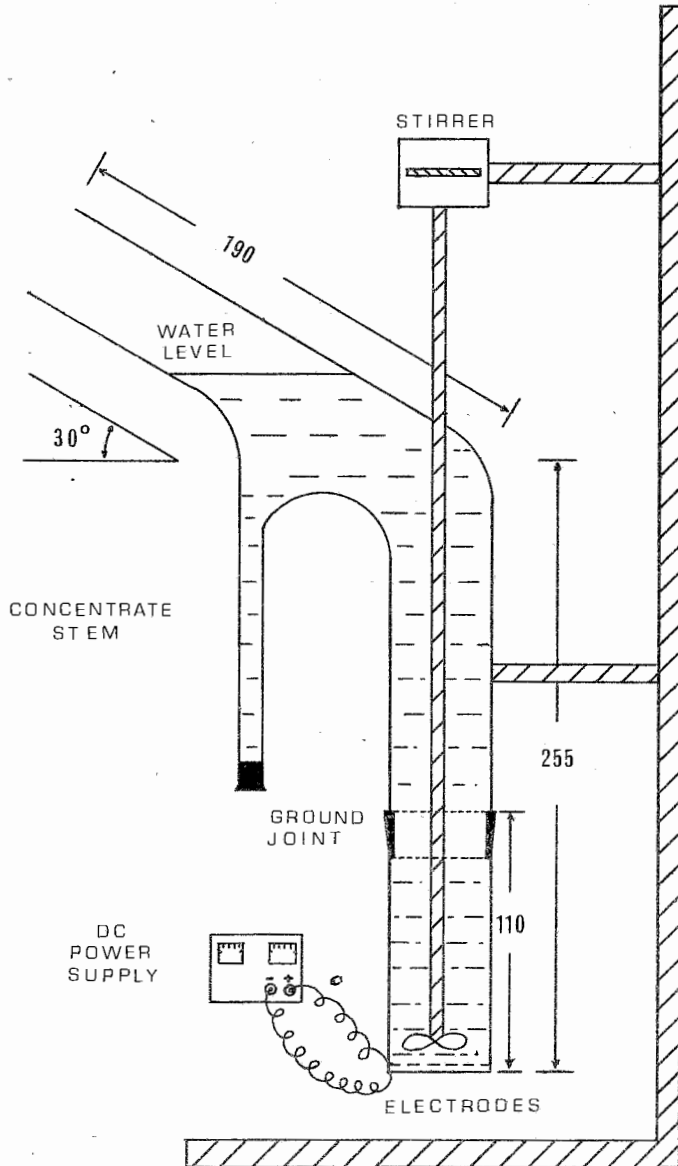


Fig. 1. Laboratory electrolytic flotation apparatus.
(All dimensions in mm).

ELECTROLYTIC FLOTATION OF CARBONATE FINES

CaO 31.30, SiO₂ 0.28 and R₂O₃ 0.09%. This was also certified by x-ray crystallographic analysis. After crushing, grinding and wet sieving, the particle size range of -45 +15 μm was taken; where the -15 μm fraction was discarded by washing and decantation, after the calculation of settling time from Stokes law.

As flotation collector was used a tall oil fatty acid (anionic collector) with the trade name Acintol FA-1, supplied by Arizona Chemical Co. According to the Company, this had rosin acids maximum 5%, unsaponifiable 3 and total fatty acids 92.8%; from which oleic acid was 44, linoleic 43, soluble 5 and other acids 8%. All the reagents were put and mixed together before flotation and then diluted to the double volume. The concentrations quoted are those of conditioning*.

RESULTS AND DISCUSSION

Initial Test

Calcite, which is the most common carbonate mineral, possesses a rhombohedral structure with the Ca⁺⁺ ions located at the corners and faces of the unit cell and the CO₃⁻⁻ ions located at the center of both the edges and the cell itself. Each cation is coordinated in the structure to six oxygen atoms of six different CO₃⁻⁻ groups. Crystal structures of magnesite and dolomite are of the same type. Other carbonates, that have a comparatively larger cation, follow the crystal structure of the aragonite type (form of CaCO₃). Crystal chemistry of sulphates, tungstates and phosphates are much more complex. Deviation in the crystal lattice of a mineral from the ideal structure can be estimated from the data obtained for its electrophysical parameters, such as Fermi level or concentration ratio of the charge carriers, since these parameters reflect such deviations. It was seen¹⁶ that minerals as calcite does change from n-type to p-type semiconductors upon dry grinding and thereby become more floatable with sodium oleate. Heating of the solid can also be expected to affect the flotation response, since upon increasing the temperature the Fermi level of n-type would be lowered, enhancing the anionic collector adsorption and vice versa, as observed with calcite, barite and fluorite.

* Experimental collaboration of Chemistry student Mr. C.T. Grekos is acknowledged.

The effect of the type of electrolyte used is also significant. Solubility is decreased due to common ion effect, when electrolytes that contain constituent ions of the salt-type mineral were added, and increased when other electrolytes were added. It is noteworthy that the responses of the individual species to the addition of an electrolyte differ much from each other. These phenomena are of particular relevance to the study of flotation chemistry, since the number of ions that are extraneous to a mineral and can be expected to be present depends both upon the type of water used and the mineralogical composition of the ore.

In a previous work⁹, it was found out that a conditioning time over 180 s was not affecting the process giving recoveries over 95%. The time of electrolysis and actually flotation time, was 300 s when collector was used. For dolomite fraction -45 +10 μm , 20 ppm of the same collector was giving recoveries of the order of 70%; the pulp density over 17 kgm^{-3} (which is indeed very low) was decreasing the mineral recovery. A current density of 100 Am^{-2} , which is the ordinary value for effluent treatment, was producing recoveries over 90% with both the electrolytic flotation laboratory cells that were constructed and tested. Also, a comparison was made for these cells and the advantages were given.

However, care was needed for the height of the cell, which was increased for this reason after the preliminary tests⁹, to avoid the transfer of fines to the surface mechanically, due to their small mass and momentum. An alternative explanation for ultrafine flotation behaviour was proposed, based wholly on the hypothesis of mechanical entrainment, which was further developed²¹.

The time of electrolysis was tested for both materials and the results are shown in Figure 2. In these experiments, the pulp density was 11.1 kgm^{-3} , current density 100 Am^{-2} , conditioning time 600 s and no collector was used. The voltage was in the range of 15-24 V. A small volume of sodium hydroxide solution, 3.7×10^{-3} N totally, was added to increase the conductivity of the medium. What is interesting from these results is that electrolytic flotation was possible without any collector.

The gas bubbles generated during electrolytic flotation were measured²². Most of the bubbles measured were in the range of 20 to 90 μm , compared with 0.6 to 1 mm of conventional froth flotation. With increasing the applied current density also the bubble size was decreased.

ELECTROLYTIC FLOTATION OF CARBONATE FINES

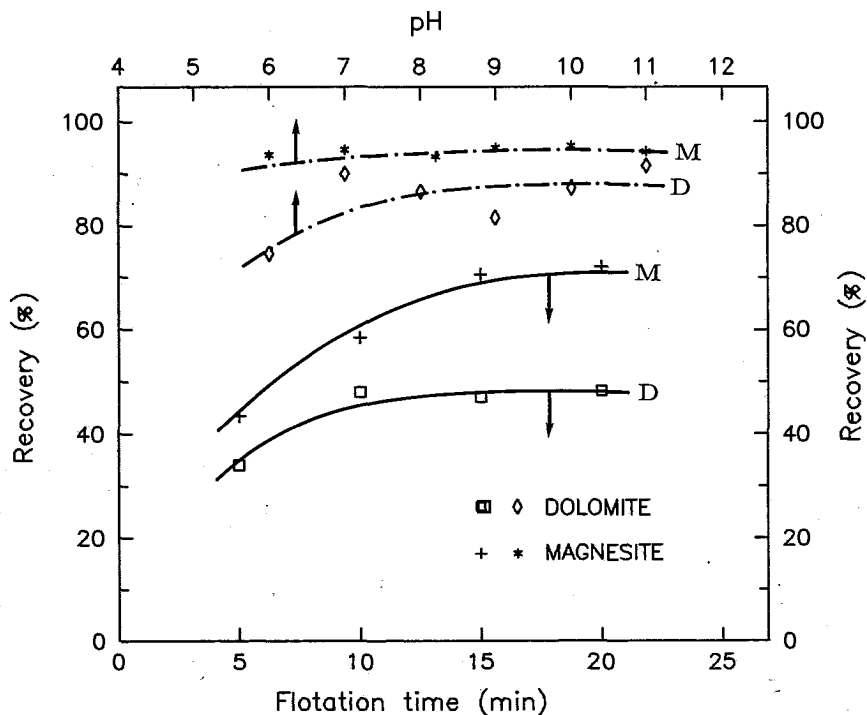


Fig. 2. Effect of electrolysis time on flotation recovery without any collector and influence of pH of solution on electrolytic flotation of magnesite-dolomite. The dotted lines refer to the upper and right axis (through the rest figures).

