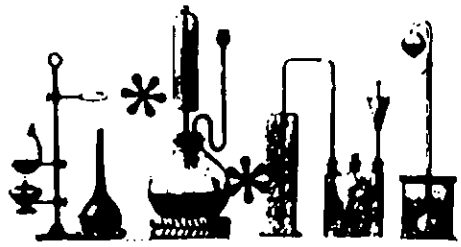
October 1980 Vol.44 No.5

Chemistry in new zealand

Official Journal of the New Zealand Institute of Chemistry, P.O. Box 1926, Christchurch.

INSIDE: Silica — In Theory & Geothermal Practice; Geothermal Corrosion; Corrosion of Fibreglass; Clay-Polymer Systems; Corrosion in Boiler Plant; Control of Industrial Cooling Systems.



New Products, Services

WATER CONDITIONING EQUIPMENT

Described as the largest water treatment company in USA, Culligan International has recently named Lennard, Tuck & Co. as NZ distributors of its water conditioning equipment.

Currently available in 92 countries, the Culligan range is comprehensive. Basically the equipment covers depth filters, de-ionizers, reverse osmosis units, desalination plants, softeners and cyclone separators. The depth filters are unique in their flow rates and economy. Typically a sand filter will operate at 13 to 23 litres/min/sq ft. of media. Culligan depth filters have flow rates almost 7 times faster than conventional sand filters and are said to produce greater clarity by removing particles down to 10 microns. The entire bed traps turbidity enabling long runs between backwash cycles which require 85% less water.

Multi-Tech is the name Culligan has given to its filtration systems for potable water supplies. For a much lower capital investment, less site preparation and reduced supervision Multi-Tech claims to give superior product water quality than conventional settling basins, open clarifiers and open sand filters. By the use of modular design, increased water demands are fulfilled with low cost and rapid installation. The systems produce potable water at flow rates from 170-3000 LPM at a conservatively estimated saving of 40%.

All units throughout the range are pre-engineered, automatic, simple to install and cover a wide selection of sizes. For example, design flow rates for softeners go up to 2,800 LPM, depth filters 1,800 LPM and de-ionizers 2,000 LPM. However, many sizes are available and at the other end of the scale Culligan equipment will condition water at 700 mls/min.

To service and promote the Culligan concept of "Treating Water Seriously", a seminar was held in Auckland recently.

These products are available at the Lennard, Tuck branches in Auckland, Wellington, Christchurch and Dunedin.

CO64 for further details, use Reader Service Card.

DISCS

The introduction of the following new discs from Tintometer Ltd, UK, is announced by Selby-Wilton Scientific Ltd.

Phosphate: The method is suitable for the analysis of most industrial waters from cooling systems, boilers and associated plant treated with phosphate based or organo-phosphorus based products. The method has distinct advantages over other techniques and is based on the reaction of orthophosphates with ammonium molybdate and potassium antimonyl tartrate to form phospomolybdic acid which is reduced to molybdenum blue by ascorbic acid. The method is listed by the American Public Health Association (APHA).

Nitrite: The presence of nitrite in water is a clear indication of pollution. Now available is a new simplified version of a nitrite test using disc 3/103 and a single tablet reagent. The test is based on the APHA recommended reagent N1 — Naphthy Ethylene Diamine.

Zinc: A new simple tablet reagent used with a new Lovibond Zinc disc 3/102 is now available for the determination of zinc, which is added to industrial cooling water as an anti-corrosion agent and it is important to periodically check that the required level is maintained.

CO60 For further details, use Reader Service Card.

DIGITAL RESISTIVITY MONITORING SYSTEM

Unprecedented accuracy in the monitoring and control of pure and ultra-pure water is now a reality with the recent introduction of the 921D Digital Indicating Resistivity Monitoring System by the Balsbaugh Center of Foxboro Analytical.

The new 921D, the first microprocessor-based resistivity monitoring system, provides adaptive automatic temperature compensation through use of a microprocessor in a digital computation system. This microprocessor computation used in conjunction with a solid-state temperature sensor in the cell provides highly accurate measurement. Once the resistivity and temperature are measured, the value at 25°C is automatically calculated and displayed on a 3-digit LED readout. This value is used to provide signals to the alarm and output circuits. A simple touch of the digital display front panel switch permits instant viewing of either the alarm set point or the process temperature with no interruption of the measurement or the output signals.

Modular in construction for easy servicing, it features all solid-state circuitry mounted on the power supply, display, and function boards. The monitor is small and compactly designed for panel mounting. The enclosure meets NEMA 3 environmental standards, say the NZ representatives, W. Arthur Fisher Ltd.

CO62 For further details, use Reader Service Card.

ION CHROMATOGRAPHY SYSTEM

Tracor Instruments, manufacturers of a photo-conductivity detector used for selective detection of halogen and nitrogen compounds in HPLC effluents, have released information to demonstrate how this detector will effectively detect low concentrations of both anions and cations by the selection of appropriate counter ions and columns.

For anion analysis column packings of low capacity (eg 0.04 milliequivalents/gram of resin) are selected. These permit the use of solvents with low concentrations of competing anions. Typically, solvents containing 5 x 10-4m phthalic acid or benzoic acid are used, say the NZ agents, Advanced Electronics Ltd, Auckland.

Several interesting chromatograms are available, illustrating the following:

1) Anion separation of a synthetic mixture of C1, NO_2, Br, NO_3, and SO_4;
2) Synthetic mixture of C1, NO_2, Br, NO_3, and PO_4;
3) SO_4 in tap water;
4) Synthetic mixture of cations giving good separation of Li, Na, NH_4 and K.

The main advantage of the detector system is that it can usually be added to existing HPLC pumps for less than $6,000, or supplied as a complete system for $12,500.

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CALCULATING PRINTER

The increased use of microprocessors has significantly raised the performance of electronic balances. As a result, peripheral instruments must also meet higher performance standards. Weight values in labs and industrial plants must be identified and recorded. But without the date, time and article number, even printed records are incomplete and can cause mistakes and misunderstandings.

This is where the Mettler GA23 comes into play. Connected to any Mettler balance equipped with an 03 Data Output, this calculating printer is suitable for the following applications:

- It continuously adds up individual values, then calculates subtotals and grand totals.
- With the touch of a button, the GA23 automatically calculates and prints out the mean value of a series of results.
- When the appropriate factor is entered, the instrument converts weight values into other units of measurements.
- The GA23 continuously compares individual weight values with a desired reference or target value.
- Calculated differences are indicated in absolute terms and in percent.

If needed, the Mettler GA23 calculating printer turns into a full-fledged office calculator than can be used all by itself.

NZ agents are Watson Victor Ltd.

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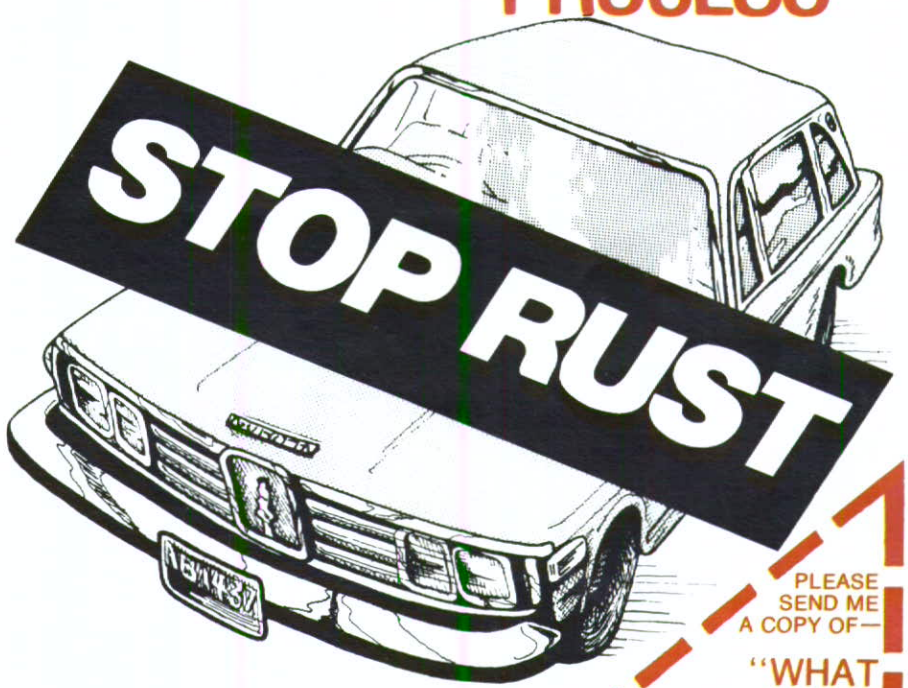

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STOP PRESS

Guest Editorial

"RUST NEVER SLEEPS"

As this issue of our Journal contains several papers on the corrosion or degradation of materials, I am pleased to have been given this opportunity to speak out on this subject as a member of the Australasian Corrosion Association.

First, why bother about corrosion at all? The second law of thermodynamics tells us that it is inevitable, that all materials will undergo degradation; so why not accept this fact, allow the material to corrode and then replace the article when it is beyond redemption? Furthermore, corrosion control measures invariably appear as a negative quantity on any balance sheet, so why trouble with the costs of protective measures? The answers to these questions are becoming increasingly more urgent nowadays, because corrosion is like a disease — it is wasteful of materials, our diminishing resources and labour; it can indirectly lead to accidents; ruin the aesthetics of an attractive structure and cost the community, both individuals and the nation, a great deal of money. And like many diseases, it never sleeps!

The 1978 Report on the "Economic Effects of Metallic Corrosion in the United States" prepared by the National Bureau of Standards as directed by the US Congress, concluded that the cost of corrosion to America is about $70 billion per annum, with avoidable costs being in the vicinity of 15-25% of this amount. Translating these figures to the NZ scene (as at 1978) then each man, woman and child in this country pays out about $160 per annum for corrosion costs, of which about one quarter could have been avoided by applying knowledge that already exists! Thus corrosion may be defined as the science explaining how productivity and values are lost! And yet who in decision-making positions, both in Government and many commercial enterprises, really seems to care about this appalling wastage of our natural and imported resources?

The Australasian Corrosion Association with eight branches throughout Australia and NZ has a very real concern for this situation. The Association fully supports the recommendation of the Hoar Report (The Committee on Corrosion and Protection, UK, 1971) which, in the NZ context, advocates the following improvements to the current situation:

- There is a need for a focal point of all corrosion and protection interests in NZ and this could best be achieved by the establishment of a National Corrosion Advisory Service, which would reinforce rather than replace existing organisations.
- More effort should be made to instruct engineers, scientists, designers and architects in corrosion and control measures during their undergraduate and professional training.
- There should be more emphasis on corrosion theory and protection measures in post-graduate research, while co-operation and exchange of information should be encouraged between research bodies.
- There should be closer links between various institutions and organisations in the corrosion field throughout Australasia.

Although these aims are admirable and long term, the immediate need is to make the public **aware** of the present unsatisfactory situation. To this end, ACA is about to launch throughout Australasia a $20,000 colour film entitled "The Corrosion Problem", and our Association hopes that chemists and all scientists will have the opportunity to view this interesting and unique presentation, which we hope will stimulate future action in the technology of corrosion mitigation.

L.H. Boulton
Imm. Past-President
NZ Branch
Australasian Corrosion Association

Comment

'Pologetic Polemics From The Pulpit

The apostrophe before the first "P" in our title this time is due to our easing the load on our sacerdotal shoulders by taking off for sister dioceses in the Pacific, particularly Tonga and Samoa, where the ' is used to indicate a glottal stop and also to modify pronunciation. Travel broadens the ecclesiastical mind: We had always felt that the motto of the Presidents of the United States "In God we trust" merited our approval — how can it be otherwise with a nation that produced Billy Graham, Oral Roberts, and other evangelists who had the ear of Presidents and built Universities? However in American Samoa we saw this sign in a shop:

IN GOD WE TRUST
All others pay cash
No checks accepted

Enquiries from the staff elicited the fact that God was not a customer, so in fact the proprietor of the store trusted no-one.

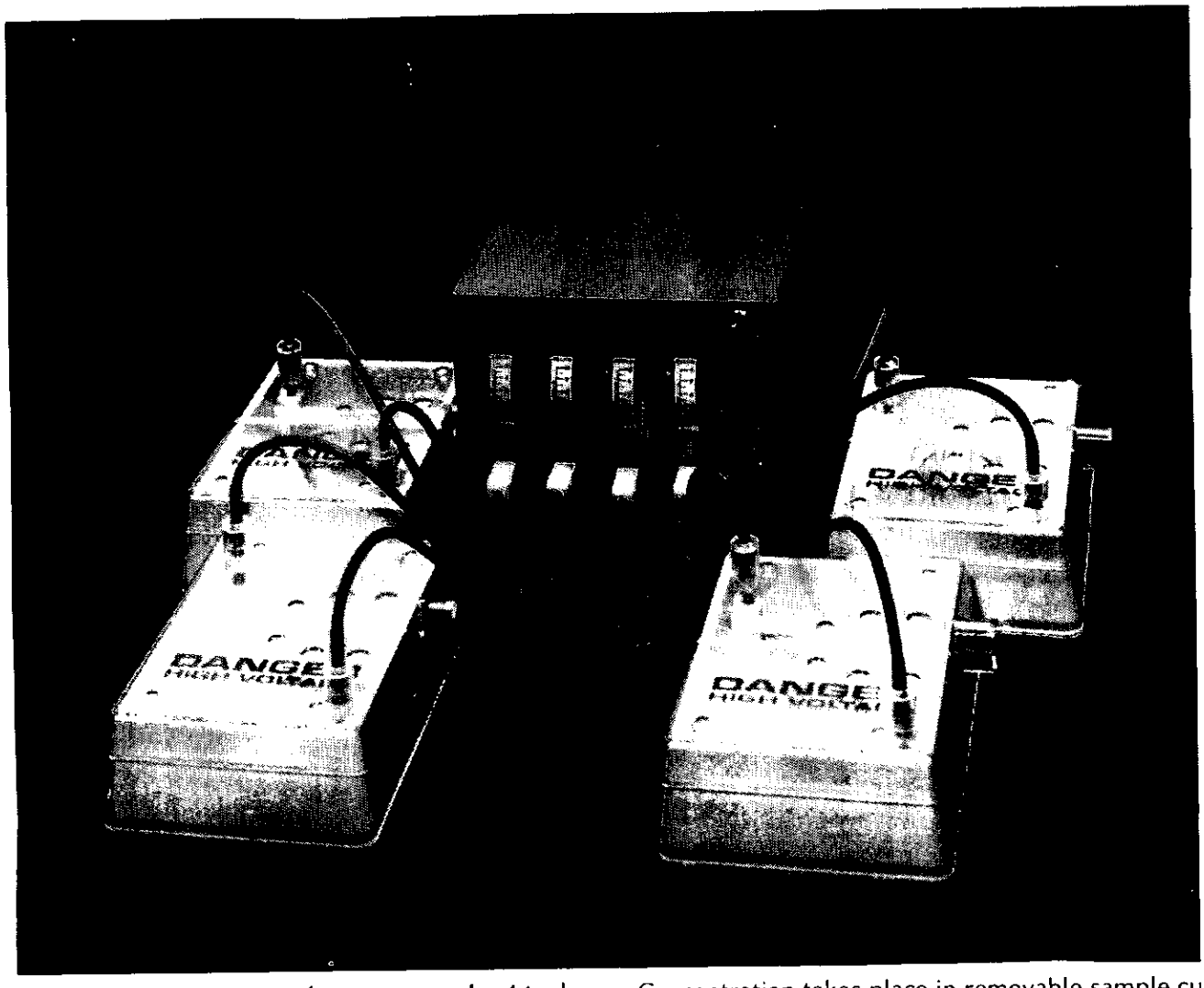
We have recently had our faith disturbed in another way. We had trusted computer readouts for changes of address and status of our members for adding to the information kindly supplied by our Branch Editors. But, alas, strong complaints from our brethren (and cistern) in the south; this information was wrong and in fact even offensive for which we are sorry. The sad lesson, and rude shock to our faith, is that we can no longer trust in the computer; like our American friends, only in God can we trust. However we need not fall back entirely on this ecclesiastical resource; we still trust many of our fellowmen and women who nobly help us with the Journal and the odd word of appreciation, which may be saying the same thing.

(As a postscript, those who do not receive this issue of Chemistry In NZ, and therefore miss the beauty of our sublime utterance, blame the computer, not US.)