The electrode material was, in this case, stainless steel. More information on the type and construction of electrodes for electrolytic flotation will be published¹.

It is known that during electrolytic flotation changes occur in the pH value of the solution near the electrodes. Since the pH exerts, generally, a great influence on the hydrophobic properties of mineral surfaces and determines the collector dissociation and the ionic composition of the pulp, this localised pH effect is important. It was also proposed that the pH of solution could be used for selective flotation of carbonates²³.

The variation of pH from 6 to 11, however, as shown also in Figure 2, did not produce any appreciable differentiation of electrolytic flotation recoveries for the two minerals individually. In these experiments

~~K.A. MATIS, G.P. GALLIOS, G.A. STALIDIS~~

20 ppm of collector was added and the time of electrolysis was 600 s; while the other parameters were as before. Solutions of sodium hydroxide or sulphuric acid were added as pH modifiers. When the collector concentration was doubled the results were not different.

Chemisorption of fatty acids or their soaps on salt-type minerals resulting in the formation of alkaline earth soaps has been advocated by a number of investigators¹⁶. It was also shown that the adsorption of oleic acid occurs at low pH values predominantly by physical adsorption and at high pH values (over approximately 6) by chemisorption. Infrared spectroscopy, in the sixties, helped for the above conclusions.

The presence of the 5.8 μm band associated with the stretching of the C=O of the -COOH group, and 6.4 and 6.8 μm bands associated with the asymmetric and symmetric stretching modes respectively of the C=O of the -COO⁻ led to the proposal of the presence both of physically adsorbed and chemically adsorbed oleate on the mineral. Washing of the mineral with acetone removed the 5.8 μm band due to the physically adsorbed oleate.

Chemisorption was proposed to occur by an ion exchange process and below the point of zero charge, oleate was suggested to adsorb on calcite and apatite electrostatically. Change in zeta potential and even sign reversal occurs at high concentrations of collector due to the formation of hemimicelles. Having as basis a hydrolytic model, a different mechanism was proposed¹⁶, which involved a combined action of ionic and hydrogen bonding of the oxygen of the polar group of the collector to the species on the mineral surface. These mechanisms essentially seek to explain the adsorption of the first layer of fatty acids on mineral. Multilayer adsorption of fatty acids on calcium minerals has been also found to exist²⁴.

However, according to recent theories¹⁸, previous IR results cannot be used to draw any conclusions regarding adsorption mechanisms. Because IR is not an in situ test and pretreatment, such as consolidation of particles (altering the double layer interactions) and even more seriously, drying will produce artifices and can yield misleading results.

It is noted finally that reverse flotation by cationic collectors (amines) is the existing technology at Mantoudi²⁵.

ELECTROLYTIC FLOTATION OF CARBONATE FINES

Use of Modifiers

Since the separation of salt-type minerals from each other is extremely difficult, particularly when the minerals contain common cations, modifiers are invariably used for obtaining selectivity. In addition to the pH modifying agents, modifiers commonly used include inorganic and organic reagents. Mechanism by which reagents act, however, have mostly remained obscure, mainly because of a lack of systematic data in the literature on their application.

Preliminary tests of modifiers (citric acid, sodium metaphosphate, etc.) addition for dolomite electrolytic flotation were reported⁹. The results were better when the addition was applied before conditioning with the collector.

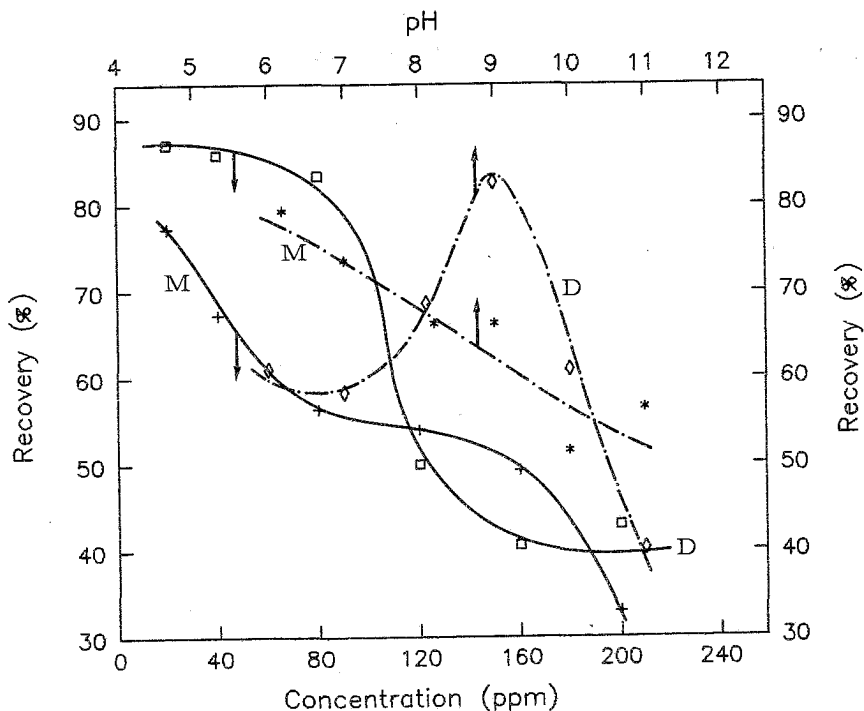


Fig. 3. Addition of carboxymethyl-cellulose to individual samples; Effect of modifier concentration (at a pH 9.5) and pH (c.c. conc. 40 ppm) on recoveries. (The symbols are the same as in Figure 2).

K.A. MATIS, G.P. GALLIOS, G.A. STALIDIS

Organic modifying agents, such as starch, tannin, dextrin, etc., have been used for a number of years for increasing selectivity during salt-type mineral flotation. These are generally characterised by their high molecular weight and the presence of a number of strongly hydrated polar groups. Carboxymethyl-cellulose was applied to the beneficiation of Satkin magnesites on a semi-industrial scale by flotation with recycled water²⁶.

Electrolytic flotation experiments were conducted with the application of carboxymethyl-cellulose as modifier to the pure minerals individually and these are presented in Figure 3. The collector concentration was 40 ppm (the rest parameters as forementioned). The results of the study of modifier concentration and solution pH are varying but at higher concentrations the lines are approaching. At certain conditions around pH 9.5 a reverse flotation is expected, as magnesite is depressed, showing also an apparent difference in recoveries for the two minerals.

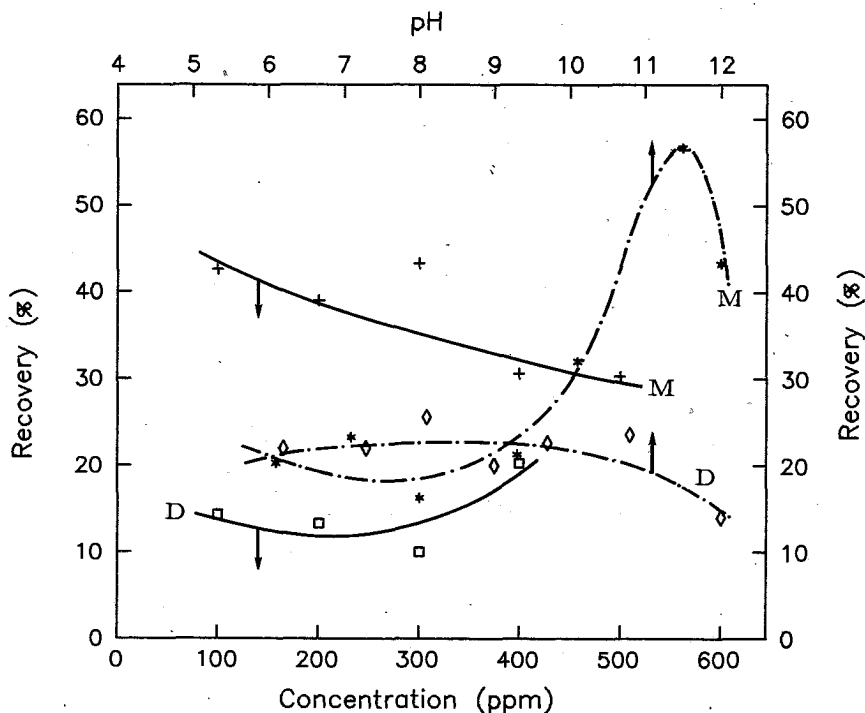


Fig. 4. Modifying action of sodium silicate without any collector. Effect of reagent concentration (at a pH of 11) and pH (with 100 ppm sodium silicate).

ELECTROLYTIC FLOTATION OF CARBONATE FINES

One of the most commonly used modifying agents in salt-type mineral flotation is sodium silicate, acting usually as dispersant. Our tests, shown in Figure 4, examined the influence of pH and modifier concentration and in this case, magnesite was the more floatable.

In practice, sodium silicate is considered to act by depressing quartz and other silicates (at relatively high concentrations and above pH 7) and by dispersing the slimes that are present in the pulps¹⁶. An increased depressing action of sodium silicate was observed on calcium minerals such as fluorite, calcite, scheelite and apatite. Both the mode of preparation of silicate and the ratio of SiO_2 to Na_2O were shown to play a role in determining the effectiveness as depressants.

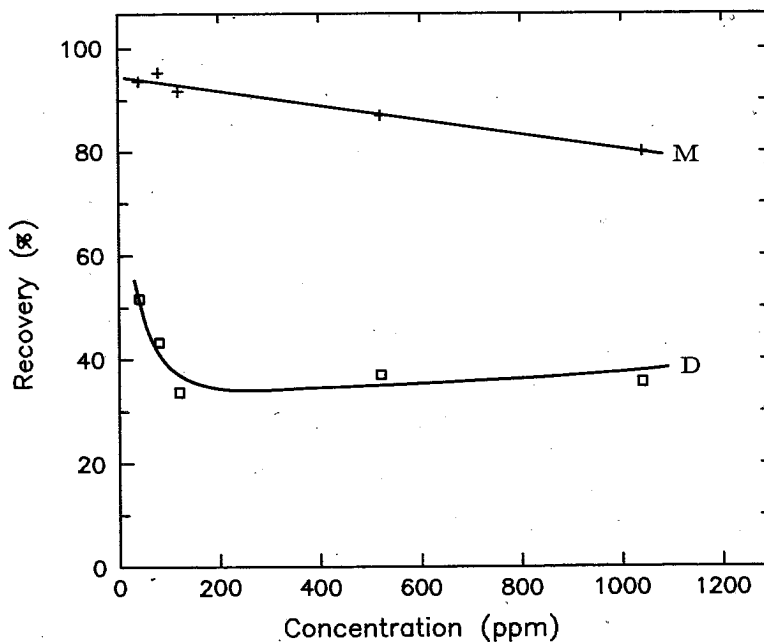


Fig. 5. Effect of concentration of added sodium fluorosilicate on electrolytic flotation.

Then, sodium fluorosilicate was tested for the two minerals, as sodium fluoride has been also widely used; the results are shown in Figure 5. The collector concentration was 40 ppm and the pH approximately

K.A. MATIS, G.P. GALLIOS, G.A. STALIDIS

11.6. It is noticed that magnesite flotation is not really affected, while dolomite is strongly depressed, having a recovery difference from 87% that of magnesite to 37% of dolomite, for 520 ppm sodium fluorosilicate.

Another inorganic reagent examined as flotation modifier was sodium pyrophosphate and the experimental results are shown in Figure 6. Again the same variables were studied, at a rather high range of modifier concentrations, showing a depressing action. However, the obtained recoveries were not much different from each other and so not encouraging.

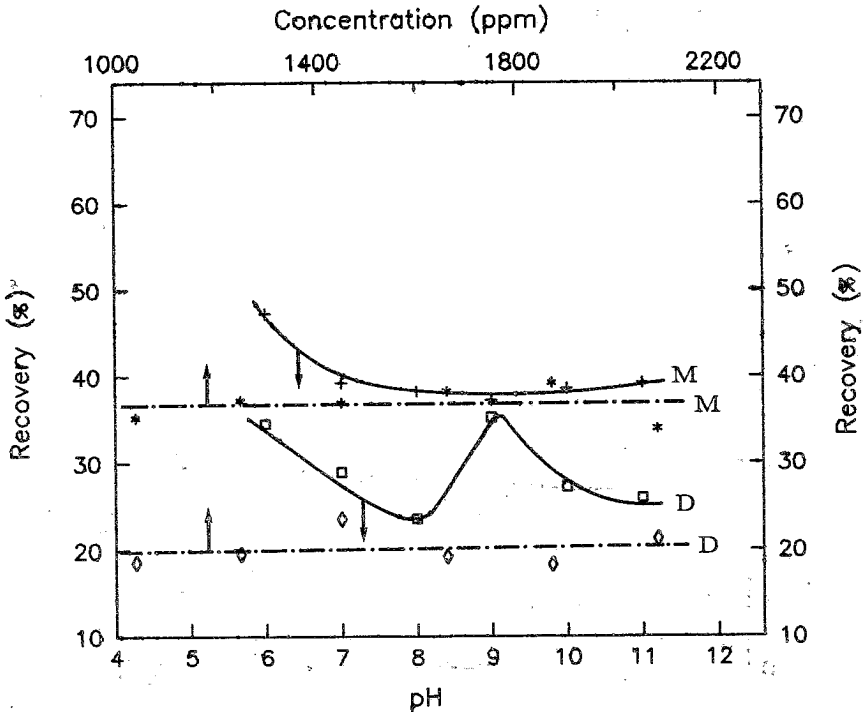


Fig. 6. Adding sodium pyrophosphate as modifier (with 40 ppm collector). Effect of pH (at a concentration of 1040 ppm) and pyrophosphate concentration (at pH 11.5).

The action of polyvalent anions, including that of phosphates and polyphosphates which are widely used as depressants for carbonate minerals, could be the result of the effect of these reagents on the surface charge

ELECTROLYTIC FLOTATION OF CARBONATE FINES

of the mineral, since they can be expected to make the minerals increasingly negatively charged and this causes a reduction in the adsorption of the anionic fatty acid collectors. Komlev¹⁶ have attributed the depressing action of the polyphosphates in the flotation of magnesite from dolomite, in addition to reduction in fatty acid adsorption, to the dispersion of dolomite slime from the magnesite surface as well as to the selective adsorption of the polyphosphate on the dolomite surface.

So, attention was paid to the use of sodium hexametaphosphate as modifier in electrolytic flotation of carbonate fines. In Figure 7 the influence of pH was looked with the addition of 80 ppm of modifier and at two collector concentrations. At a pH of 8 the difference in recoveries is from 50% that of magnesite to around 24% of dolomite. Also, the increase of modifier concentration showed a decrease in recoveries, mainly with 40 ppm collector, as shown in Figure 8.