And an ecclesiastical footnote: By royal decree, Sunday is the day of worship in Tonga, which suits the mainstream Christians, but puts the Seventh Day Adventists on a spot. However there is a way out of this diabolical dilemma. The SDA's say "Look at the map, and see the twisted line; we are not really one hour ahead of NZ, but 23 hours behind. Though King Taufa'ahu Tupou IV says it is Sunday, it is really Saturday and we are right after all, and the only ones who are right." Is there a moral in this story?

S.G. Brooker.

electrophoretic sample concentrator



The concentrator consists of a power supply, 4 tanks, and 20 cups. The molded tanks have a hollow central septum which separates the buffer chambers and supports one or two sample cups. Tube fittings allow cooling water to be passed through the septum when desired. The power supply provides controlled power (wattage) individually to each of the four tanks. All tanks are run at the same power, which can be set at either one or three watts*. Electrode connection is made through an interlock system in the cover to disconnect the power if the unit is inadvertently opened without turning off the power supply.

Concentration takes place in removable sample cups in a molded electrophoresis tank. Each cup has a large and small well covered at the bottom with a special cellulose dialysis membrane allowing passage of ions with molecular weights smaller than 3,500. The two wells are immersed in oppositely charged buffer chambers. For simple concentrations, both wells and the area connecting them are filled with a 10 ml unconcentrated sample. Sample ions migrate to the small (0.2 ml) concentration well and may be removed through plastic tubing with a syringe, after the overlying buffer has been pipetted off.

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October 1980

What's Happening

The Institute is very short of copies of issues of **Chemistry in NZ** for October and December 1979. Anyone who has copies to spare is invited to send them either to the Editor at 6 Koraha St, Remuera, Auckland, or Chemistry Dept, University of Auckland, or to the Registrar, Box 1926, Christchurch.

* * *

Royal Society on 2,4,5-T in NZ: After presentations made at the Annual Meeting of Fellows at which papers were read by **Prof McQueen,** Medical Research Council Toxicology Unit, Dunedin; **Mr I.R.C. McDonald,** Chemistry Division, DSIR; and **Dr D.M.O. Becroft,** Pathologist in Charge, Princess Mary Laboratory, Auckland, the RSNZ issued a press release stating that there were few grounds for regarding 2,4,5-T itself as having any important health hazards. The contaminant dioxin is extremely poisonous, but at the concentration currently present in the herbicide as distributed in NZ the possible hazard represented by dioxin appears negligible. It was also stated that sunlight, 2,4,5-T, and solvents used contribute to rapid breakdown of dioxin. It will be interesting to see how well this pronouncement from a learned group is accepted by environmentalists and other vocal groups. (Copies of the assessment are available from the Royal Society, Box 12249, Wellington).

* * *

Mike Kingsford, Convener of the NZIC Public Affairs Committee, has received an assurance from the Human Rights Commissioner that any concern over non-graduates having the same opportunities in the teaching profession as graduates is based on a misunderstanding. "Qualifications are usually stressed as one of the most relevant criteria" the Commissioner says.

The Commissioner has also ruled that fluoridation of water does not constitute a breach of human rights.

* * *

Strike upsets the American Chemical Society: Because of a continuing hotel and restaurant workers' strike in San Francisco, the American Chemical Society 180th National Meeting held concurrently with the 2nd Chemical Congress of the N. American Continent, scheduled for August 24-29, was transferred at short notice to Las Vegas, Nevada.

* * *

In a hand-out from the **USSR on science and technology,** we are informed that a group of scientists in Yakutia, a remote district in Northern Siberia, has discovered metallic aluminium in minute particles of 1mm diameter in basaltic rocks. The report goes on to say that 'A famous Soviet petrographer' and mineralogist, Academician **Vladimir Sobolev,** called the discovery of the Yakutian scientists "sheer absurdity" due to the disregard of the "fundamentals of elementary chemistry" .... and cast aside the evidence as "vulgar misinformation".' However a commission set up confirmed the find as the 'first fact of native aluminium discovery recorded in world science'.

* * *

Energy extracts: In audited tests conducted by General Motors on a number of their vehicles on roads around the North Island, it was found that LPG gave significant savings over petrol, and CNG showed better still, e.g. with a Commodore 6 costs per km were LPG 3.88c; CNG 3.02c; Petrol 4.90c. ---The Minister of Energy in a radio talk-back show over Radio Pacific, Auckland, said that for a motorist doing less than 10,000km per year, the saving would not warrant the cost of conversion. ---We talked with officials of one large company which has a number of vehicles converted to LPG and they could not confirm these savings, which may have been due to not having installed conversion units which matched with cars.

A writer in "Science" (USA) says "It takes about ¼ acre of cropland to provide enough food for the average person in the third world. It would take almost 8 acres to grow enough grain to run an average American automobile entirely on grain derived alcohol."---Workers at Massey University have been experimenting running vehicles on vegetable oil produced in NZ (rapeseed oil) and found some difficulties with the fuel injection system. Tallow converted to methyl or ethyl esters could be an alternative. ---An article in the "New Scientist" for August 21 cites the work of **Melvin Calvin,** who won the Nobel Prize for his work on photosynthesis in 1961, and **Sir George Porter** of the Royal Institution, London, who predicts that in two years ways will be found to split water into H and O by the action of sunlight. Thus an ideal fuel could be obtained.

* * *

Contact lens may be a hazard in the laboratory says "Chemical and Engineering News", since any chemicals getting into the eyes are harder to remove. It is therefore all the more important that people with contact lenses wear safety glasses.

HAMILTON AWARD 1981

The Hamilton Award is presented by the Royal Society of NZ for "scientific research carried out in NZ or in the Islands of the South Pacific which has been published within 5 years preceding the last day of January 1980. Such publications may consist of one or more papers and shall include the first investigation published by the author. No candidate shall be eligible for the prize who prior to such period of 5 years has published the results of any scientific investigation in a recognised scientific journal."

No award will be made unless in the opinion of the RSNZ Council, there is evidence of scientific work of great merit. The 1980 prize was awarded to Dr R.M. Lewitt for his work on medical image processing.

Nominations should be sent to the General Secretary (Box 1926 Christchurch) by November 30. At least 2 copies of the relevant publication and a supporting statement should accompany the nomination.

Our man with Shell Oil NZ Ltd, **Alan Turner,** has been responsible for the technical content of the company's new booklet "The Shellman Guide to Safe Handling and Use of Petroleum Products", which is a good thing. Copies are available from Shell offices, depots, and some service stations, or direct from their Head Office, Box 2091, Wellington.

* * *

The main topic of interest in Otago/Southland at present is the possible construction of a new aluminium smelter in the area. There has been substantial local comment both for and against the proposed project says Branch Editor **Stuart Gray.** If the project proceeds as planned, it will have a considerable impact on the Dunedin area.

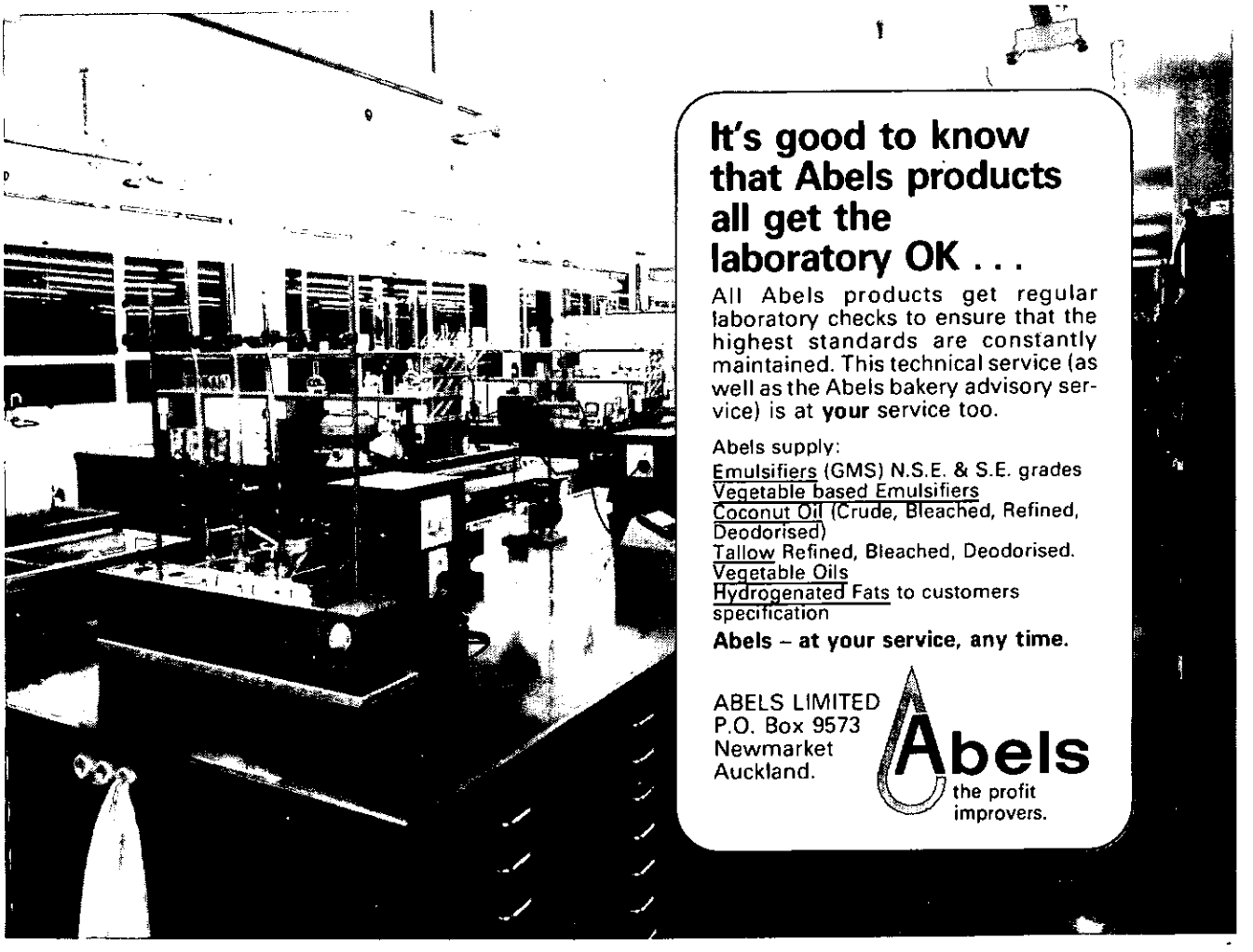
Golden Jubilee Issue

The February 1981 issue of CHEMISTRY IN NZ will be a special issue devoted to the history of the Institute as the Journal's contribution to the Golden Jubilee celebrations. Although the Institute was actually formed in November 1930, the first President, Prof W P Evans was not appointed until the following February, so that February 1981 may well be considered the actual date when we should celebrate the event.

It will be a specially enlarged issue and any members who have reminiscences or documents that would be of interest in this connection are asked to communicate with the Editor at 6 Koraha St, Remuera, Auckland 5.

List of Members

An updated list of members will be published in the Yearbook which comes out in November. Any member who feels that his or her entry in the alphabetical list OR the occupational breakdown is incorrect, should immediately advise the Registrar, Box 1926, Christchurch. "Immediately" is the operative word, as the publication schedule for the Yearbook is fairly tight.



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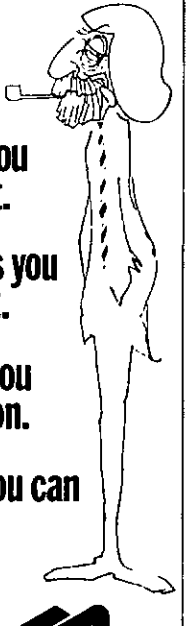

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People

We would pay our tribute to the contribution that **Gavin Fletcher** has made to the Institute. He took over from **Prof W.E. Harvey** as General Secretary in 1977, and has not been content at any stage merely to carry out the mechanics of the job, but has had many innovative ideas, to some extent drawn from his experience with other organisations, and these are reflected in the progress of the Institute. Gavin is a busy man, with his demanding job in the Applied Research Office at the University of Auckland, his keen interest in the Kiwanis organisation, and as one who does not take his home responsibilities lightly, but such people are often the ones that produce ideas which are of lasting value. It is the Editor's personal contention, after nearly 40 years continuous service to the Institute in some capacity or other, that the period of office of the President of only one year hardly allows him or her time for much innovation and we are therefore dependent a good deal on the Secretary — and the Registrar — for this. In Gavin we have been well served and his place will be hard to fill.

We apologize for some errors in our August issue, which were due to taking information from a computer readout — a genuine excuse this time. **Dr Marion Robinson** is Professor in Human Nutrition in the School of Home Science at Otago; **Prof Fastier** has retired, while KP and Chem Industries for which **Mrs Simpson** works are the same company.

Two chemists have recently been appointed principals of Christchurch High Schools. They are **Messrs J.D. Murdoch** (Cashmere) and **W.G. Swan** (Linwood).

A recent visitor to the Campus of the University of Canterbury was **Dr J.I. Vargas,** Director of Industrial Technology in the Brazilian Ministry of Industry and Commerce. Dr Vargas, a Cambridge graduate and former professor of Chemistry spoke on chemical and industrial development in Brazil.

Dr Don House has recently returned from a period of study leave spent at Stirling, Scotland, and Neuchatel, Switzerland. **Dr Alan Hopper** recently attended a conference at Santa Cruz, California and **Prof Leon Phillips** was a speaker at the Australian Spectroscopy Conference in Sydney.

Mr A. MacDonald, has recently been appointed Laboratory Manager with B.J.N. Holdings Ltd., Auckland. He is a very active member in the Auckland Branch of the Oil and Colour Chemists' Assn., and is acting as an unofficial liaison officer between OCCA and the NZIC. **Mr P.Y. Phang** B Sc (Singapore) has joined the staff of T.J. Sprott and Associates Auckland. **Mr M.W. Phillips** M Sc (Waikato) is now an analyst with Flinders-Cook Technical Services Ltd., Auckland. **Mr J. Child** now has the position of Technical Officer with the Natural Gas Corp. Hawera. **Miss T.H. O'Connell** is now with Waitaki-NZ Refrigerating Co at Wairoa, H B. **M.L. Jansen** has gained his Ph D from Calgary, Alberta, and is now with the Building Research Assn., Porirua. **Mr B.I. Mattingley** is at Cawthron Institute Nelson. **Mr R.S. O'Mahoney** is now at Waitakere College, Auckland.

Prof R.C. Cambie (Chemistry Department, Auckland University), national representative for the Chemistry of Natural Products Network, will be attending the Co-ordinating Board Meeting of the Regional Network and the 4th Asian Symposium on Medicinal Plants and Spices, to be held in Thailand during September 1980. He has been invited to present a paper at the Symposium.

Mr B.E. Cavitt has transferred from the Ministry of Agriculture and Fisheries, Mt Maunganui to the Environmental Lab., Health Dpt., Auckland. **Dr M.L. Daroux,** of the University of Auckland, is now at the University of Southhampton, England. The new address of **Dr J.D. Featherstone,** previously at the Dental Research Unit, Wellington is Eastman Dental Centre, 625 Elmwood Avenue, Rochester, N.Y. 14620, USA. **Prof B.J. Welch,** previously of the University of NSW, Sydney, is now Professor and Dept. Head, Dept. of Chemical and Materials Engineering, University of Auckland.

Mr N. (Nick) E. Jarman, General Manager of the Fishing Industry Board since 1976, has received the prestigious J.C. Andrews Award for 'eminence in food technology' for 1980. Previously he had been Technical Manager at the Alliance Freezing Works in Southland. He has represented NZ at Codex Alimentarius meetings concerned with both meat and fish. (Being an old boy of Christchurch Boys' High School like ourselves no doubt put his foot on the first rung of the ladder of success — Ed.) The award is made annually by the NZ Institute of Food Science and Technology. He has recently been appointed to the Scientific and Technical Advisary Group (STAG) of the International Frozen Food Association.

Dr D.W. Smith, Waikato University is on leave until January 1981, during which time he will visit a number of institutions abroad. **Dr P.J. Morris,** also of Waikato, is at the Physical Organic Laboratories, Murdoch University, Perth, WA until January.

Shell Oil (NZ) Ltd has welcomed to their laboratory **Janet Chrobock** from South Africa, while another immigrant from South West Africa, **Mr Goldsmith,** is joining the BP (NZ) Ltd laboratory at Seaview.

At Unilever (NZ) Ltd the chief chemist, **Mr Paul Milsom,** has been promoted to Product Development Manager and **Mr Andrew McQuillan** has left Development to become Production Manager, Powders.

Mr N.R. Edmonds took over the appointment of Course Supervisor, Chemistry Section of the Applied Science Department, Auckland Technical Institute from **Mr L.H. Boulton** at the end of the second term.

Gavin Fletcher resigns from the position of Executive Officer, Applied Research Office, University of Auckland at the end of September to become Director, Heavy Engineering Research Association. In his new position he will be based at the Association's offices at the Manukau City Centre and will be working on services to the heavy steel and structural industry. An unfortunate consequence to this change of job is that Gavin has had to resign as General Secretary of NZIC.

Mr T.R. Butler has joined the NZ Fertiliser Manufacturers' Research Association as a Chemical Engineer. He was previously in the Research and Development Engineering Section of UEB Industries Ltd.

Dr Roger Whiting has joined the staff of the Auckland Regional Authority Water Laboratory as Scientist (analytical). Roger completed his PhD in chemistry in 1975 at Auckland University under **Dr G.A. Bowmaker** researching nuclear quadrupole resonance.

After completing his doctorate Roger worked as a chemist for Roan Consolidated Mines in Zambia for 2½ years. He returned to NZ and worked for Nylex Fletcher Ltd as Chemist and Production Superintendent for 2½ years before taking up his present position.

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Meet The President

Dr Ellis

Dr A.J. Ellis, Assistant Director-General, DSIR, is now President of the Institute. He received his primary and secondary education in Invercargill before proceeding to the University of Otago where he graduated M.Sc. (1st) in Chemistry in 1953. This was the same class as a previous Institute President, **Dr C.L. Davey,** Director of MIRINZ.

Dr Ellis worked first in the Dominion Laboratory, DSIR, Dunedin, on food chemistry, and later in Wellington on paint chemistry. In 1956 he returned to Otago University to complete a PhD in hydro-thermal geochemistry, a topic which occupied much of his later career in Chemistry Division, DSIR, Lower Hutt. From the late 1950s as Section Head in Geochemistry his job was to build up a team in Lower Hutt and Wairakei to service the geochemical requirements of the geothermal areas in the North Island.

An international team was recruited to undertake basic chemical research on the properties of high temperature water solutions so as to be able to interpret quantitatively the many analytical chemistry results on natural water and steam compositions. Other geochemical activities included mineral survey and development work, and chemical volcanology. In the mid-1960s he studied geochemistry at Imperial College and electrotype chemistry at Southampton University on a Nuffield Fellowship.

In the late 1960s and early 1970s Dr Ellis was associated with many overseas geothermal developments, as a consultant for the United Nations and other international organisations in countries such as Chile, Turkey, El Salvador, Guatamala, Taiwan and Japan. He also represented the Department at many coferences overseas in Europe and North America.

He became Director, Chemistry Division, DSIR, in 1971. The decade following was one of rapid expansion, particularly in the industrial chemistry, mineral development, energy areas and with an increasing need for services in the health and forensic science areas. Time for personal chemistry became limited but some studies on water chemistry, and environmental chemistry were completed.

In 1979 he was appointed Assistant Director-General, DSIR, with administrative responsibilities for Applied Mathematics, Chemistry and Physics and Engineering Divisions, Auckland Industrial Development Laboratory, Christchurch Industrial Development Laboratory, Industrial Processing Division, Wheat Research Institute. In this situation he is concerned with the development of work programmes and policy in the chemical processing and general manufacturing areas, transport, wood processing and various other scientific services.

He is an executive member of several organisations, including Consumer Council, TELARC, Meat Research Institute of NZ, Logging Industry Research Association, Research Institution for Textile Services. He is a Fellow of the Royal Society of NZ and recently completed a lengthy period on its Council, lately being Treasurer and Vice-President.

Dr Ellis is 50 and is married with 4 children, 2 of whom are still at home. The time for hobbies appears to be getting less and less but he is a reasonably effective woodworker and has been known to build a house in his spare time. He recently took 3 months' long service leave to tour Europe with his wife, something he recommends that all executives do about once every 5 years.

As President during the Institute's 50th Jubilee year, he looks to the collaboration of Branches and of members in showing the community the importance of chemistry to our economy and in our everyday life.

Silica — In Theory And Geothermal Practice

(1979 Mellor Lecture, to Wellington Branch, NZIC)
H.P. Rothbaum,
Chemistry Division, Department of Scientific and Industrial Research, Private Bag, Petone, New Zealand.

SUMMARY

Silica scales deposited by geothermal discharge waters prevent pollution control and therefore limit worldwide development of geothermal energy. Several novel methods for preventing silica-scaling are described, namely removal of silica with quicklime, elimination of air, acidification of the discharge waters and a treatment with ferric sulphate. The last method is the most promising, as it removes arsenic and also eliminates scaling; in addition it is relatively cheap and may result in recovery of much waste energy in the form of clean hot water. It is possible that this method may form an economic alternative to re-injection of the discharge waters.

Background laboratory work on the mechanism of silica polymerisation between 5°C and 180°C is described. We suggest that silica monomers preferentially react with polymers. At high temperatures far larger polymers (molecular weight 10^9) are formed than at low temperature (molecular weight 10^6). The reaction shows almost no temperature co-efficient, because there are so few polymers present at high temperatures.

The Mellor lecture commemorates the almost incredible coincidence that in the 1890's the University of New Zealand produced two geniuses, one of whom, Rutherford, became the greatest physicist of his age, while the other, Mellor, turned out to be the world's leading inorganic chemist. The latter's magnificent "Comprehensive Treatise on Inorganic Chemistry" is now over 50 years old and summarises the total conventional wisdom of classical inorganic chemistry; it reminds us of much that we tend to overlook today.

Dr Mellor would certainly have approved of a talk on silica, the most common inorganic material on the earth's crust. When water percolates through hot rocks, it becomes saturated with quartz at elevated temperatures; on cooling, the supersaturated silica monomers in solution can either polymerise (leaving the total silica concentration unchanged) or they can deposit as silica scales. In practice, depending on conditions, both these reactions occur to varying degrees, and one result is the beautiful silica terraces formed in geothermal areas. Mellor[1] correctly quotes the silica solubility at several temperatures, and states that silica can polymerise to colloidal silica of molecular weight greater than 30,000. What he could not foretell, is that these reactions undoubtedly limit development of conventional geothermal energy all over the world, because of deposition of hard silica scales from geothermal discharge waters. These scales will also hamper the proposed universal use of geothermal energy, in which water is heated by pumping it into fractured hot dry rocks.[2]

Discharge waters from existing geothermal power stations contain from 500 to 1000 g/t (the old units were ppm) of silica, while its solubility at 100°C is 370 g/t and at 20°C only 110 g/t of amorphous silica. While silica itself is not toxic, the resulting scales cause severe operational problems; in addition, harmful impurities such as arsenic and boron cannot be removed from the discharge waters by conventional chemical water treatment methods. Furthermore, the very large amounts of waste heat in the waters cannot be dissipated in conventional cooling towers, nor can any of this waste heat be recovered usefully in heat exchangers. Several methods have been used for disposing of geothermal discharge waters, and these have recently been reviewed by Defferding and Walter.[3] They include:

1. In the Wairakei power station in New Zealand, the main drain consists of two parallel channels used alternately. Silica scale is removed mechanically from the drain (Fig. 1) and the water is finally discharged into the Waikato River. However, the river has now reached its limit for acceptable thermal and chemical pollution, and further geothermal schemes will not be permitted to use this simple discharge system.
2. At Cerro Prieto in Mexico, the discharge water is piped into a lake, in which silica separates out; evaporation just balances inflow. Further extension of the power station is limited by the size of the lake.

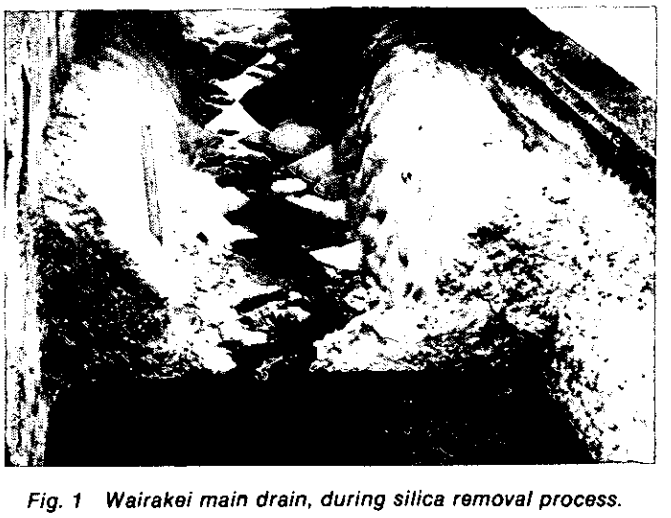


Fig. 1 Wairakei main drain, during silica removal process.

Dr H.P. Rothbaum studied at Victoria University, receiving a BSc (1946), MSc (1947) and BA (1951) and at Liverpool University, where he obtained a PhD (1956) in electrochemistry. He has worked at Chemistry Division, Department of Scientific and Industrial Research since 1947, with spells away at CSIRO, Melbourne (1953), Liverpool University (1954-56) and National Physical Laboratory, London (1964-66). He has invariably found that any applied development project will soon lead to some interesting chemical problem which one may not have suspected; he then tries to do some basic chemistry and bench-type development, as well as being involved in the joint pilot-plant work with chemical engineers. Such projects included vapour pressure determinations leading to work on salt production, measurement of bacterial heat-outputs resulting in theories of spontaneous combustion and industrial moisture control of wool and phosphorus oxidation studies ending up with new fertiliser formulations. Similarly, silica polymerisation chemistry was inevitably involved with geothermal pollution control.

All these "development" projects aim for better use of ever-diminishing uses of energy supplies in the hope of finding a reasonably acceptable balance between growth and conservation.

Dr Rothbaum's main hobby is playing the viola in chamber music groups, mostly led by his wife who is a violin teacher. Given this noisy family background, it is surprising that his son is shaping up as a keen cellist.

3. In Ahuachapan, El Salvador, geothermal discharge waters are high in boron, which is detrimental to tropical citrus agriculture. The waters are therefore reinjected at about 150°C into porous rock. This system has performed satisfactorily over a number of years, and also returns waste heat to the reservoir; however at this temperature it is less efficient and considerably more costly than the simple system used in Wairakei. At Otake, in Japan, reinjection is carried out at a lower temperature, and as a result there are severe problems with silica deposition in the porous rock, and blockages in the reinjection wells. In the Philippines, reinjection is being tried because of the high boron content of the geothermal discharge waters. At Ohaki, New Zealand's proposed second geothermal power station, it is also intended to reinject the discharge waters, because of their high arsenic content and large thermal pollution load; however, so far reinjection at Ohaki has not been completely proven in practice.

We have investigated several other alternatives for coping with the discharge waters; these are:

A. Treatment of the waters with slaked lime, to precipitate calcium silicate, together with some arsenic.[4]

B. Reinjection of the discharge waters without ex posure to air.[5]

C. Acidification of the discharge waters to reduce the rate of scale formation.[6]

D. Treatment of the discharge waters with ferric sulphate;[7] this simultaneously acidifies the waters (as in option C) and forms a floc of ferric hydroxide, which co-precipitates the arsenic.

This paper summarises these new alternative approaches, and also describes our work on the polymerisation rate of silica in water between 5°C and 180°C; the mechanism of polymerisation is discussed and we speculate how this is related to deposition.[8]

Method A:

Beaker tests in the laboratory showed that when freshly slaked lime is added to the hot discharge waters, calcium silicate is precipitated; this readily settles out and can be filtered off. Depending on the dose rate (300-800 g/t CaO) all or part of the silica is removed, and all or part of the arsenic is co-precipitated. This process was investigated in pilot-plant trials at both Wairakei and Ohaki. Fig. 2 shows the pilot plant in the Wairakei geothermal field (at this stage modified for acidification tests, see method C). Finally the Ministry of Works and Development built a pilot-plant which was 10 times as large, and they continually desilicated the discharge from a well in Ohaki for 2 weeks.

This method worked satisfactorily, but proved to be rather expensive; furthermore, if the total outflow from

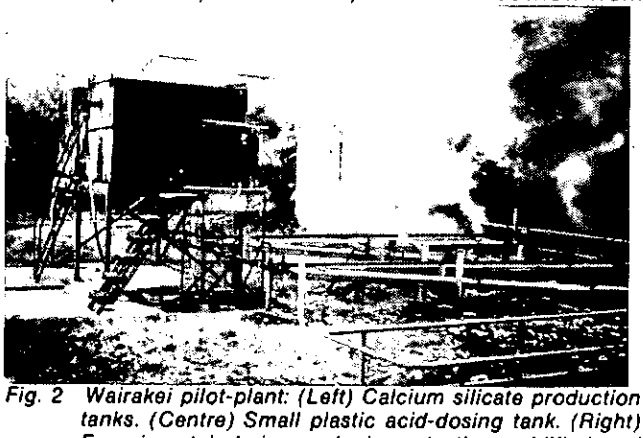


Fig. 2 Wairakei pilot-plant: (Left) Calcium silicate production tanks. (Centre) Small plastic acid-dosing tank. (Right) Experimental drains and pipes, testing acidified and normal discharge water.

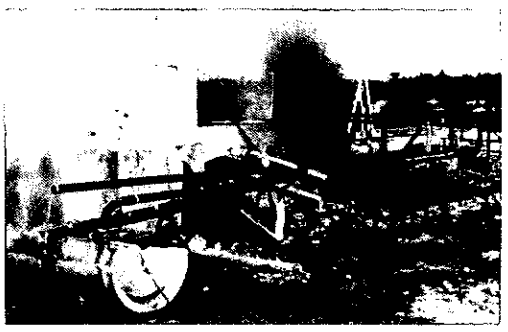


Fig. 3 Experimental flash unit in Ohaki, and experiment on the effect of aeration of geothermal discharge water on silica scaling rates.

Wairakei were treated, about 80,000 tonnes/annum of arsenical calcium silicate would be produced. Calcium silicate is a very useful high-temperature insulant, but as the total Australasian annual demand is only 5,000 tonnes, there would be a severe disposal problem. Currently a firm is designing a plant to manufacture arsenic-free insulating blocks, using about one-tenth of the Wairakei flow; they intend first removing arsenic from the water with ferric sulphate (see method D).

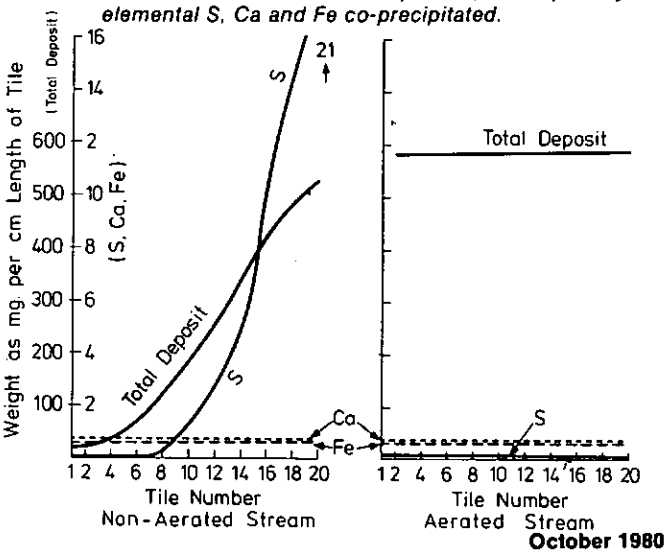
Method B:

McDowell[5] showed that if air is kept out of geothermal discharge waters, the rate of deposition of silica scales is greatly reduced. This is the simplest method of coping with discharge waters, especially for reinjection at temperatures well above 100°C. For example, successful reinjection in El Salvador probably depends on absence of air. However, at lower temperatures, exclusion of air is probably not sufficient to eliminate scaling.

We have investigated scaling rates[8] including experiments on the effect of aeration: Fig. 3 shows a small flash-unit that was built in Ohaki to deliver unaerated water to test pipes and an open field-tile drain, in which the water rapidly aerated. A second field-tile drain simultaneously tested fully aerated water, which had been stored for two hours to allow the silica in solution to polymerise. Results from these two tests (which lasted for one month) are shown in Fig. 4. In the first drain, as the water is aerated, deposition rates increased by a factor of 20. Elemental sulphur in the scales is an indicator of aeration, as the traces of H_2S in the water are oxidised. In the second drain, where the water was fully aerated, deposition is uniformly high along the whole length. The H_2S in the water has long ago been oxidised and any elemental sulphur has distilled off.

Fig. 4 also indicates that while aeration greatly increases the silica deposition rates, aeration does not affect the amount of impurity Ca and Fe co-precipitated as $CaCO_3$ and $Fe(OH)_3$. This suggests the importance of

Fig. 4 Effect of aeration of geothermal discharge water on amount of silica scale deposited, and quantity of elemental S, Ca and Fe co-precipitated.