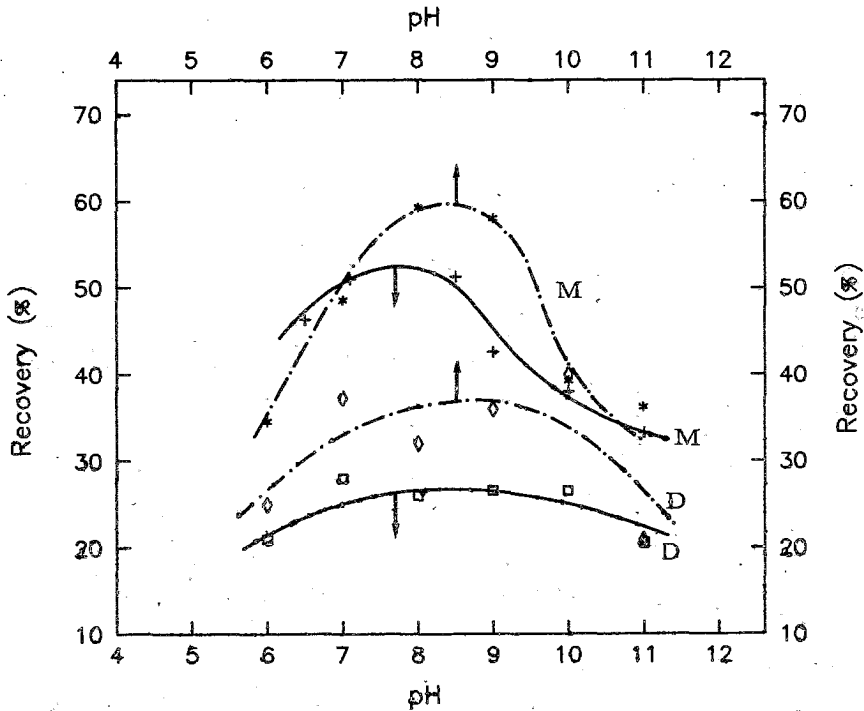


Fig. 7. Effect of pH when sodium hexametaphosphate is used as modifier, with 20 and 40 ppm of collector.

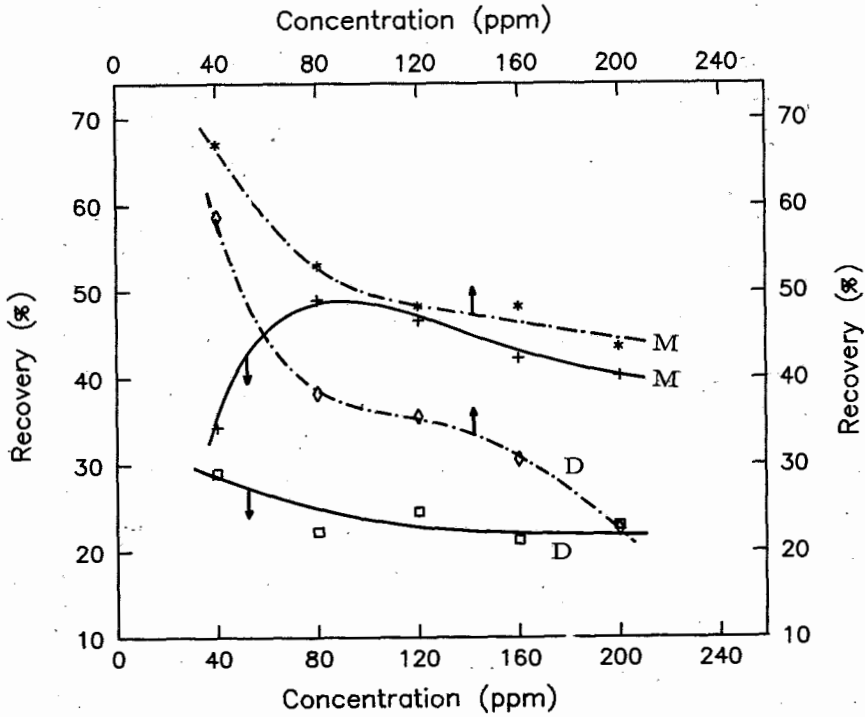


Fig. 8. Effect of sodium hexametaphosphate concentration at pH 8, with 20 and 40 ppm collector.

When inorganic and organic modifying reagents are introduced together, the possibility exists for the presence of interactions between these reagents that can affect the final flotation response of the system considerably. In couple of preliminary experiments, mixtures of modifiers were introduced: in the first, sodium hexametaphosphate 80 ppm, sodium silicate 200 ppm, collector 20 ppm, pH 11 and in the second, sodium hexametaphosphate 80 ppm, carboxymethylcellulose 100 ppm, collector 40 ppm, pH 9.5. But the results for the two minerals were showing recoveries without any appreciable difference and not far from the experimental error.

Artificial Mixtures

Following the above work on the individual pure carbonate minerals and the necessary conclusions that were extracted on the use of the modifying agents for the selective separation of the carbonate fines by

ELECTROLYTIC FLOTATION OF CARBONATE FINES

fatty acid electrolytic flotation, experiments were carried out for artificial mixtures of these minerals. The average results from duplicate experiments are shown in Table, where sodium fluorosilicate, sodium hexametaphosphate and carboxymethyl cellulose were applied to different concentration ratios of the two carbonates. With the last modifier, magnesite was expected in the underflow, i.e. a reverse flotation and the data obtained from chemical analysis are given in both the concentrate and tails.

It was observed that the grade of magnesite, which was improved in comparison with the initial concentration, if it is compared with the calculated (expected) % grade from the experiments with the individual minerals, shown also in the Table, are less. However, magnesite recoveries in all the cases were better. From the theory²⁷, it is known that there is an inverse relationship between recovery and concentrate grade. Certainly, as shown from the results with the different initial concentration ratios, having a number of flotation stages separation will be improved; further investigation is warranted. From parallel experience in froth flotation of carbonates, it is felt that it is more a problem of the given system for selective flotation than of electrolytic flotation.

It is already known¹⁶ that selective separation, which is required commercially, of calcite from apatite, or of fluorite from barite or scheelite by flotation is not easily achieved. It was also shown that the differences between flotation characteristics of various salt-type minerals (like calcite, fluorite and apatites) might not be any greater than those between samples of a single mineral from different deposits. The use of modifying agents is therefore essential to achieve selectivity in these systems.

Concluding, the similarity in the response of various minerals to flotation techniques is often attributed to their comparable surface chemical composition and in many cases to the high surface activity of the collectors usually employed to float them. In addition, interactions of dissolved anions or cations from one mineral with other minerals in the pulp as well as with collector species can be considered to contribute towards the poor selectivity. This is the reason why all these aspects have been extensively discussed.

K. A. MATS, G. P. GALLIOS, G. A. STALINS

TABLE

Selective Batchwise Experiments of Mixtures of Pure Ores with Modifiers

A. Sodium Fluorosilicate: Concentration of collector 40 ppm,
modifier 520 ppm, pH 11.5

Magnesite 80% - Dolomite 20%	$R_M = 98.4\%$	$G_M = 84.2\%$	$\text{calc.} = 90\%$	
60	40	100	67.6	78
40	60	100	48.1	61

B. Sodium Hexametaphosphate: Con.col. 20 ppm, modif. 80 ppm, pH 8.0

Magnesite 80% - Dolomite 20%	$R_M = 74.9\%$	$G_M = 85.8\%$	$\text{calc.} = 89\%$	
60	40	81.7	70.4	76
40	60	82.3	47.6	58

C. Carboxymethyl Cellulose - Reverse Flotation: Con.col. 40 ppm, modif. 100 ppm, pH 9.5

Magnesite 80% - Dolomite 20%		Concentrate	$R_D = 70.1\%$	$G_D = 23.3\%$
		Tails	$R_M = 42.3$	$G_M = 85$
50	50	Concentrate	$R_D = 70.2$	$G_D = 58.7$
		Tails	$R_M = 50.6$	$G_M = 62.9$

NOTE: Pulp density 11.1 gl^{-1} , current 100 Am^{-2} , addition $\text{NaOH } 3.7 \times 10^{-3} \text{ N}$, conditioning time 600 s, electrolysis 600 s. For the case C, no individual recovery data for these conditions were available for comparison reasons.

R refers to recovery, G to grade, calc. to calculated values of grade and the subscripts M and D to magnesite and dolomite, respectively.

ELECTROLYTIC FLOTATION OF CARBONATE FINES

The existence of fine mineral particles complicates more the whole matter. As the particle size is reduced two characteristics begin to dominate: the specific surface becomes large and the mass of the particle becomes very small. The relationship between the physical and chemical properties of fine particles and their behaviour in flotation was examined, among others, by D.W. Fuerstenau et al¹⁰. Certain phenomena, as low flotation rate, high reagent consumption and rapid oxidation, affect the recovery. Other phenomena affect the grade, such as fine particle entrainment and non specific collector adsorption. While there are some affecting both, as froth stabilisation and higher dissolution.

The problem of processing mineral fine particles poses an immense challenge today to the researchers, with the increasing demand for minerals and the continuously diminishing grade of ores. The application of conventional separation methods is generally uneconomical or inefficient. Electrolytic flotation, a process coming principally from effluent treatment, offers certain advantages and particularly, the production of fine gas bubbles. Interesting results were obtained with the artificial mixtures of magnesite-dolomite fines, showing better recoveries of magnesite compared with the individual tests. In this way, work on this field is going on in our laboratory and the research program is continued.

Περίληψη

Δυνατότητα εφαρμογής της ηλεκτρολυτικής επίπλευσης στην ανάκτηση λεπτών τεμαχιδίων ανθρακικών ορυκτών.

Κ.Α. Μάτης, Γ.Π. Γάλλιος και Γ.Α. Σταλίδης
Εργαστ. Γεν. & Ανόργ. Χημ. Τεχνολογίας, ΑΠΘ

Η ηλεκτρολυτική επίπλευση, που χαρακτηρίζεται από την παραγωγή λεπτών αέριων φυσαλίδων με ηλεκτρόλυση, εφαρμόσθηκε σ' αυτή την εργασία για την ανάκτηση λεπτών τεμαχιδίων μαγνησίτη και δολομίτη, κλάσματος -45 +15 μμ. Ύστερα από μια σύντομη εισαγωγή στο πρόβλημα των λεπτών τεμαχιδίων ορυκτών, ανασκοπείται γενικά η επίπλευση των ορυκτών τύπου άλατος, γιατί πιστεύεται ότι έχει ελκύσει μικρό ενδιαφέρον σε σύγκριση με τα θειούχα, οξείδια και πυριτικά συστήματα. Καλύπτονται οι διάφορες φυσικοχημικές ιδιότητες, οι σχετικές με την επίπλευση, όπως η κρυσταλλική δομή, το επιφανειακό φορτίο, η διαλυτότητα, η συμπεριφορά κατά την προσρόφηση συλλεκτών, τροποποιητών (ενεργοποιητές, παρεμποδιστικά, διασπαρτικά), κ.ά. Ο διαχωρισμός των ορυκτών αυτής της ομάδας μεταξύ τους είναι εξαιρετικά δύσκολος, λόγω παρόμοιας συμπεριφοράς κατά την επίπλευση, έτσι για να επιτευχθεί εκλεκτικότητα χρησιμοποιήθηκαν τροποποιητές. Τέτοια αντιδρα-

στήρια, που δοκιμάσθηκαν σε ανεξάρτητα καθαρά δείγματα ορυκτών και σε τεχνητά μίγματα αυτών (Πίνακας), ήταν η καρβοξυμεθυλοκελλουλόζη, το πυριτικό νάτριο, το εξαμεταφωσφορικό νάτριο, το φθοροπυριτικό νάτριο και το πυροφωσφορικό νάτριο. Παράμετροι που εξετάσθηκαν ήταν ο χρόνος επίπλευσης, το pH του διαλύματος, η συγκέντρωση του συλλέκτη (εμπορικό λιπαρό οξύ) και των τροποποιητών σε σχέση με την ανάκτηση των ορυκτών. Με τα μίγματα βρέθηκαν καλύτερες ανακτήσεις, σε σύγκριση με τα ανεξάρτητα πειράματα, αλλά χειρότερη καθαρότητα συμπυκνώματος. Τα αποτελέσματα θεωρήθηκαν ενθαρρυντικά και η εργασία σ' αυτό τον τομέα συνεχίζεται.

REFERENCES

1. K.A. Matis and G.P. Gallios: in "*Mineral processing at a Crossroads*", Advanced Study Institute, B.A. Wills (Director), Falmouth, U.K., Mar. 24 - April 4 (1986).
2. A.M. Gaudin et al: *AIIME*, Tech. Publ. 414, 3 (1931).
3. D.W. Fuerstenau: "*Fine Particles Processing*", (ed.) P. Somasundaran, SME/AIME, N.York, p. 669 (1980).
4. V.I. Klassen and V.A. Mokrousov: "*An Introduction to the Theory of Flotation*", Butterworths, London, p. 123 (1963).
5. A.F. Colombo, as in ref. 3, p. 1034.
6. M. Szatkowski and W.L. Freyberger: *Trans. IMM*, 94, C 61 (1985).
7. K.A. Matis: *Techn. Chron. (Scient. Edit. Chem. Eng.)*, 4, 19 (1979)(Gr.).
8. K.A. Matis and J.R. Backhurst: in "*Solid-Liquid Separation*", (ed.) J. Gregory, Ellis Horwood, London, p. 29 (1984).
9. K.A. Matis, G.A. Stalidis and G.P. Gallios: *Techn. Chron. (Scient. Edit. - Chem. Eng.)* 5, 4, 35 (1985).
10. K.A. Matis and G.P. Gallios: *Chim. Chron. - New Series*, 14, 219 (1985).
11. P. Hogan, A.T. Kuhn and H.F. Turner: *Trans. IMM* 88, C 83 (1979).
12. V.A. Glembotskii et al: XI Int'l Miner. Proces. Cong., Cagliari (1975).
13. Y. Fukui and S. Yuu: *Chem. Eng. Sci.* 35, 1097 (1980).
14. N.V. Tyabin et al: *Teoret. Osnov. Khimich. Tekhnol.* 13, 880 (1979).
15. J.D. Miller et al: in "*Principles of Mineral Flotation - The wark Symposium*", Australasian IMM, Victoria, p. 31 (1984).
16. H.S. Hanna and P. Somasundaran: in "*Flotation - A.M. Gaudin Memorial Volume*", (ed.) M.C. Fuerstenau, SME/AIME, N.York, p.197 (1976).
17. D.W. Fuerstenau: as in ref. 15, p. 7.
18. P. Samasundaran: in "*Discussion on Flotation*", XV Int'l Miner. Proces. Cong., Cannes, p. 129 (1985).
19. W. Stumm and J.J. Morgan: "*Aquatic Chemistry*", Wiley - Interscience, N.York, p. 161 (1970).
20. K.A. Matis, Th. N. Balabanidis, G.P. Gallios: 9th Nat'l Symp. Chem., Athens (1984) (Gr.).

ELECTROLYTIC FLOTATION OF CARBONATE FINES

- 21.C.E. Hemmings: *Trans. IMM* 89, C 113 (1980).
- 22.K.A. Matis: *Chim. Chron. - New Ser.* 9, 71 (1980).
- 23.J.J. Prédali: *Sciences de la Terre, Mém.* 27 ENSG, Nancy (1973).
- 24.C. Du Rietz, as in ref. 12.
- 25.Th. Gambopoulos et al: *US Patent* 3, 976, 251, Aug. 24, (1976).
- 26.N.I. Baranovskii: *Ogneupory* 1, 37 (1978).
- 27.B.A. Wills: "*Mineral Processing Technology*", Pergamon Press, Oxford, p. 20 (1985).

OPTIMISATION OF A MULTIPRODUCT BATCH PROCESS

P.A. PILAVACHI

*ICI-Europa Ltd, Belgium **

(Received December 19, 1986)

SUMMARY

A computer model was developed to simulate an existing multiproduct batch process. This was used to determine the bottlenecks and to explore possible ways of increasing plant capacity by investigating the effect of modifications. Factors taken into account included delays due to equipment waiting times, delays due to random equipment failures and several other uncertainties. It was shown that different operating policies and some plant modifications could substantially increase the capacity.

Key words : Modelling, GPSS language, operating policies, operating procedures, bottlenecks, waiting times, equipment failures, stochastic situations, discrete event, statistics.