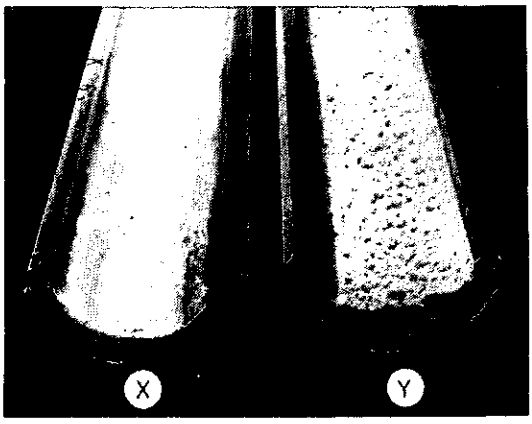


Fig. 5 Tiles after acidification experiment: X is acidified discharge water at pH 4. Y is normal discharge water at pH 8.2

X Y

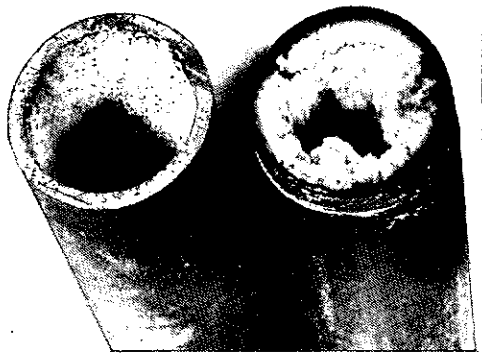


Fig. 6 Pipes after acidification: X is acidified discharge water at pH 4. Y is normal discharge water at pH 8.2.

nucleation, by traces of insoluble compounds, on the rate of silica scale formation. Furthermore one may speculate that air oxidises traces of ferrous compounds in geothermal waters to $Fe(OH)_3$ and in this way is responsible for initiating silica scaling.

Method C:

Extensive field tests[6] compared rates of silica scaling from geothermal discharge waters at the natural pH of 7 to 8 and sulphuric acid — dosed water at pH 4. Fig. 2 shows a typical experiment in progress and Figs. 5 and 6 show results of tests that had lasted two months. The effect of acidification is quite dramatic, and has reduced scaling by a factor of 100. Provided corrosion does not become a problem, acidification may provide an answer to geothermal scaling problems. In addition, the acidified, treated waters could be passed through heat-exchangers, to recover clean hot water, for industrial or home-heating use. In further tests the effect of pH values intermediate between 4 and 8 will be investigated.

We are not certain why acidification slows down scaling so much, but we believe that solubilisation of nuclei of $CaCO_3$ and $Fe(OH)_3$ (see Method B) may have a large influence.

The tanks shown in Fig. 2 were also used to investigate the effect of storage of geothermal waters for various periods, to allow time for silica to polymerise.[6] It had been claimed by Japanese authors[9] that storage of geothermal discharge waters for one hour, reduced silica scaling by a factor of 10. However, in our tests, polymerisation of silica had no effect on the quantity of scale produced, although in two experiments the scales formed from stored waters were rather softer than the scales from fresh waters.

Method D:

Arising out of the acidification work (Method C), we have developed jointly with chemical engineers, a new treatment method which simultaneously removes arsenic from geothermal discharge waters and stops silica scaling.[7] The water is treated with small amounts of ferric sulphate at elevated temperatures, where hydrolysis and flocculation occur far more quickly than at ambient temperatures. The ferric sulphate hydrolyses to sulphuric acid (which prevents silica scaling) and ferric hydroxide; the latter forms a floc, which co-precipitates nearly all the arsenic, and is collected by dissolved air flotation. The chemical engineers did an impressive development project, in using dissolved air flotation (previously only applied at ambient temperatures) between 80 °C and 90 °C. Arsenic from the floc can be quantitatively recovered and possibly used in timber preservatives, while the remaining ferric hydroxide is redissolved in sulphuric acid and recycled. As sulphuric acid is the only chemical consumed, the process seems quite economic. The acidified, treated waters could (as in Method C) be used for recovering clean hot water.

IPD (Industrial Processing Division) have run a successful pilot-plant using the ferric sulphate process in Wairakei, and we believe that this method may be a viable alternative to re-injection in certain situations.

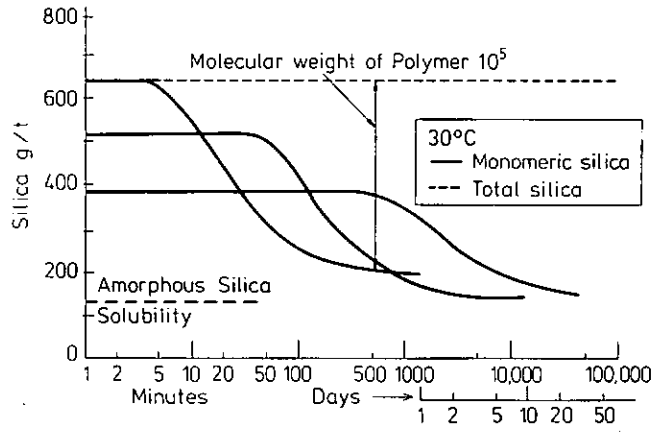


Fig. 7 Polymerisation of silica, determined at 30°C. Also molecular weight of polymers formed.

Polymerisation Of Silica:

Apart from these applied projects, we also studied the mechanism of silica polymerisation over a wide range of temperatures in the laboratory.[8] Figs 7 and 8 show typical silica polymerisation rate curves (each with 3 different initial silica concentrations) at 30 °C and 180 °C, the latter under pressure in gold bags. The figures also show the total silica concentration, and the molecular weight of the polymers remaining in suspension. Several points may be noted:

(i) Induction periods, before the silica polymerisation reaction commences, become larger at higher temperatures.

(ii) Once polymerisation has begun, there is almost no effect of temperature on the reaction rate. This is a most unusual and unexpected result, as most chemical reaction rates, over a temperature interval of 150 °C would increase approximately 2^{15} i.e. over 10,000 times.

(iii) At 30 °C the molecular weight of the polymers formed is approximately 10^5 and no silica deposition occurs.

(iv) At 180 °C the molecular weight of the polymers is approximately 10^9 and polymerisation leads to deposition.

These results suggested a rate equation and a physical picture of the reaction mechanism.[8] Silica monomers react very slowly with themselves, but rapidly with silica polymers. This accounts for the long induction periods before sufficient polymers

Silica (Cont)

are present. Furthermore, as much larger polymers are formed at high temperatures, there are considerably fewer polymers to react with monomers; this explains the absence of a temperature coefficient and longer induction periods at high temperatures. Much more work would be required to elucidate completely the mechanism of silica polymerisation.

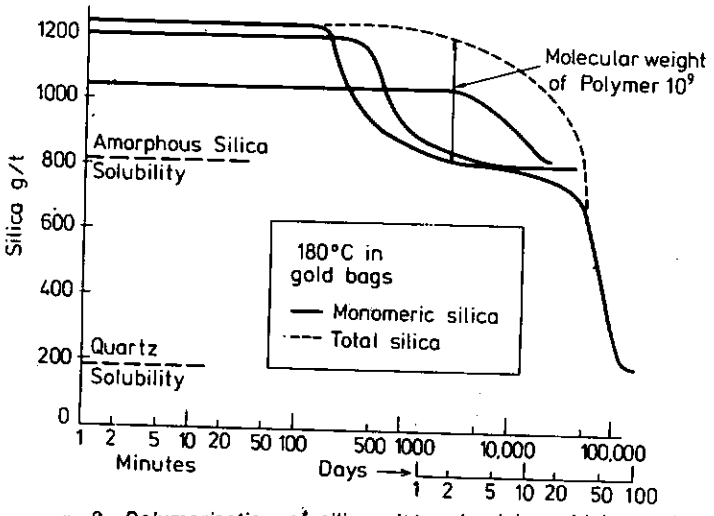


Fig. 8 Polymerisation of silica, determined in gold bags at 180° C. Also molecular weight of polymers formed.

Our picture of silica scaling is also one of silica monomers reacting with scale already formed by previous nucleation. In practice we find scaling in different geothermal fields is very dependent on local conditions of silica concentration, salinity, impurity content and pH. In addition, flow patterns of the water are important, with increased deposition rates when turbulent flow occurs. Our studies have led to the generalisation that large silica polymers in the water cling preferentially to pipes or drains, and monomers then react with the initial soft scale to cement or harden it. However, ultimately each geothermal field must be studied individually, and treatment methods must be devised in each instance to suit local water properties, and local idiosyncracies of finance and politics.

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GEOTHERMAL CORROSION

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Department of Chemical and Materials Engineering
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ABSTRACT

This article reviews a current research project on geothermal corrosion using electrochemical and metallurgical techniques. The mechanism of the anodic and cathodic processes, which are strongly influenced by the presence of hydrogen sulphide, can be determined from a study of the electrode kinetics.

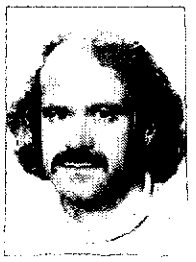
Introduction

Hot geothermal fluids are a valuable source of energy exploited in New Zealand for domestic heating (as in Rotorua), industrial processes (Kawerau), and generation of electricity (Wairakei). Geothermal fluids originate from water in contact with hot rocks and they contain a variety of dissolved substances taken up by chemical reaction with the rock minerals. These constituents remain dissolved in the hot water or steam when it reaches the surface and often cause problems due to scaling, deposition, corrosion and pollution when the geothermal water is released into the environment. Geothermal fluids usually do not contain oxygen, but corrosion of metals is promoted by constituents such as carbon dioxide and hydrogen sulphide which provide enough acidity for sustained corrosion. In chemically pure steam, as produced in conventional boilers in thermal power stations, iron and steel form a passive layer of the black oxide magnetite, Fe_3O_4. However, in contact with geothermal fluids, steel may corrode to form iron sulphides (H_2S present) or suffer pitting attack (Cl^- present). Ferrous alloys used for turbine blades, rotors and condensers may suffer stress corrosion cracking, corrosion fatigue or hydrogen embrittlement.

Since there is no economic alternative to the use of steel and ferrous alloys for the handling of geothermal fluids, it is necessary to monitor corrosion rates carefully and design equipment to minimise the effects of the corrosion which is predicted to occur. In order to gather corrosion data useful for engineering design and maintenance, extensive corrosion testing has been carried out both in New Zealand (by DSIR[1]) and overseas[2], and a great deal of empirical information has been accumulated. However, the corrosion reactions themselves are still not fully understood and there are many corrosion processes which are difficult to explain and control. Corrosion involves surface reactions which depend on the properties of the metal and the constituents of the corrosive medium. At the surface itself adsorbed intermediates such as hydrogen atoms and thin passive films such as Fe_2O_3 can play a major role.

This article reviews some research on geothermal corrosion being carried out at the University of

Dr Bruce G. Pound is a research officer in the Department of Chemistry at the University of Auckland. He obtained his PhD in electrochemistry at Victoria University and his general research interests are directed towards the thermodynamics and electrochemical kinetics of metal/water systems. He has worked in the field of high temperature electrochemistry and his present position is involved with research into geothermal corrosion.



Dr Graham A. Wright is Associate-Professor in Chemistry at the University of Auckland. His current research is in the field of electrochemical kinetics, including metal passivation and corrosion, and semi-conductor electrode mechanisms.

Dr Roy M. Sharp is a senior lecturer in the Department of Chemical and Materials Engineering at the University of Auckland. He is a metallurgist, a graduate of Oxford University, and he has research interests which encompass various properties of material, including corrosion behaviour.

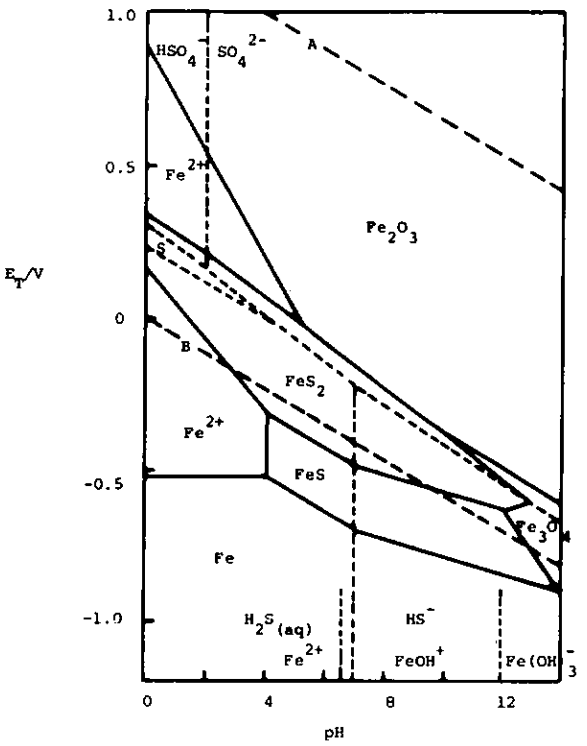


Fig. 1:
Potential-pH Diagram for Fe/S/$H_2$0 System at 298 K. The conditions selected apply to cold condensate at the Broadlands Corrosion Test Rig operated by DSIR (Fe^{2+}) = 10^{-4} mol l^{-1}, (H_2S + HS^-) = 10^{-3} mol l^{-1} Line B represents the equilibrium H_2/H^+ for 101 kPa hydrogen pressure, and line A represents the $H_20/0_2$ equilibrium for 101 kPa oxygen pressure (but 0_2 is normally absent or present only in trace amounts). S^{2-} was not considered since experimental evidence [10] indicates that its existence is unlikely in aqueous solutions.

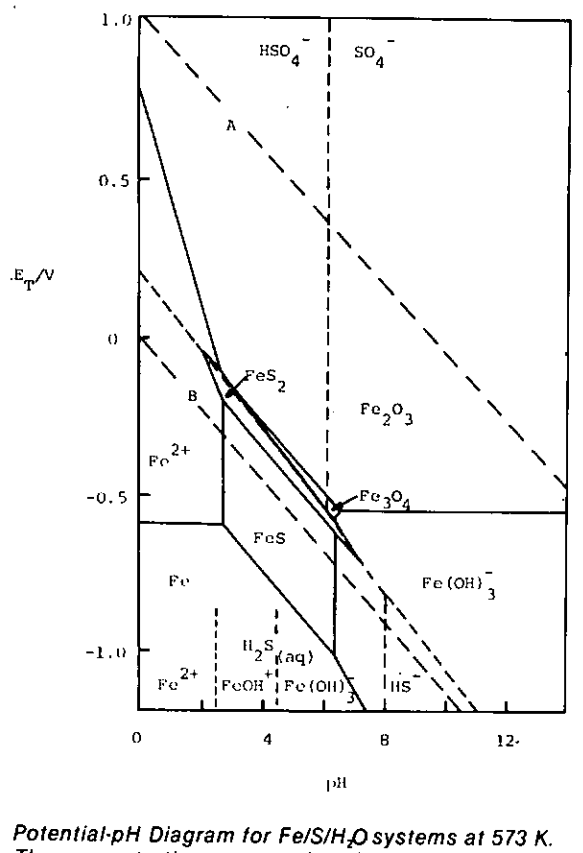
Auckland under a contract from the NZ Energy Research and Development Committee. The approach has been to investigate the mechanism of the corrosion reactions on steel and other alloys using electrochemical and metallurgical techniques.

Electrochemical Phase Diagrams

Corrosion equilibria may be represented by potential-pH (Pourbaix) diagrams[3] in which the thermodynamic limits of stability of a metal and its corrosion products are shown in terms of pH and equilibrium potential of the electrochemical reaction. Potential-pH diagrams for the Fe/S/H_2O system under different conditions have been presented by various workers.[2—8] The diagrams shown in Figs. 1 and 2 were constructed[9] for the composition of Broadlands geothermal condensate (condensed steam phase).

Phase diagrams can be used to predict corrosion products if the pH and electrode potential can be estimated. In non-aerated condensate at 298K (Fig. 1), for example, the corrosion potential will lie between the region of Fe metal and line B which represents the discharge of H^+ to H_2. Since FeS is the predominantly stable species near neutral pH, it is predicted that this compound will be the corrosion product. Ferrous sulphides occur in various crystallographic and stoichiometric forms ranging from an iron-rich phase, $Fe_{1+x}S$ (mackinawite), through stoichiometric FeS (troilite) to a sulphur-rich phase, $Fe_{1-x}S$ (pyrrhotite). Mackinawite is known [11] to be thermodynamically unstable relative to troilite, and pyrrhotite can exist over a composition range (x = 0 to 0.14),[12] so it is convenient to show only the stoichiometric form, troilite, in the phase diagram. Nevertheless, a predicted ferrous sulphide product is consistent with DSIR tests in which mackinawite was found to form on carbon steel in condensate at Broadlands.[1]

The effect of temperature on corrosion products in the Fe/S/H_2O system has been examined from potential-pH diagrams constructed[9] for various temperatures in the range 298 to 573 K. The stability region of FeS_2 (pyrite) appears to decrease rapidly with increasing temperature. This occurs to such an extent that whereas FeS_2 was stable over a greater region than FeS (troilite) at 298 K, the situation is reversed at 573 K (Fig. 2). At temperatures up to 573 K, both troilite and Fe_3O_4 (magnetite) are thermodynamically stable.