ABBREVIATIONS AND TERMINOLOGY

A, B = Reactants; N = Neutraliser; P = Product; R = Reactor; S = Stripper; T = Storage tank. - *Indices* : m = number of reactors or neutralisers; n = number of products; q = number of strippers.

INTRODUCTION

On a production process, the performance could be defined as the proportion of the time that the plant is running at normal rates. There is 100 % capacity performance, when there is complete access to all required equipment at all times. If the annual capacity performance is quoted as e.g. 85 %, the potential annual production is simply 85 % of the normal rate. Reduced capability in batch processes can be due to equipment failures or to waiting times if the downstream equipment is occupied.

* present address to which correspondence should be sent:
*Commission of the European Communities Directorate-General for
Science, Research and Development, 200 rue de la Loi, B-1049 Brussels.*

P.A. PILAVACHI

When many batch operations are involved in a multiproduct plant, the process is complex and it is almost impossible to predict the effects of delays due to failures, waiting times and planned process modifications. For this reason, a computer program is required to model the process.

The model can be used during the design stage or during operation of the plant to reveal existing bottlenecks, to investigate different plant operating policies and to obtain capacity figures before plant modifications. However, scheduling methods can significantly improve the productivity and cost effectiveness of batch processes and should be considered first before investigating process details ¹.

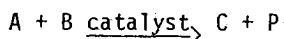
The program was developed in GPSS computer simulation language ². The elements of modelling included statistical distributions for the process steps derived from the actual plant. They handled stochastic situations and performed discrete event and continuous modelling. Such an analysis required that all factors which appeared to affect the plant operation should be identified, relevant data collected and the overall capacity calculated. More specifically, the following information was required : The process description together with the plant operating procedures and policies; the frequency of change of product; the occupation times for all batch equipment; the throughput of each product in all continuous equipment; the capacity of the storage tanks; the equipment failures and delays; the equipment cleaning policies and cleaning times required when a product was changed or when equipment was fouled; other information specific to the plant. A similar study for a different process has since been presented by Felder and Kester ³.

The detailed data required for the simulation are, however, best illustrated in the example which follows.

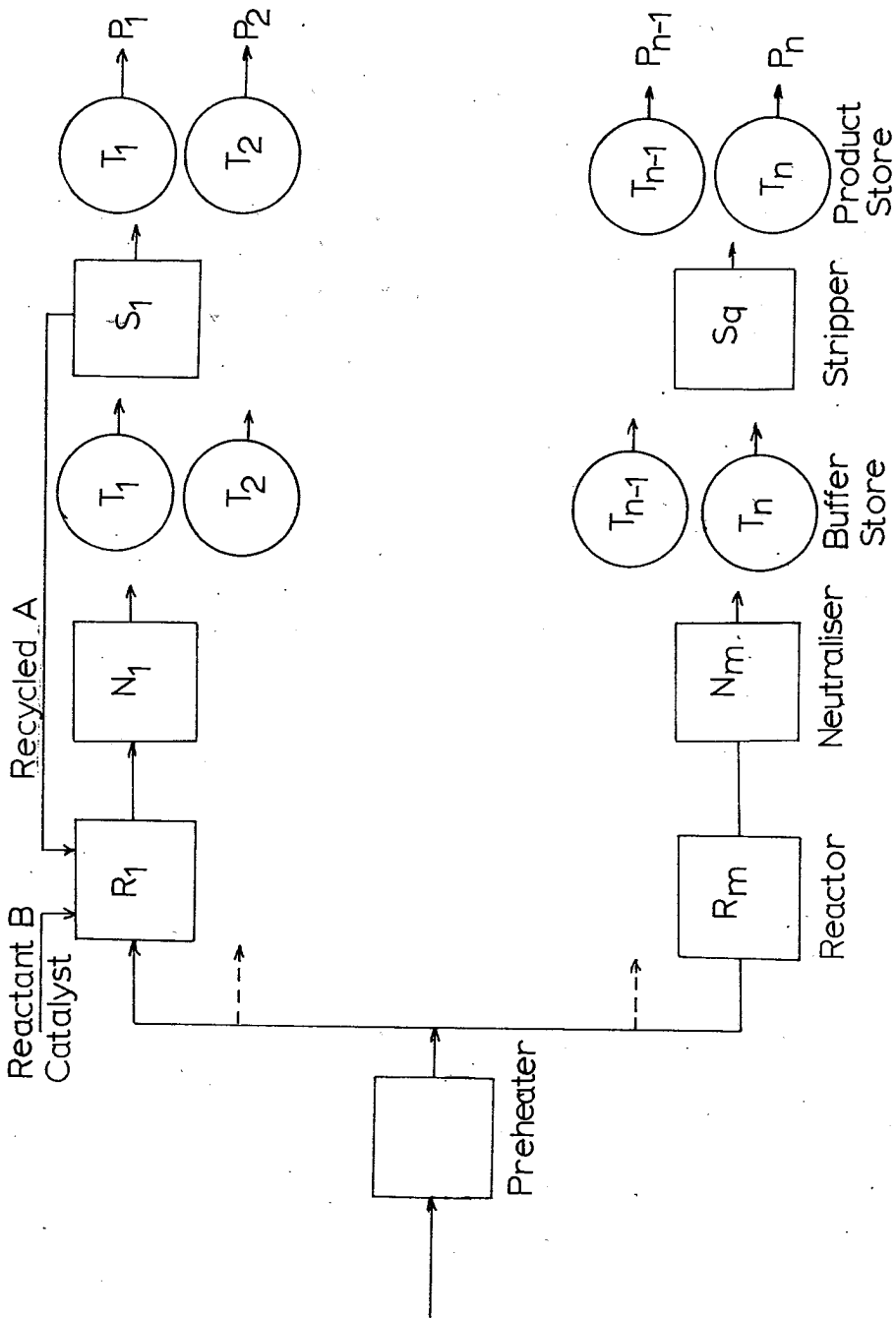
PROCESS DESCRIPTION

A flow diagram of the process considered is presented in figure 1.

Several chemical products are manufactured in batch reactors (R_1 to R_m) according to the reaction scheme.:



where P stands for the product.



OPTIMISATION OF A MULTIPRODUCT BATCH PROCESS

FIG. 1. Flow diagram of the process.

P.A. PILAVACHI

Reactant A is fed to the reactor via a preheater. According to the existing scheme, one preheater serves all the reactors, but can only be used for one reactor at a time. Simultaneously, reactant B and the catalyst as well as recycled reactant A are added to the reactor.

At the end of the batch, the reactor content is emptied into a neutraliser so that the excess of reactant B is neutralised with NaOH. Following neutralisation, which is also batch, the crude product is emptied into the buffer tank, which corresponds to the product concerned. Then, it is stripped continuously in one of the strippers (S_1 to S_q) in order to remove the water obtained from neutralisation as well as the excess of reactant A, the latter being recycled to the reactor. The distillation bottom product is mixed with filter aid and then filtered. Finally, the filtrate is stored in the corresponding final product storage.

METHODOLOGY

The computer model operates in the following way: First it stores all the information provided by the user of the program i.e. reaction times, neutralisation times, storage capacities, and others. It then calculates the processing times, taking into account not only all the unit occupation times but also the delays due to waiting times, equipment failures and others.

When a reactor is empty, the model checks whether the preheater for reactant A is available. If this condition is true, it occupies the preheater for a fixed period, while reactant A is fed into the reactor, and then carries out the reaction. The reaction time depends on the product processed. When the reaction is completed the model checks whether the corresponding neutraliser is empty and also that no other reactor content is being discharged into another neutraliser. This is one of the existing limitations of the plant. If both of these conditions are met, it then discharges the reactor content into the neutraliser and carries out the neutralisation. The reactor then becomes available again. If the product has to be changed, a reactor cleaning time is allowed for.

After neutralisation the corresponding buffer storage spare capacity is checked and, provided it is greater than the reaction batch size, the neutralised product is emptied into the buffer store. If this

OPTIMISATION OF A MULTIPRODUCT BATCH PROCESS

conditions is not met, the neutraliser has to wait till the storage capacity becomes available.

When a stripper is available, the model selects the fullest buffer store (i.e. the one with the highest percentage of its capacity occupied). It then strips the content of this buffer store, until the store is empty or stripping time exceeds the predetermined time when the stripper has to be cleaned. Then the stripper is cleaned and another buffer store is chosen.

Plant capacity is then computed for a range of production strategies.

At a later stage, modifications to actual performance were considered and built into the program. Then, the model showed how different hypothetical plant modifications and operating policies could increase plant capacity. The aspects examined were at the point where a bottleneck occurred. Amongst the modifications considered were: adding storage capacity, reducing failure rates, producing a smaller variety of products, reducing batch reaction times (through changed operating conditions; for examples see Results section), and others.

The computer program incorporates a random number generator subroutine. This selects randomly, within limits set by the indicated probability, the choice of products in each reactor, the mean time for repairs and the mean period between failures. The program could then calculate the plant capacity.

Each time the random number generator subroutine is called, it operates on a seed number, provided by the user of the program. When the seed number is changed, there is a change in the sequence of events e.g. choice of products with different batch reaction times, choice of failures with different repair times, etc. This results in different computed capacity figures. All cases had therefore to be run several times using, each time, a different seed number.

THEORETICAL MODEL

The following describes in detail the plant operating data as well as the assumptions made for the computer model:

Products

Several products are manufactured (P_1 to P_n)

Preheater of reactant A

- . According to the existing scheme at the actual plant, one preheater serves all the reactors, but can only be used for one reactor at a time. (This of course gives less flexibility and creates a restriction, but was originally designed in this way to reduce capital investment).
- . When a reactor is charged, the preheater is occupied for a predetermined period.

Reactors

- . Each product can be produced in some reactors only, as indicated in table I.

TABLE I : Product-reactor matrix

Product	Products produced in reactor			
	R ₁	R ₂	... R _{m-1}	R _m
P ₁	Y	Y	... Y	Y
P ₂	N	Y	... Y	N
.
.
P _{n-1}	N	N	... Y	N
P _n	N	Y	... Y	N

Y = Yes, N = No

- . The probability of having a product manufactured in a reactor is calculated from plant data on the number of batches in each reactor. Then, the computer program randomly selects the product to be manufactured in each reactor with the probability concerned.
- . Average batch reactor times for each reactor are considered (the exact batch reactor time could be found were a reactor model to be available).
- . When reaction ends, only the contents of a single reactor can be emptied at a time. This can only then be emptied into the corresponding neutraliser provided it is not occupied.
- . There is a product change in each reactor with an equal probability every 1, 2, 3,, 13 days. This was calculated from plant data and is shown graphically in fig. 2.
- . When changing the product to be processed, the reactor is cleaned. A different cleaning time is taken into account for each product.

OPTIMISATION OF A MULTIPRODUCT BATCH PROCESS

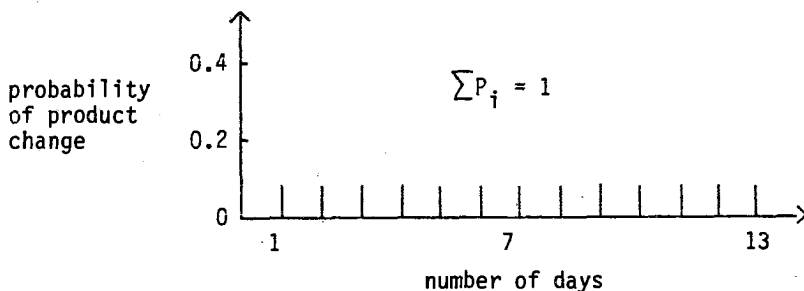


FIG. 2 : Product change in each reactor with an equal probability every 1, 2,, 13 days.

Neutraliser

- . The occupation time of the neutraliser is taken into account. This includes not only the neutralisation time, but also the time for charging and the time for discharging.
- . When neutralisation ends, the content of the neutraliser is discharged into the buffer storage which corresponds to the product processed. However, it will not be discharged if the space available in the storage tank is less than the neutralizer's batch size.

Buffer Stores

- . Only total buffer storage capacities for each product are considered. These are calculated from individual storage capacities.

Final product stores

- . The capacities of the final product stores are selected to be large enough that there will not be a bottleneck. This is justified since with good production planning their capacity is not a real limitation.

Strippers

- . When a stripper is available, the content of the most loaded buffer store is chosen (provided this is higher than a specified minimum). It then strips until the storage tank is empty (provided it does not strip for longer than a predetermined period and there is no stripper failure).
- . The throughput of each stripper depends on the product processed and on the stripper concerned. However, only average throughput values are considered.
- . Strippers are assumed to fail at widely varying intervals and for variable durations; the probability distributions of both were determined from plant data.

P.A. PILAVACHI

- . After a predetermined period of continuous stripping the stripper operation is stopped and the unit is cleaned. Cleaning times are taken into account.
- . The stripper is also cleaned whenever there is a change of product to be stripped.

Filters

- . The filters are considered to have a performance of 100 % i.e. they are considered to have no failures and are not responsible for any delays whatsoever.

Productive days

- . Scheduled plant shutdowns are taken into account for the calculation of the productive days. The most important shutdowns are due to scheduled maintenance, holidays and others.

Failure Analysis

Data from the plant showed that the main factors for failures and delays commonly encountered were due to : Main equipment mechanical failures, equipment leaks, equipment blockages, pump failures, valve failures, pipework blockages, general piping and flange leaks or ruptures, control system failures (or maloperations), changeover failures (e.g. installed spare does not start although it was all right yesterday); service failures due to steam supply, cooling water supply, heating oil supply (e.g. due to failure of the boiler), instrument air supply, electric power supply (e.g. due to strikes) or others; failures or delays due to lack of manpower, operator errors, computer failures, instrument failures, product quality failures, quality monitoring equipment failure and many others.

For each unit, statistical data on "*failure repair time*" and "*period between failures*" were obtained from the existing plant. All failure data were taken from one particular year. The repair times were grouped in seven categories according to their length, and the probability of occurrence of each category was computed (the split into seven categories was arbitrary). The period between failures was also split into seven categories, while their probability of occurrence was also computed. Failure analyses were made for all the reactors and neutralisers as well as for the heat exchanger.

OPTIMISATION OF A MULTIPRODUCT BATCH PROCESS

Typical results of a failure analysis for a reactor are shown in figure 3. As shown on the graph, the highest probability of occurrence was for a mean repair time of 4 units of time. There was also a 15 % probability for a repair time of 1 unit of time, etc. All probabilities should, of course, sum up to 1. A similar analysis made for the "period between failures" for the same reactor is also presented in figure 3.

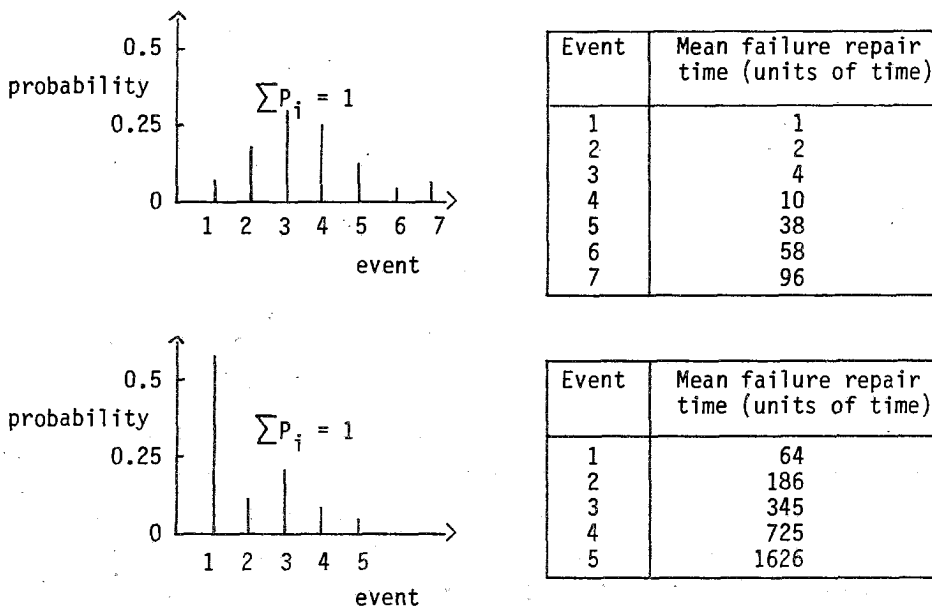


FIG. 3 : Typical failure analysis for a reactor.