Potential-pH Diagram for Fe/S/H_2O systems at 573 K. The concentrations are as given for Fig. 1.

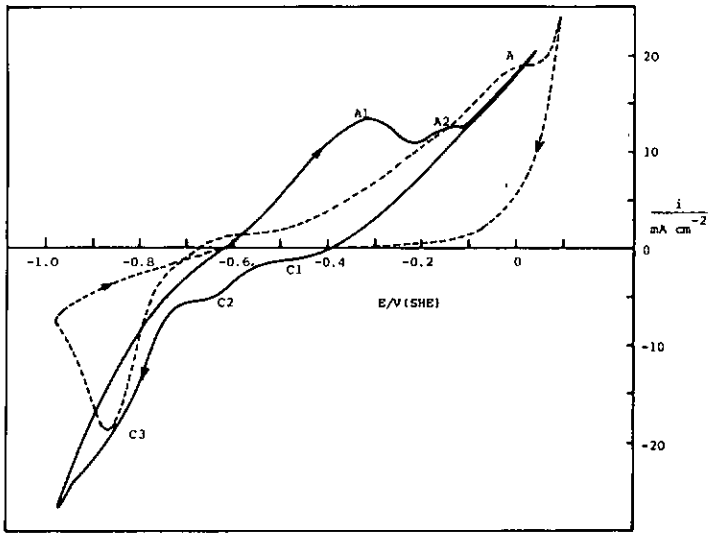


Fig. 3: Cyclic voltammogram of Iron in a Solution Containing NaCl and $NaHCO_3$.
(Cl^-) = 0.032 mol l^{-1}
(HCO_3^-) = 0.003 mol l^{-1}.
----- No H_2S, ———— H_2S present (0.055 mol l^{-1}, pH = 5.8)
Potential sweep rate = 100mV s^{-1}.

Aeration of geothermal media is known[1] to result in quite different corrosion products. In the presence of air, the corrosion potential can lie between the Fe region and line A which represents the equilibrium

$$O_2 + 4H^+ + 4e^- = 2H_2O \quad (1)$$

The potential-pH diagram at 298 K shows that Fe_2O_3 (haematite) is stable over a wide region and is therefore a likely corrosion product. However, it has been found[1] that the oxide formed under conditions of near-neutral pH is Fe_3O_4. In terms of the potential-pH diagram under these conditions, magnetite must be regarded as a meta-stable phase.

Anodic Reactions

The anodic oxidation reaction in the corrosion process and the surface films produced depend on both the potential of the metal and the nature of the corrosive medium. The potential regions in which the anodic and cathodic reactions occur can be found from cyclic voltammograms, obtained by linearly sweeping the potential of the test metal and following the current response.

The cyclic voltammogram of iron[9] in an aqueous solution containing NaCl and $NaHCO_3$ is shown in Fig. 3. As the potential of the iron is scanned in the positive direction, a film of oxide forms on the surface. This process is indicated by the shoulder, A, in the anodic current and the large cathodic peak which corresponds to subsequent reduction of the film. The sharp increase in current following A corresponds to a breakdown of the film; pitting occurs and passivation of the iron does not take place.

When the direction of the potential sweep is reversed, higher currents result as shown in Fig. 4, signifying that the pits continue to grow. Eventually pit growth is reduced and the current exhibits a steep decrease. The

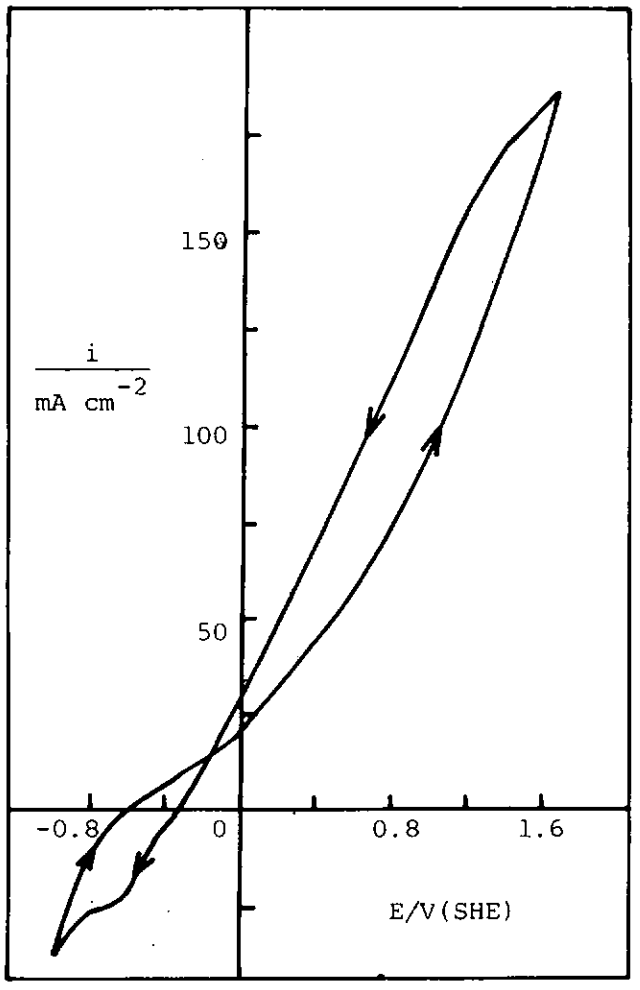


Fig. 4: Cyclic voltammogram showing pitting region of iron. Solution composition as indicated in Fig. 3. Potential sweep rate = 100 mV s^{-1}.

role of chloride in the pitting of metals is well documented and the occurrence of pitting on iron in the Cl^-/HCO_3^- solution is therefore to be expected. A scanning electron microscope examination of the iron confirmed that pits had formed extensively over the surface.

In the presence of H_2S, the anodic reactions on iron occur at higher rates as apparent from Fig. 3. A black solid product which was identified by x-ray diffraction as the iron sulphide, mackinawite, is formed in the potential ranges of A1 and A2 (Fig. 3) according to the reaction:

$$(1+x)Fe + H_2S \rightarrow Fe_{1+x}S + 2H^+ + 2e^- \quad (2)$$

The mackinawite is non-adherent and readily spalls from the metal surface. Despite this high loss of material, a thin film of the sulphide remains on the iron and is available for reduction back to iron at sufficiently negative potentials. The cathodic reduction of the mackinawite gives rise to the series of arrests, C1-C3, observed in the cyclic voltammogram.

The corrosion potential, E_{corr}, of iron in the solutions containing H_2S corresponds to the potential at which i = O in the cyclic voltammogram. The value of E is -0.62 V which lies in the FeS (troilite) region of stability in the potential-pH diagram shown in Fig. 1. Since troilite is thermodynamically stable with respect to mackinawite, we conclude that mackinawite is a metastable reaction product whose appearance is controlled by kinetic factors rather than thermodynamics.

Mackinawite itself was electrochemically oxidised[9] in the absence of H_2S using a carbon paste electrode. The paste consisted of a finely ground mixture of mackinawite and graphite in 10 mol l^{-1} ammonium acetate solution. In principle, this type of electrode allows most of the solid to undergo reaction because of the close contact with the electron-conducting graphite.

The potential sweep curve for the anodic oxidation of mackinawite is shown in Fig. 5. Two oxidation steps are observed and an x-ray diffraction examination identified sulphur as the dominant product at both peaks. The conversion of mackinawite can be considered to proceed according to the reaction:

$$Fe_{1+x}S \rightarrow S + (1+x)Fe^{++} + 2(1+x)e^- \quad (3)$$

in which the formation of sulphur evidently takes place on the surface of the iron sulphide particles. The second oxidation peak appears to correspond to a reactivation of the sulphur-forming reaction, possibly due to a change in the composition of the underlying iron sulphide.

Cathodic Reactions

In a neutral, deaerated solution in the absence of H_2S, the cathodic reaction involves the evolution of hydrogen.

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^- \quad (4)$$

When H_2S is present, hydrogen is formed by the reduction of H_2S, [13]

$$2H_2S + 2e^- \rightarrow H_2 + 2HS^- \quad (5)$$

giving rise to an increased cathodic current as shown in Fig. 3. Stirring of the solution promotes the transport of H_2S to the iron surface and thereby causes a substantial increase in the current. It can be seen from Fig. 3 that the hydrogen-evolution current also depends on the potential applied to the iron. Potential-step experiments

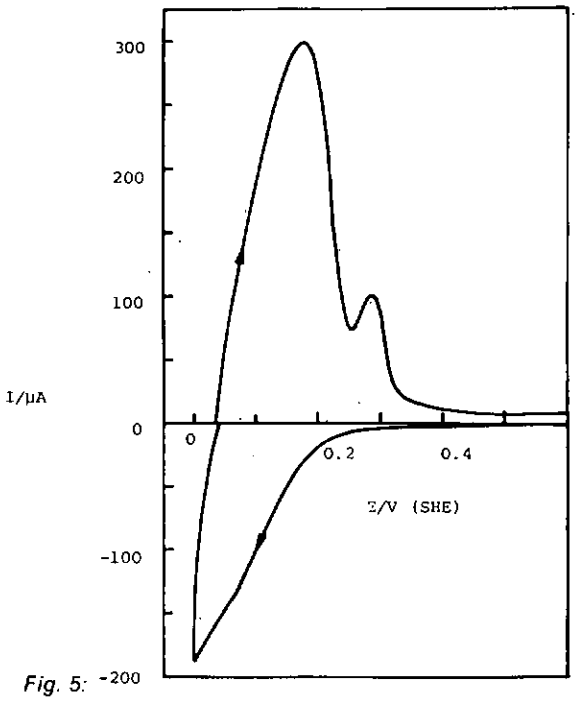


Fig. 5: Oxidation of Mackinawite at the Carbon Paste Electrode
Potential sweep at 0.1 mV/s using 1 mg $Fe_{1+x}S$ + 30 mg graphite (particles 30 to 50 m) in 10 mol l^{-1} NH_4OOCCH_3 at 20°C.

have established that the rate of H_2S reduction is controlled partly by the transfer of charge and partly by the diffusion of H_2S to the metal surface. By measuring the AC impedence of the electrode reaction over a wide range of frequencies, we have shown that the formation of hydrogen by reaction (5) involves adsorbed hydrogen atoms, H(ads). Their presence on iron in solutions containing H_2S was detected by use of an anodic potential-step technique in which the charge, Q_A (Fig. 6), passed was attributed to the oxidation of adsorbed hydrogen. The mechanism of reaction (5) is then as follows:

$$H_2S + e^- \rightarrow H(ads) + HS^- \quad (6a)$$

$$\text{and } H_2S + H(ads) + e^- \rightarrow H_2 + HS^- \quad (6b)$$

$$\text{or } H(ads) + H(ads) \rightarrow H_2 \quad (6b')$$

At sufficiently negative potentials, Q_A is greater than that expected for a monolayer of adsorbed hydrogen on the iron surface. It is assumed that some H(ads) dissolves in the metal to form interstitial hydrogen atoms which diffuse into the bulk metal. The excess charge is then associated with the oxidation of these atoms after they diffuse back to the surface. Undoubtedly, some hydrogen remains trapped in the bulk metal at grain-boundaries and dislocations, and consequently is not available for oxidation.

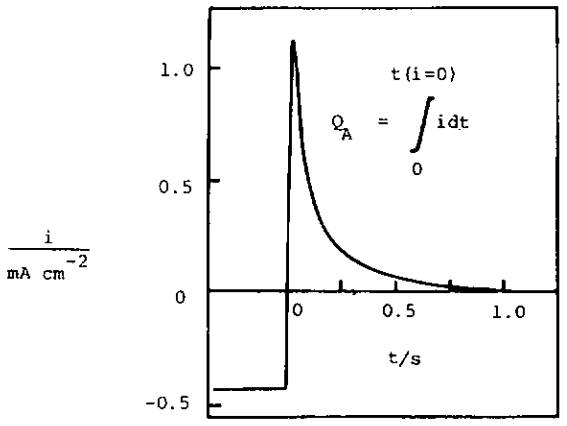


Fig. 6:
Current-time transient for the oxidation of H(ads) Hydrogen was formed at -750 mV (SHE) for 20 s and then the electrode potential was stepped to —620 mV (SHE). Solution composition as in Fig. 3, with 0.06 mol/l H_2S Q_A = 0.4 mC cm^{-2} which is equivalent to 2.7 x 10^{15} H(ads) cm^{-2}.

Electrochemical Measurement Of Corrosion Rate

From our investigations on the electrochemical kinetics of the corrosion processes, it was a logical step to develop an electrochemical instrument for measuring corrosion rates. Electrochemical techniques for measuring corrosion rates are attracting increasing attention,[2] mainly because of their ability to provide a direct value of the corrosion rate at the time of measurement. One such method, the polarisation resistance technique[14] involves the measurement of the electrochemical resistance R_p associated with the corrosion reaction. R_p is related to the corrosion current, I_{corr}, by the expression

$$R_p = B/I_{corr} \quad (7)$$

where B is a parameter derived from the kinetics of the electrode reaction.

TABLE 1 Comparison of Corrosion Rates obtained from Polarisation Resistance and Weight-Loss Methods[15]

Unstirred solutions, pH 6.0 to 6.4, 17 °C

	Time hours	Weight-Loss μm yr^{-1}	Polarisation Resistance μm yr^{-1}
0.3% NaCl	500	33	27
	600	32	28
0.3% NaCl + H_2S (sat)	500	172	158
	600	165	185

The geothermal fluids used for electricity generation in New Zealand generally have relatively low conductivities (typically κ = 0.02 S m^{-1})[9] which results in the measured resistance, R, being the sum of the electrochemical resistance and a solution resistance term which may not be negligible. Thus,

$$R = R_p + a/\kappa \quad (8)$$

where a is a cell constant for a particular polarisation resistance probe. We have found, however, that reliable corrosion rates can be obtained by using suitable probe configurations for which the solution resistance term can be neglected (i.e. by making 'a' small).

Laboratory experiments[15] show that the polarisation resistance and weight-loss techniques give similar corrosion rates (Table 1) for low carbon steel in simulated geothermal condensates. Both methods gave approximately constant corrosion rates over a four-week test period and also showed that there is a marked increase in the corrosion rate of steel with the addition of H_2S. This behaviour is consistent with the effect of H_2S on the cyclic voltammograms; furthermore, the steady corrosion rate of the steel is clearly associated with the lack of protection afforded to the iron by the loose mackinawite film.

Acknowledgements

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Corrosion of Fibreglass

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Healing Industries Ltd

ABSTRACT

The chemical corrosion mechanism of iron and mild steel in aerated fresh water and sea water is compared with the breakdown of glass fibre reinforced polyester (FRP).

The phenomenon of osmosis as related to FRP under aqueous conditions is explained in terms of the chemical and physical mechanisms involved.

The effects of the many variables in terms of raw materials and environmental conditions both during and after fabrication of FRP structures are examined.

The theme is thus to examine the causes, methods of prevention and finally methods of repair of affected FRP structures.

Introduction

The corrosion of ferrous and many other metals has been well studied. Iron or steel in neutral, aerated water, for example, corrodes to form insoluble ferrous hydroxide.

$$2\,Fe \rightarrow 2\,Fe^{++} + 4\,e^-$$

$$2\,H_2O + O_2 + 4\,e^- \rightarrow 4\,OH^-$$

$$Fe^{++} + 2OH^- \rightarrow Fe(OH)_2$$

This is soon oxidised by atmospheric oxygen to form ferric hydroxide which loses water to form the familiar red-brown rust.

$$4\,Fe(OH)_2 + O_2 + 2H_2O \rightarrow 4Fe(OH)_3$$

$$4\,Fe(OH)_3 \rightarrow 2\,Fe_2O_3\,H_2O + 4H_2O$$

The corrosion reactions are electrochemical in nature. Fibreglass which is the term frequently used to describe glass fibre reinforced polyester (FRP) also corrodes in an aqueous environment. Like metals it, too, undergoes a chemical reaction with the aqueous environment to form compounds which eventually lead to a breakdown of the FRP structure.

The text of this article relates to FRP as used in the marine environment and, more particularly, to its use in the pleasure boat field, although many of the effects described apply equally well to the use of FRP in swimming pools, spa pools and FRP tanks for holding water and dilute aqueous solutions.

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He came to NZ from UK to join this company in 1977. Previously he had been technical manager for a Scottish paint manufacturing company. His first appointment was in England as laboratory assistant with an international paint and adhesive manufacturer. From that beginning he progressed to chemist and then for 7 years was works manager. He has post degree qualifications in chemistry, is a graduate of the Plastics and Rubber Institute (UK) and holds a Diploma in Management Studies.

In recent years the pleasure boat industry around the world has seen a truly dramatic shift away from the more conventional materials of construction, wood and steel. Ferrocement and aluminium have been more widely used, but the real revolution has been the use of fibreglass reinforced polyester. FRP boat hulls are now produced in their thousands every year.

Wood rots and steel rusts, but FRP, it was claimed, did neither and was regarded as the wonder material for boat construction. It is strong, having an excellent strength to weight ratio, can be shaped or moulded easily to any design and lends itself to both mass production and "one off" construction. Perhaps what is more important from a cost point of view, especially in large scale production of one design, is that the labour cost is much lower than when using timber.

Unfortunately, there has been growing concern in recent years as many examples of blistering of the underwater surfaces of FRP boat hulls, swimming pools and spa pools have become evident. This corrosion is known to proceed by a physiochemical process of both chemical reaction and osmosis. The boating fraternity in their own inimitable way have coined the term "boat pox" to describe this effect.

In order to understand the phenomenon of osmosis in this context, it is necessary to examine the laminating process by which an FRP boat hull is made.

FRP boat hulls are produced by a process called **contact moulding**[1] in which the first stage is the production of a mould, often of FRP, the shape of the hull required. Most small and medium sized boat hulls are produced by the use of a female mould, which means that the mould is the outer former and the boat hull laminate is laid up on the **inside** of the mould and removed when sufficiently set or cured. For larger boat hulls of, say, 40 feet and over, the male moulding technique is usually more convenient[2]. Here, the mould or **plug** is the inside and the laminate is produced on the outside of the **plug.** For reasons of space, however, consideration will be limited to the more widely used female moulded types.

The Gel Coat

In the case of a female moulded hull the first layer of material applied to the mould is a resin rich, often coloured, product referred to as the gel coat. This coat of resin is allowed to gel or set up but not completely cure before subsequent layers of resin and reinforcement glassfibre are successively laid up onto the gel coat.

The gel coat is a high quality polyester resin designed to have sufficient flexibility to withstand cracking without the need for reinforcement.

The durability of FRP mouldings is mainly dependent upon the quality of its exposed surface. Every possible precaution must be taken to prevent underlying glassfibres from coming too near to the surface where they will be liable to attack by water and moisture. The function of the gel coat therefore is to provide a resin rich working surface designed to protect the underlying fibreglass laminate from water and moisture. It becomes obvious, therefore, that the gel coat is one of the most important components of a laminated boat hull.

Application of the Gel Coat

The gel coat can be applied by brush, roller or spray. The thickness of gel coat is vitally important and should be within the range 500 — 550 microns (20 — 22 thou)[3].

The Laminate

After the gel coat has sufficiently set up, there comes the layup of polyester resin and fibreglass which forms the main strength of the hull. There can be many variations on the materials used. Fibreglass is most common, but many other reinforcements, such as carbon fibre, dynel acrylic, and, often, sandwich construction

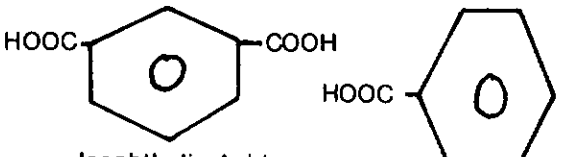
are used. The latter technique involves the sandwiching of other lightweight materials, such as balsa wood or foam, between fibreglass reinforced polyester, and is popular for racing yachts where ultra lightweight is all important[2].

The layup of fibreglass reinforced polyester resin can be effected by the hand layup process or by spraying. After the layup is complete and sufficiently cured, the hull is removed from the mould and trimming and finishing operations take place. The moulded hull is not yet fully cured and a suitable period of post curing in a warm dry environment is needed to assist good future performance.[4]

Types of Materials

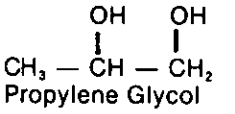
The different types of materials used to produce a polyester resin gel coat and a laminating resin are numerous and a few of the various types of reinforcements have already been mentioned.

The polyester resin alone can be of many different chemical types, such as orthophthalic and isophthalic acid derived, propylene glycol or neopentyl glycol based and so on, all of which impart different properties[5].

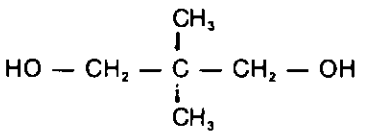


Isophthalic Acid

Orthophthalic Acid



Propylene Glycol



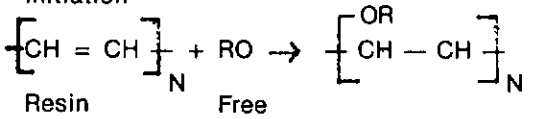
Neopentylglycol

In a typical polyester gel coat formulation, as well as the resin there would typically be pigments, a thixotrope, flow control additives, an accelerator and, as with all polyester resins, a catalyst, which is usually an organic peroxide, such as methyl ethyl ketone peroxide.

The curing or polymerisation reaction proceeds by a free radical mechanism —

Catalysing Polyester Resin

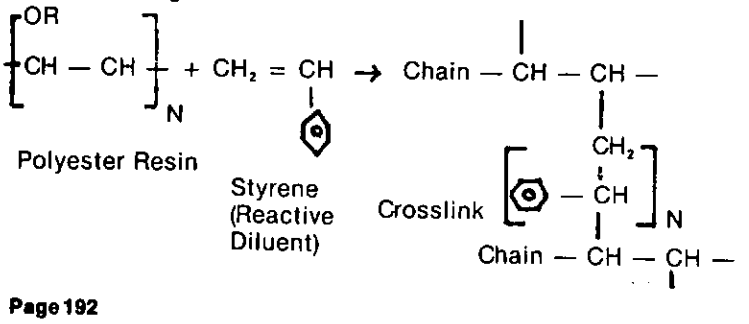
Initiation



Resin

Free Radical

Cross Linking



Polyester Resin

Styrene (Reactive Diluent)

Crosslink

There are many types of fibreglass as well, differing both in their physical form and in the chemical treatment of their surfaces.

Examples are:
1. Woven glass cloth
2. Chopped strand mat
3. Gun stock roving
4. Surfacing tissue

To hold the individual strands of glassfibre together, they are treated with a "binder". Typical binders are PVA (polyvinyl acetate) and polyester resin.[6]

What Causes Osmosis?

The text book describes osmosis as the process where two solutions of differing concentrations, separated by a semipermeable membrance. cause liquid to flow from the weaker solution into the stronger solution to even out the two different concentrations. This, of course, happens in nature all the time and is, for example, how a tree gets water from its roots to its upper branches.

Osmosis on a Boat Hull

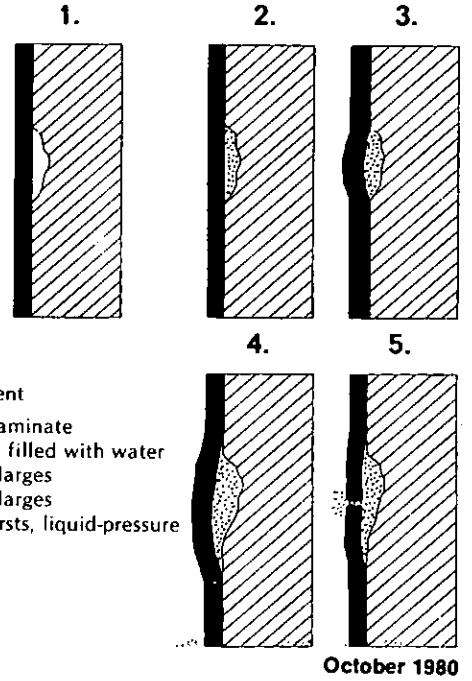
On an FRP boat hull, the gel coat behaves as a semipermeable membrane. In this respect a polyester gel coat may not be the best water resistant coating available, but it is the only material which can be used in the manner employed as part of the moulding process.

Water permeates the gel coat in very small quantities. This water can then dissolve various water soluble materials from, for example, the glass fibre binder, the free peroxide catalyst, or components from undercured resins, to produce a solution.

As only small amounts of water may be involved behind the gel coat (between the gel coat and the back up laminate) the resultant solution can become very concentrated. The solution, in practice, is usually acidic, probably because of hydrolysis of some of the PVA binder.

There now exists an osmotic cell situation. A concentrated solution on one side of a semipermeable membrane (the gel coat) and a more dilute solution on the other side — the sea or fresh water lake.

A positive driving force or pressure — osmotic pressure — now develops, drawing in more water to attempt to dilute the concentrated solution between the gel coat and the laminate. If available, more water



Air entrapment

1. Gelcoat laminate
2. Airbubble filled with water
3. Blister enlarges
4. Blister enlarges
5. Blister bursts, liquid-pressure decreases

soluble-materials dissolve, genefating more concentrated solution, and exerting further osmotic pressure.[7] This pressure deforms the gel coat, producing blisters which can burst, exposing the laminate directly to water attack. Pressures of up to 5 atmospheres have been recorded in osmotic blisters. The long term effect can be loss of laminate integrity and eventual structural failure.

This is the basic physical corrosion mechanism for fibreglass. The corrosion of fibreglass has had the same net result as the corrosion of iron or steel: it has by chemical reaction destroyed the structure.

Prevention of FRP Corrosion

As in the prevention of the corrosion of iron or steel, it is necessary to arrest the corrosion reactions of FRP.

If water can be prevented from reaching the interface of the gel coat and fibreglass/resin layup then neither the chemical step of the corrosion process nor the physical step (osmosis) can proceed and the corrosion reaction will be prevented. Clearly, also, if the source of readily water soluble materials could be removed then neither of the corrosion steps referred to could proceed. A combination of these two approaches is, in fact, desirable.

Factors related to FRP corrosion prevention can be considered in two stages (a) during manufacture, and (b) after manufacture.

(a) **During Manufacture**

The Gel Coat: The choice of gel coat is important and both in laboratory and practical trials isophthalic based types have shown superior water resistance.[8]

Deep coloured gel coats absorb heat more quickly than light colours and since the corrosion is accelerated by higher temperatures, dark colours should be avoided.

Undercuring of gel coats can be a serious and common problem. Because geographic and seasonal temperature variations affect the rates of set up, catalyst levels are varied. Decreasing the amount of catalyst to cope with warm conditions may result in the degree of cross-linking being unsatisfactory. Over catalysing in cold conditions is also detrimental as free catalyst residues remain.

Film thickness of gel coat has already been listed as important. Too thin a film presents a much reduced water resistant barrier; excessively thick films lead to star cracking of the gel coat and rapid water ingress.

The entrapment of air bubbles in the gel coat creates cavities in which water may accumulate and, in effect, represent low film thickness at the point of the air bubble.[1]

Another common problem is pinholing which may occur when the gel coat does not correctly wet the mould and surface tension effects create a small pinhole through which water can penetrate.[1] A further cause of pinholing is when entrapped air bubbles in the gel coat burst and the gel coat sets or gels before the small crater produced has time to flow out. Correct gel coat production and cure cycles overcome the problem.

The Laminating Materials: As with the gel coat resin the correct selection of a good quality laminating resin designed for marine use together with correct catalyst level is also required for optimum water resistance.

After applying the gel coat to the mould, the time interval before applying the back up resin and reinforcement can be critical for good laminate/gel coat adhesion. If the back up resin is applied too quickly, styrene monomer from the resin may wrinkle the gel coat and the first layer of glassfibre reinforcement may penetrate the soft gel coat. This, in turn, can lead to "wicking" (water passing by capillary action along fibreglass strands through to the laminate).[9]

If applied after an excessive time the bond between the gel coat and lay up may be poor as no "solvent cementing" takes place.

As shown, hydrolysis of water sensitive binders on fibreglass have a detrimental effect upon performance and the type of fibreglass employed should, therefore, be carefully considered.

During consolidation of the laminate a lightweight (weight/unit area) glassfibre should be used as the first layer behind the gel coat. This should not be excessively hard rollered. Both precautions are to prevent heavy glass fibre slivers penetrating the gel coat which can lead to "wicking".[9]

Equally important during lamination is the need to avoid "dry patches" where polyester resin does not, through insufficient consolidation, wet-out the fibreglass.[1]

Only dry, correctly stored, (fibreglass is hygroscopic) reinforcement should be employed. Moulding conditions need to be warm, dry, free from direct sunlight and draughts for uniform successful cure conditions.

(b) **After Manufacture**

Post Curing: When the boat hull is removed from the mould it is rigid enough to handle but still far from fully cured. If left exposed to the elements at this "green stage", serious undercuring may result. A system of post curing under dry warm conditions is very important for optimum performance. The Plastics Institute of Australia suggests the following minimum post curing times under cover.[4]

Temp. °C	Days
15 — 20	14 or more
20 — 25	10 — 14
25 — 30	8 — 10

Painting/Water Resistant Coatings: To add further protection against water penetration much research into suitable auxiliary water resistant paint and resin systems has been undertaken and experience has shown that suitably water resistant coatings have very beneficial effects.[10]

Conclusion:

The corrosion of fibreglass proceeds by a combination of physical osmotic processes and chemical hydrolysis reactions. The risk of this corrosion may be reduced by careful attention to fabrication and post construction conditions and by the use of correctly applied and selected water resistance coatings.[11]

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Clay-Polymer Systems: A Brief Survey*

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Interest in the clay-polymer interaction goes back a long way, being prompted by the known biostability of soil organic matter ("humus") which, for the most part, consists of a mixture of polymeric organic species, referred to as humic substances[1]. Indeed, I need not remind soil chemists of the importance and relevance of the clay-polymer interaction to such soil conditions as biological activity, fertility, mineral cycling, profile development, and structural stability. Jacks[2] went so far as to state that this interaction is ".. as vital to the continuance of life as, and less understood than, photosynthesis". If this seems a little far-fetched, we have only to recall that, with the possible exception of some desert and polar soils, surface soils are, in essence, clayor mineral-organic complex systems.

It was not until the early 1940's, however, that the chemistry of clay-organic reactions came into its own, following closely on the general acceptance and elucidation of the crystallinity and structures of the main groups of clay minerals.[3] The rapid advances in clayorganic chemistry which have been made since then were aided by the application of modern instrumental techniques, in conjunction with the more conventional Xray diffraction and electron microscopy, to the study of these reactions. Thus, for many systems involving organic micromolecules we have been able to deduce the mode of bonding and the orientation of the adsorbed species at the clay surface.[4]

Although this kind of information forms the basis of interpreting the behaviour of organic macromolecules at clay mineral surfaces, additional variables enter the picture. These essentially arise from the fact that besides being long, polymer molecules are flexible and polyfunctional. They may, therefore, adopt various conformational states in solution and at the clay surface to which they can become attached by numerous segment-surface bonds. In addition, steric and accessibility factors come into play during the interaction process. For these reasons, clay-polymer systems can, at best, be described in semi-quantitative terms.

For the sake of brevity, I shall confine my remarks to the interactions of kaolinite and montmorillonite with selected synthetic and naturally occurring polymers of the charged and uncharged type, in an aqueous environment.

Dr Theng was educated initially in Indonesia and later at the University of Adelaide where he graduated B.Ag.Sc. with first class honours in 1961 and Ph.D. in 1965. Prior to his appointment as Scientist with the Soil Bureau, he held positions at the University of Western Australia, the University of Leuven, Belgium, and with CSIRO Division of Applied Mineralogy. He has published a book, 29 scientific papers and two monographs, one of which "The Chemistry of Clay-Organic Reactions" was awarded the Adam Hilger Prize for 1972.