RESULTS

The computer model was run for a simulated period of 1 year. The agreement of model results with existing plant data validated the model. A further indication of the validity of the model was obtained with computer results which indicated that the fraction of each product manufactured does not change considerably from case to case and compares well with the fraction of each product produced at the actual plant. This is illustrated in table II.

The model was used to determine the bottlenecks and to explore possible ways of increasing plant capacity by investigating the effect of modifications. Factors taken into account included delays due to

P.A. PILAVACHI

equipment waiting times, delays due to random equipment failures and several other uncertainties. It was shown that different operating policies and some plant modifications could substantially increase the capacity.

TABLE II : Comparison of model runs with plant data

Product	Fraction of each product manufactured		
	All assumptions for the existing process apply		Actual Plant data
	Seed No. 1	Seed No. 2	
P ₁	.206	.202	.196
P ₂	.037	.050	.037
.	.	.	.
.	.	.	.
P _{n-1}	.0	.004	.004
P _n	.021	.011	.008
Total	1.00	1.00	1.00

The computer printout provided tables with statistical information. The information obtained from these tables directed the modifications to be considered and the next computer runs to be made. The statistical information included :

- . Time reactors are waiting for the respective neutralisers to be available;
- . Time reactors are waiting for the preheater to be available;
- . Time reactors are waiting for another reactor to empty;
- . Time neutralisers are waiting because the respective buffer stores are full;
- . Daily production of each product and cumulative daily production of all products;
- . Total yearly production of each product.

The computer model was run for several cases. On the one hand, run 1, for which all assumptions for the existing process apply, and, on the other, runs 2 to 8, for which all assumptions apply except the one indicated. These runs are summarised in table III.

OPTIMISATION OF A MULTIPRODUCT BATCH PROCESS

TABLE III : Effect of variations on base case

Run	Description of the simulated case	Capacity increase %
1.	All Assumption for the existing process apply (no modification applied)	0
2.	Reaction time of each product in each reactor is reduced by 20 %	17
3.	All failures are eliminated	9
4.	Only boiler failures are eliminated	1
5.	One storage capacity creating a bottleneck is increased	2
6.	Less frequent change of reactant A with an equal probability every 8, 9,, 20 days	3
7.	Less frequent change of reactant A with an equal probability every 1, 2,, 27 days	1
8.	Only the major products are produced	1

If the reaction time in all reactors is reduced by 20 %, the capacity increases by about 17 %. However, a further time decrease of 10 % gives a further capacity increase of only 6.7 %. This non linear increase is due to the decreasing availability of the neutraliser (when the reactor and neutralisation times become comparable, the reactor waiting times increase).

While reduction of reaction times may be straightforward, however, it may not always give the desired result. For example in the case of simple non-reversible reactions or reversible endothermic ones, reaction time could be reduced by using higher temperatures, (although for reversible exothermal or for multiple reactions, temperature increase is not the optimal operating policy for a reactor). However, increase of the reactor operating temperature may require more energy consumption. In this way, a possible capacity increase may be accompanied by a higher reactor operating cost and perhaps a higher production cost per unit of product. Modelling is necessary to identify the optimum strategy, and may require analysis at the reactor level to be introduced into the

process model. An overview of batch reactor models, the input needed to generate these models and also the type of payback that might be gained from their use is described by Wilson⁴.

CONCLUSIONS

Simulating an existing multiproduct batch process, it was shown to be possible to increase plant capacity in a number of ways. The conclusions may seem to be qualitatively obvious. However, the model allows quantitative estimates and a priority classification of the possible modifications, e.g.

- . Reduced reaction time. By reducing the reaction time in all reactors by 20 %, we can increase the capacity by about 17 %.
- . Fewer plant failures. In the hypothetical situation where all failures are eliminated, the capacity increases by about 9 %. Boiler failures alone account for a capacity loss of 1 %.
- . Increased storage capacity. By increasing the storage capacity of one buffer store which was creating a bottleneck, the plant capacity increases by 2 %.
- . Less frequent reactant changes.
- . Producing fewer products.

In future, the model will be applied to obtain capacity figures in the case of other major plant modifications. It will also be applied to other processes.

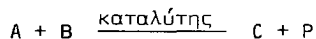
ΠΕΡΙΛΗΨΗ

Βελτιστοποίηση της διαδικασίας παραγωγής σειράς προϊόντων κατά παρτίδες.

Αναπτύχθηκε μοντέλο υπολογιστή με το οποίο προσομοιάζεται υφιστάμενη διαδικασία παραγωγής κατά παρτίδες που ακολουθείται για σειρά προϊόντων. Το μοντέλο έδωσε τη δυνατότητα να ερευνηθούν οι επιπτώσεις διάφορων μεταβολών και χρησιμοποιήθηκε για τον εντοπισμό των θέσεων συσσώρευσης (bottlenecks) και την αναζήτηση τρόπων με τους οποίους είναι δυνατόν να αυξηθεί η παραγωγική ικανότητα. Στους παράγοντες που λήφθηκαν υπόψη περιλαμβάνονται καθυστερήσεις λόγω αναμονής των μηχανημάτων, καθυστερήσεις λόγω τυχαίων μηχανικών βλαβών και διάφορα άλλα απρόβλεπτα.

P. A. PİLAVACHI

Στο σχήμα 1 δίδεται το διάγραμμα ροής της υπόψη διαδικασίας. Τα διάφορα χημικά προϊόντα παράγονται κατα παρτίδες σε αντιδραστήρες (R_1 έως R_m) σύμφωνα με την αντίδραση:



όπου το P αντιπροσωπεύει το προϊόν.

Το πρόγραμμα καταρτίσθηκε στη γλώσσα GPSS (για προσομοίωση) (2). Τα στοιχεία με βάση τα οποία καταρτίσθηκε το μοντέλο περιλαμβάνουν στατιστικές κατανομές για τα στάδια της παραγωγής, τα οποία είναι τα στάδια που ακολουθούνται στην υπάρχουσα εγκατάσταση. Με τα στοιχεία αυτά υπάρχει δυνατότητα χειρισμού στοχαστικών δεδομένων και είναι δυνατή η μοντελοποίηση τόσο διαδικασίας κατά παρτίδες όσο και συνεχούς διαδικασίας. Η ανάλυση αυτή περιλάμβανε τον προσδιορισμό κάθε στοιχείου που επηρεάζει τη λειτουργία της εγκατάστασης και τη συλλογή των σχετικών δεδομένων και τελικά τον υπολογισμό της ολικής παραγωγικής ικανότητας.

Το μοντέλο χρησιμοποιήθηκε για την προσομοίωση χρονικής περιόδου ενός έτους. Η συμφωνία των αποτελεσμάτων του μοντέλου με τα δεδομένα από την υπάρχουσα εγκατάσταση επαλήθευσε το μοντέλο.

Πραγματοποιήθηκαν υπολογισμοί για διάφορες περιπτώσεις. Τα αποτελέσματα συνοψίζονται στον πίνακα II. Όπως φαίνεται, ακολουθώντας διάφορες πολιτικές για τη λειτουργία και με ορισμένες τροποποιήσεις της εγκατάστασης είναι δυνατόν να αυξηθεί σημαντικά η παραγωγική ικανότητα.

Μελλοντικά, το μοντέλο θα εφαρμοστεί για τον υπολογισμό της παραγωγικής ικανότητας σε περίπτωση που επέρχονται άλλες σημαντικές μεταβολές στην εγκατάσταση. Θα εφαρμοσθεί επίσης και σε άλλες διαδικασίες παραγωγής.

REFERENCES

1. Ku H.M. et al, *Chem. Eng. Prog.*, 35, August 1987.
2. Greenberg S., *GPSS Primer*, Wiley-Interscience 1972.
3. Felder R.M. and Kester P.M., *Chem. Eng. Prog.*, 84, June 1983.
4. Wilson J.A., *Proc. Eng.*, 45, June 1987.