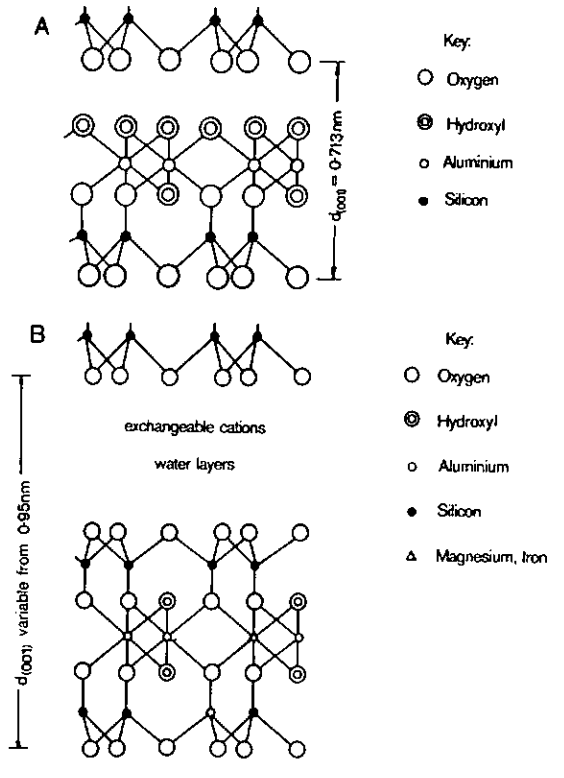
**ICI Prize lecture delivered to Wellington Branch, NZIC, March 1980.*

The Clay Minerals

Clay minerals belong to the class of layer silicates because their crystals are made up of layers formed by condensation of sheets of $Si(O,OH)_4$ tetrahedra with those of $Al(OH)_6$ octahedra. Condensation in a 1:1 proportion gives rise to the two-sheet (diphormic) type minerals, exemplified by kaolinite (Fig. 1A). Similarly, the three-sheet (triphormic) type clays of which montmorillonite is an example, arise from a 2:1 condensation, the octahedral sheet being sandwiched between two inwardpointing tetrahedral sheets (Fig. 1B). A crystal is composed of di- and tri-phormic layers which are continuous in the horizontal *(a b)* plane and stacked in a more or less regular array along the vertical *(c)* axis. There is scope, in these structures, for isomorphous replacement, that is, the replacement of Si^{4+} and Al^{3+} by cations of similar size and co-ordination number but of different (usually lower) valency. When this occurs, the structure acquires a (permanent) net negative charge, or a positive charge deficiency, which is balanced by sorption of extraneous (exchangeable) cations.

There is little isomorphous replacement in kaolinite and the few exchangeable cations (3-8 meq/100g) are located on external crystal surfaces which have an area of 30-50 m^2/g. Kaolinite crystals, therefore, show no interlayer expansion (swelling) in water and polymer adsorption is confined to the external crystal surface. Each layer is about 0.72 nm thick and this also represents the repeat distance along the *c*-axis, referred to as the basal or d(001) spacing (cf. Fig. 1A). On the other hand, much substitution occurs in the montmorillonite

Fig. 1: A, the layer structure of kaolinite, viewed along the a-axis. The indicated layer thickness of about 0.72 nm also represents the basal or d(001) spacing because there are no extraneous, interlayer species. Summation of the anionic and cationic charges in the structure, as depicted, shows that the layer is electrically neutral. In reality, most if not all kaolinites carry a net negative surface charge.
B, the layer structure of montmorillonite, showing the presence of isomorphous replacement in the octahedral sheet and the occupancy of the interlayer space by exchangeable cations and water molecules. The thickness of each layer is about 0.95 nm but the basal spacing is variable and commonly greater than 0.95 nm.



structure, giving rise to a high exchange capacity (80-100 meq/100g). Here, the exchangeable cations are distributed over the external crystal and interlayer surfaces. The thickness of an individual layer is about 0.95 nm but the basal spacing is variable, depending on the nature of the interlayer cation and its hydration properties (cf. Fig. 1B). With small, monovalent alkali ions (Li^+, Na^+) occupying exchange sites, montmorillonite crystals show extensive interlayer swelling in water and so expose a large surface area (about 800 m^2/g) which is accessible to most polymers.

Aspects Of Polymer Adsorption

The adsorption of an uncharged, linear homopolymer onto a clay surface is generally accompanied by the desorption of numerous solvent (here water) molecules, initially present at the surface. The translational entropy so gained provides the driving force for adsorption as the enthalpy change of the process is commonly very small and, in some instances, may even be positive. Adsorption also leads to a change in polymer conformation in that the macromolecule which, in solution, tends to adopt a random coil form, would uncoil and spread out at the clay/water interface. This gives rise to a surface conformation in which contiguous sequences of adsorbed segments ("trains") alternate with three-dimensional "loops" extending away from the surface, the polymer chain terminating in two freedangling "tails" (Fig. 2). Thus, although the net segmentsurface interaction energy, ϵ is small (about 1 kT), the total energy of adsorption can be very large indeed because of the numerous segment-surface contacts. The fraction of segments in trains, p, is therefore an important parameter which, for unchanged polymers, ranges from 0.3 to 0.5.

The strong interaction of uncharged polymers with clays means that a large amount of material can be removed from dilute solutions and hence, the adsorption isotherms are typically of the H- ("high affinity") type (cf. Fig. 7). By the same token, the rate of desorption is very low, so much so that adsorption is often regarded as being "irreversible" in the sense that there is only a small probability for all train segments to be simultaneously detached from the surface and remain so sufficiently long for the polymer to move away from the interface. We might also expect the amount and strength of adsorption to rise with the size or molecular weight of the macromolecule. Although this is true in many instances, the opposite behaviour, that is, one in which uptake apparently decreases as molecular weight increases, is by no means uncommon. This is because clay-water systems are essentially "porous" and molecules beyond a certain size range would be physically excluded from some pore surfaces.

The interactions of charged polymers with clays are, if anything, more complex than those involving uncharged species. Apart from the variables already mentioned, polyelectrolytes can undergo a stretchingcoiling transformation in response to changes in solution pH and added electrolyte. As we shall see later, this effect is of great importance and relevance to the use of polyelectrolytes as aggregating/flocculating agents of clay and colloidal dispersions.

Positively charged polymers or polycations are adsorbed by clays largely through electrostatic interactions between the cationic groups on the polymer and the negatively charged sites at the mineral surface. The value of ϵ is therefore much greater than 1 kT and adsorption leads to a rapid collapse of the polymer chain onto the surface with very little looping (p greater than 0.7). The adsorption-desorption behaviour of polycations parallels that of uncharged species, remarked on earlier.

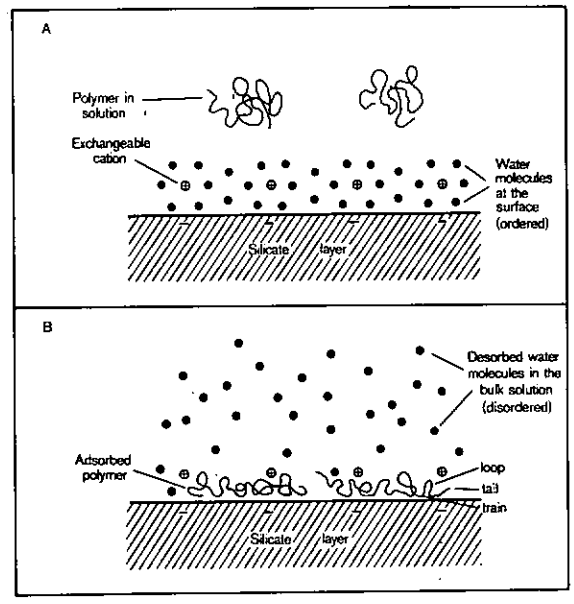


Fig. 2: Diagram illustrating the desorption of numerous water molecules from the clay surface which accompanies the adsorption of a single uncharged linear polymer molecule, giving rise to a net gain in entropy by the system. The change in polymer conformation from a random coil in solution to a more or less extended one at the surface, is also indicated.

On the other hand, negatively charged polymers or polyanions tend to be repelled from the clay surface and little, if any, adsorption occurs. However, appreciable uptake can take place at low solution pH and/or high ionic strength when the charge on the polymer is effectively neutralised by protonation and/or screened by the electrolyte. Adsorption is also promoted by polyvalent cations, occupying exchange sites at the clay surface, which can act as a "bridge" between the anionic groups on the polymer and the negatively charged sites on the mineral. Polyanions may also adsorb onto the clay crystal edges by "anion exchange" (when aluminium, exposed at these sites, acquires a positive charge at acid pH values) or by "ligand exchange" (when the anionic groups of the polymer enter the inner co-ordination layer of edge aluminium, forming a co-ordination complex with it). Nevertheless, the proportion of train segments is relatively small unless the system is allowed to dehydrate, when other modes of bonding, e.g. van der Waals interactions, become operative. Also, unlike their charged and positively charged counterparts, polyanions do not enter the interlayer space of montmorillonite-type minerals. However, intercalation may occur at low pH values when the polyanion behaves and adsorbs like an uncharged species.

Formation And Properties Of Clay-Polymer Complexes

By way of illustrating the above principles, we will cite some experimental data on the clay-polymer interaction, taking polyvinyl alcohol (PVA), cationic polysulfone (CPS), and soil fulvic acid (FA) as representatives of an uncharged polymer, a polycation, and a polyanion, respectively.

The adsorption of PVA by montmorillonite, as influenced by the nature of the exchangeable cation and by ionic strength[5], is shown in Figs. 3 and 4. These results may be rationalised in the following way. In water (zero ionic strength), Na^+ montmorillonite crystals can swell to give basal spacings greater than 13 nm whereas the calcium and cesium forms do not expand beyond a d(001) value of about 1.9 and 1.5 nm, respectively. The extensive interlayer swelling of the sodium clay may also be reduced to the level of its calcium and cesium counterparts by electrolyte (here $NaNO_3$) addition. On

this basis and the known coil dimension of PVA in solution, the polymer can presumably gain unrestricted entry into all (external and internal) crystal surfaces of Na+ montmorillonite, giving rise to a relatively large uptake. By the same token, interlayer entry would be severely restricted for the calcium clay and probably impossible for the cesium clay. The amount adsorbed is correspondingly reduced as compared with the sodium clay. The effect of ionic strength may be similarly explained, that is, in terms of the relative accessibility of interlayer surfaces to the polymer. The complex with Na+ montmorillonite at maximum adsorption of PVA (about 0.8 g/g; Fig. 3) has a basal spacing of about 3 nm, corresponding to an interlayer separation of about 2 nm (cf. Fig. 1B). For an interlayer area of about 750 m^2/g this amount is compatible with a rather flat, extended monolayer of PVA on each of two opposing interlayer surfaces, with an average loop length of 1 nm and a *p* value of about 0.5.

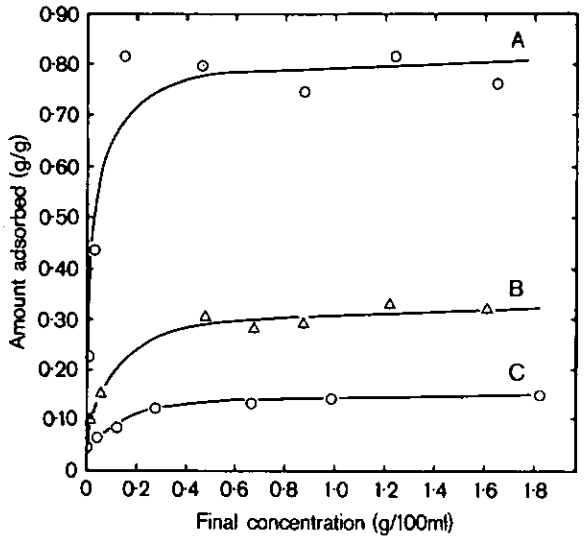


Fig. 3: Adsorption of polyvinyl alcohol by monmorillonite saturated with different (exchangeable) cations: A, sodium; B, calcium; C, cessium (after Greenland[5]).

As indicated earlier, polycations adsorb by electrostatic interactions with the clay surface. This results in mutual charge neutralisation and chain collapse, as evidenced by the studies of Ueda and Harada.[6] Using a Na+ montmorillonite with a cation exchange capacity (CEC) of 62.4 meq/100g, these workers followed the changes in CEC and anion exchange capacity (AEC) of the complex with CPS, as adsorption progressed. The data, summarised in Table 1, show that the AEC increases with the amount adsorbed whilst the CEC declines. As the parent clay has no measurable AEC, the development of an AEC, that is, of positive charges, by the complex can be ascribed to cationic groups contained in the loops and tails of the adsorbed polymer. By the same token, the decrease in CEC must be due to neutralisation of the negative surface charges by train segments. The difference between the total amount adsorbed and the AEC would therefore represent the amount of segments in trains. Interestingly, up to a surface coverage of about 0.5, all or nearly all of the polymer segments are adsorbed in the form of trains (*p* about 1); even at full coverage, only some 25% of the segments are contained in loops and tails.

Fig. 5 shows the isotherms for the adsorption at pH 7 of FA by montmorillonite saturated with different polyvalent cations.[7] The data are consistent with a cationbridge type of interaction in that the affinity of FA for the clay surface is closely related to the ionic potential

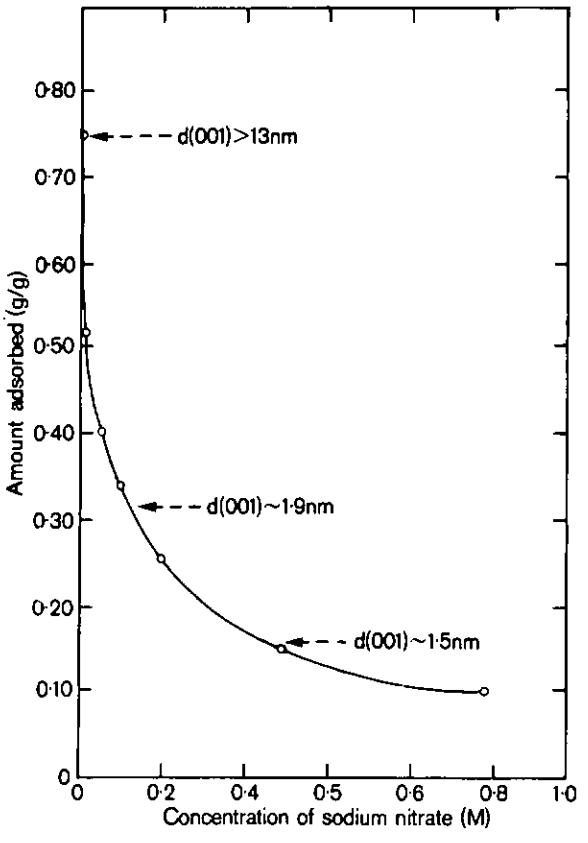


Fig. 4: Adsorption of polyvinyl alcohol by Na+ monmorillonite in the presence of $NaNO^3$ solutions of different concentration. The basal spacings of the parent clay are also indicated. The values of greater than 13 nm, about 1.9 nm, and about 1.5 nm correspond, respectively, to the spacings of Na+, Ca^{2+}, and Cs+ montmorillonite in water (after Greenland[5]).

of the respective cation. The linearity of the isotherms would indicate that fresh sites are being created as adsorption progresses. Since there is no interlayer uptake, these sites are presumably located between clay crystals within a "domain" or in the "pores" between individual clay domains (cf. Fig. 9). However, if the solution pH is taken below 4, the ionisation of the carboxyl groups on FA is suppressed and intercalation can occur (Fig. 6).[8]

The above considerations apply to the interactions of clays with biopolymers. Thus, the adsorption of proteins is pH-dependent, generally reaching a maximum close to the isoelectric point of the protein (Fig. 7) at which point the material is least soluble and so tends to accumulate at the clay/solution interface[9]. Proteins, at least the globular type, apparently retain their gross native conformation on adsorption. The adsorption of enzymes by clays commonly leads to a reduction in their respective activity and the pH-optimum for activity is shifted to more alkaline values. There is also a change in the kinetics of the enzyme-catalysed reaction in that the maximum velocity and the Michaelis-Menten rate constant are reduced. Complex formation between clays and proteins, especially when intercalation occurs, tends to "protect" the adsorbed species from enzymic attack.

As might be expected, the adsorption of nucleic acids and nucleoproteins by clays is sensitive to solution pH, generally decreasing with an increase in pH. Like most proteins, nucleic acid can intercalate into montmorillonite (without undergoing a great deal of conformational change) and so become stabilised against microbial decomposition. The strong adsorption of viruses by clays and soils is actually an advantage in that little material gets into the ground water system.

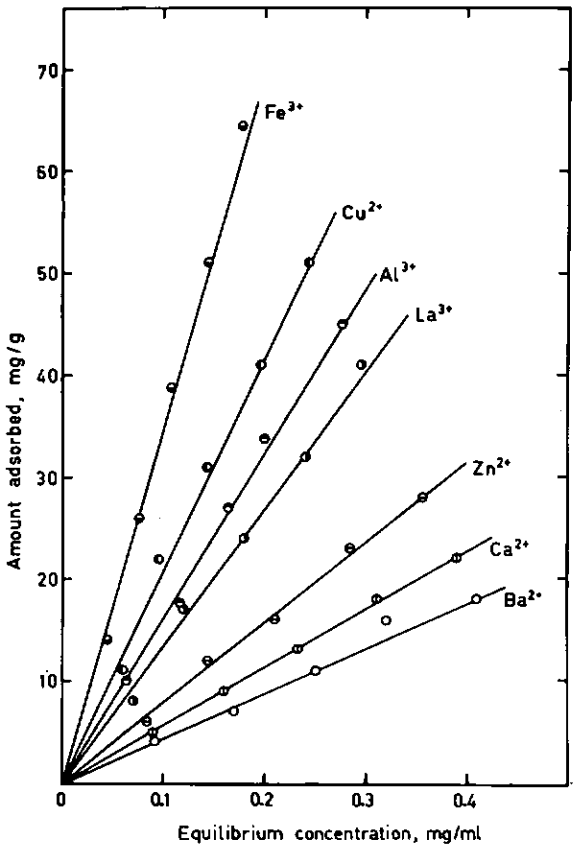


Fig. 5: Isotherms for the adsorption at 293 K and pH 7 of fulvic acid by montmorillonite saturated with different cations. The slope of the isotherms, a measure of the affinity of the polymer for the surface, is related to the valency: radius ratio (i.e. ionic potential) of the respective cation (after Theng[7]).

Polysaccharides, an important component of soil organic matter, may be uncharged, positively, or negatively charged; their interactions with clays would vary accordingly.

Some Practical Applications

The clay-polymer interaction has found many and varied practical applications in agriculture and a number of chemical industries.

One is the use of polymers as flocculants of dilute clay and colloidal dispersions, in which the particles are separated by relatively large distances. Flocculation involves both attachment of the polymer onto the particle surface and the bridging of several particles by the adsorbed molecule. Since uncharged polymers exist as randomly coiled units rather than extended chains in solution (cf. Fig. 2), they are generally not very effective as flocculating agents. Polycations, as we have seen, can neutralise the charge on clay particles and so serve as effective coagulants; however, because of their rapid collapse onto the clay surface, only limited interparticle bridging can be achieved. On the other hand, polyanions are effective flocculants, especially in the presence of polyvalent cations. This is because only a few segments of the polymer chain are involved in adsorption, the majority being present in the form of long loops and tails. In other words, polyanions have a relatively large "grappling distance" and this facilitates the formation of interparticle bridges [10].

Polymers have also been used as "soil conditioners", that is, materials capable of increasing the mechanical strength and water-stability of soil aggregates. Here the uncharged, polyvinyl alcohol type is found to be very effective since it can spread like a "coat of paint" over the surface of soil/clay particles which are already in close proximity to each other[5]. Its effectiveness can be greatly increased by introducing the polymer, at strategic positions, into pores of a certain size range (Fig. 8)[11]. As might be expected, the larger the molecule the more effective it is in stabilising soil aggregates.

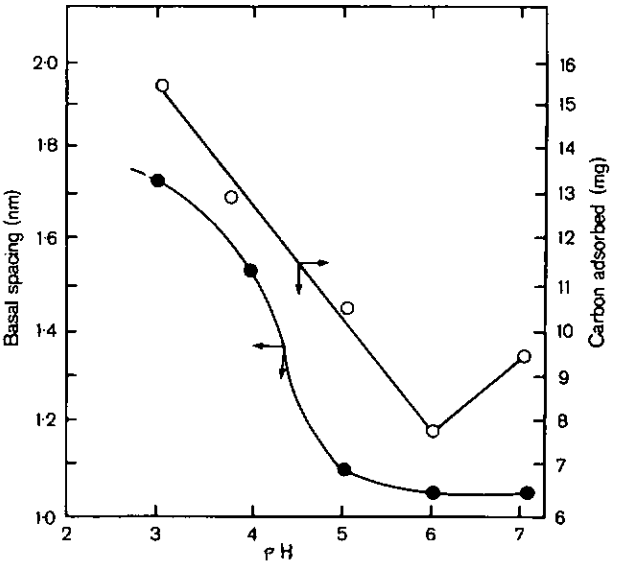


Fig. 6: The effect of solution pH on the adsorption of fulvic acid by Na+ montmorillonite, the amount adsorbed being equal to 2 x mg carbon. Note that appreciable intercalation (interlayer uptake) only occurs below pH 4 (after Schnitzer and Kodama[6]).

For reasons stated above, polyelectrolytes are relatively ineffective as aggregate stabilisers.

Industrially, clays enjoy a substantial application for the filling and reinforcement of polymer systems, such as elastomers, polyethylene, polyvinyl chloride and other thermoplastics, and as a coating agent for various types of paper. All things being equal, the efficiency of a filler in improving the physico-mechanical properties of a

Fig. 7: Isotherms for the adsorption at 298 K of lysozyme by montmorillonite at different solution pH values, ranging from 1.9 to 10.3. Highest uptake occurs at pH 10.3 close to the isoelectric point of lysozyme (after McLaren et al.[9]).

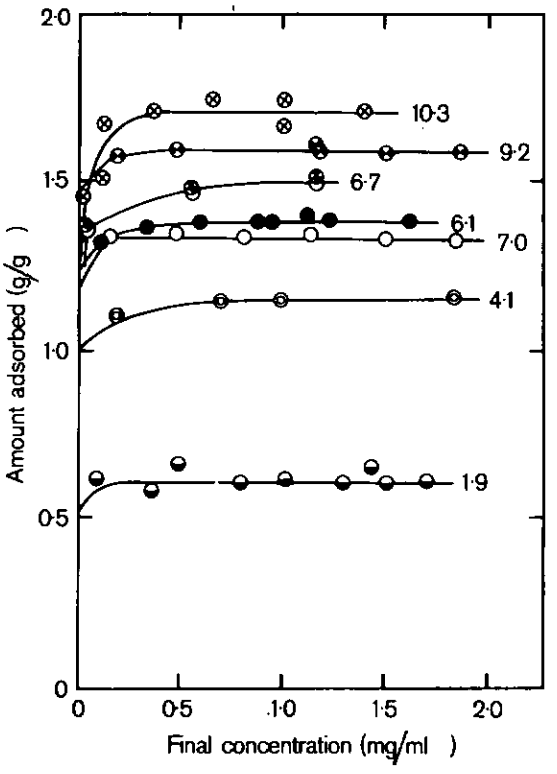


Table 1

Adsorption of a cationic polysulfone (diallyldimethylammonium chloride - SO_2 copolymer; molecular weight 16.7 x 10^4) by montmorillonite at a suspension concentration of 1.5 g/100 cm^3 and 303K[6]

Amount adsorbed (meq/100 g)	CEC (meq/100 g)	AEC (meq/100 g)	Amount in trains (meq/100 g)	Sum of B + D (meq/100 g)	Proportion of segments in trains (p)
A	B	C	D=A-C		D/A
0	62.4	0	0	62.4	1
8.56	49.6	0	8.56	58.1	1
18.5	44.6	0	18.5	63.1	1
33.6	30.7	0.97	32.6	63.3	0.97
40.7	24.5	3.85	36.8	61.3	0.90
43.5	23.9	5.34	38.2	62.1	0.88
47.9	21.4	6.68	41.2	62.6	0.86
46.6	23.7	6.37	40.2	63.9	0.86
57.7	15.8	13.2	44.5	60.3	0.77
58.5	14.4	15.1	43.4	57.8	0.74
63.0	12.8	15.5	47.5	60.3	0.75
64.3	11.1	18.2	46.1	57.2	0.71

Clay-Polymer Systems (Cont)

polymer system is primarily determined by the degree of its dispersion in the polymer matrix. Because clay surfaces are essentially hydrophilic, raw or untreated clay is not readily dispersible in, or rapdly wet by, the organic

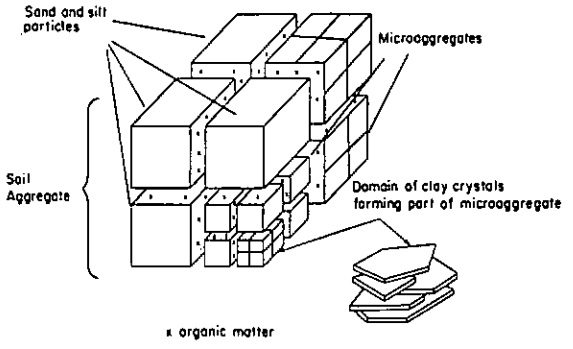


Fig. 8: Block model of a soil aggregate showing clusters of oriented clay crystals forming a domain, of domains forming a microaggregate and of microaggregates to form aggregates. The various structural units (domains, microaggregates, sand and silt particles) are bound together by soil organic matter. Introduced polymers would act in a similar fashion (after Greenland and Hayes[11]).

phase. In order to make the mineral and organic phases mutually compatible, it is often necessary to render the clay surface organophilic prior to blending or compounding the filler with the polymer. This can be done by attaching a suitable organic compound to the filler surface, by exchanging the inorganic cations with organic counterparts, or by treating the mineral with organosilanes (Table 2)[12]. Perhaps the most effective way of achieving compatibility is to graft a suitable polymer onto the filler surface and/or encapsulate the mineral particles with a polymer layer (Table 3)[13]. It seems obvious, from what has been said, that clays cannot be regarded as mere extenders, that is, as chemically inert materials. Furthermore, clays are known to catalyze a variety of organic reactions including those which lead to polymer formation[7].

Table 3

Some mechanical properties of high-and low-density polyethylene (HDPE and LDPE) containing 20% of different fillers[13]

Filler type	Stress yield (kg/cm)		Elongation at break (%)		Impact strength (kg m/m)
	HDPE	LDPE	HDPE	LDPE	HDPE
None	289 ± 4	90 ± 3	1300	700	2.63
Untreated hydrite 10 (H 10)[a]	282 ± 5	96 ± 4	100	200	1.23
Freeport kaolin OX-3[b]	285 ± 3	109 ± 1	40	140	1.30
Commercial reactive encapsulated kaolin	286 ± 3	96 ± 4	25	160	1.23
SRF Carbon black	318 ± 2	110 ± 1	50	84	1.00
H 10 + 4% isoprene [c]	300 ± 2	110 ± 3	90	210	-
H 10 + 4% piperylene [c]	300 ± 4	111 ± 2	140	140	1.32
H 10 + 4% styrene [c]	299 ± 4	111 ± 6	45	190	1.56

[a] From Georgia Kaolin Company.
[b] Coated with an organophilic compound, same average particle size as hydrite 10.
[c] Polymerization terminated by ammonia; encapsulating polymer oxidized before use.

Table 2

Modifications in some properties of polymers and plastics induced by the incorporation of an organo-titanium kaolinite filler, obtained by reacting the clay with tetraisopropyl titanate and oleic acid[12]

Property	Polymer or plastic										
	HDPE	Epoxy	Acetal	SAN	Nylon 6	Poly-propylene	Propylene copolymer	Rigid PVC	ABS	Impact PS	Phenolic
Tensile strength	+	+	0	-	0	+	+	0	+	+	0
Tensile yield	0	+	0	0	0	0	+	0	0	0	0
% Elongation	-	-	-	0	-	-	-	-	0	-	0
Tensile modulus	+	0	+	+	+	+	0	+	+	+	0
Hardness	0	+	0	0	0	0	0	0	+	0	0
Heat distortion	+	+	+	0	+	+	+	+	+	0	0
Melt flow	0	0	+	0	0	0	0	0	-	0	0
Izod impact	0	0	-	0	0	0	0	-	-	-	0
Optimum concentration	30	50	30	30	60	30	30	20	30	25	

Plus and minus signs denote a positive and negative change in property, that is, an advantage and disadvantage, respectively. Zero sign means that there is no significant alteration in property on incorporating the filler.
HDPE=high density polyethylene; SAN=styrene acrylonitrile polymer; PVC=polyvinyl chloride; ABS=acrylonitrile-butadiene-styrene resins; PS=polystyrene.

CORROSION IN BOILER PLANT AND CONDENSATE RETICULATING SYSTEMS

C.J. Miller
Gamlen Chemicals (N.Z.) Ltd

Having spent many hours with boiler plant owners and operators, it is our experience that our two biggest problem areas are;

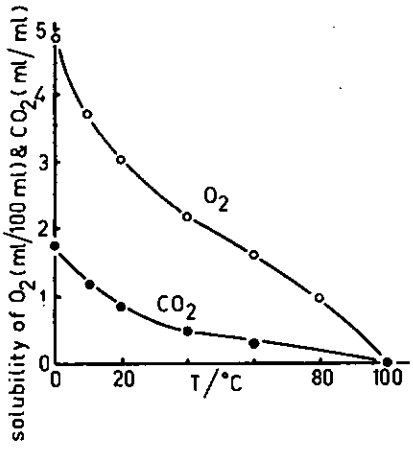
i) Corrosion of boilers due to oxygen
and
ii) Condensate line corrosion, due to carbon dioxide.

This is not to say that these two gases are the only sources of trouble, but in practice, if their behaviour is understood and the knowledge applied to installation design, a major step forward in plant longevity will be realised.

Oxygen

Fig. 1 shows the solubilities of oxygen and carbon dioxide in water. Clearly, at ambient temperatures of 15-21°C oxygen is quite soluble and if water at this temperature is fed directly into a boiler the oxygen will come out of solution. This oxygen will start corrosion cells. Boiler design is an important factor and severe pitting has been observed in boilers where the feed water distributor directed the make up water directly on to the generating tubes. Presumably the manufacturer imagined that the boiler would be fed with oxygen free water, but the plant layout was designed by someone who did not realise this. Subsequent models of the boiler employed a feed distributor which fed the water through laterally drilled holes, thus severe localized corrosion was minimized.

Fig. 1



Oxygen Free Water

The cost of installing dearating equipment is high and need not be considered on small plant, however **any** steam raising plant must be fed with water containing the lowest practical level of dissolved oxygen.

From Fig. 1 it may be seen that the solubility of oxygen at 80-90°C is only 0.8 — 0.6 ml/100ml, thus by maintaining the feed water at this temperature the oxygen levels will be minimized.

Fig. 2 illustrates a practical feed tank design. It is not expensive or sophisticated, however, it is a little different from the open 200 l drums sometimes seen. The design incorporates the following points:

i) Live steam is added directly to the feed water to mechanically agitate as well as heat the water to promote the removal of oxygen.

ii) The cold make up water and condensate return are both introduced below the surface of the water thus preventing cascading which tends to maintain oxygen levels in the water.

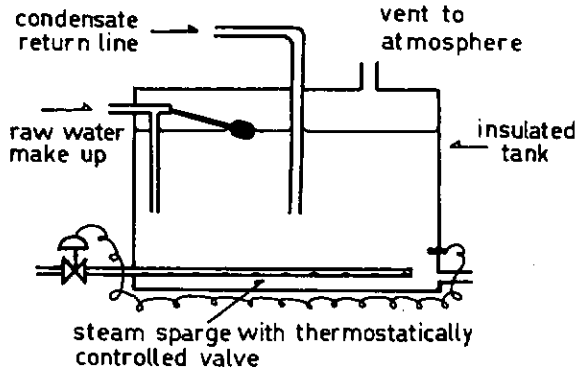
The feed tank must be located in a position to give a satisfactory head to the feed pump, as with elevated temperatures cavitation of the pump will occur.

Chemical Scavenging

Once the majority of the oxygen has been removed it is practical to use chemicals to scavenge any remaining oxygen from the water.

Scavenging agents should be introduced directly to the boiler via the make up line, as they will react with atmospheric oxygen if added to the feed tank.

Fig. 2 A Practical Feed Tank Layout



Sodium Sulphite

This material is economical in use and if catalysed with, say 0.3% of a suitable cobalt salt will rapidly react with any oxygen to form sodium sulphate. $2SO_3^{2-} + O_2 \rightarrow 2SO_4^{2-}$. It does, however, raise the total dissolved solids of the water but for small installations this is generally acceptable. Theoretically, 7.88 mg/kg of pure sodium sulphite reacts with 1 mg/kg of oxygen but in practice 12-13 mg/kg are required.

Feeding should be done on a continuous basis with provision for slug dosing on shut down.

Hydrazine

Hydrazine (N_2H_4) is toxic and thus requires care in handling; it is expensive but does not require high dose levels. It does not affect the total dissolved solids of the water as its end products, after reacting with oxygen, are water and nitrogen.

$$N_2H_4 + O_2 \rightarrow 2H_2O + N_2$$

1 mg/kg of hydrazine reacts with 1 mg/kg of oxygen but, as for sulphite, more than the theoretical levels are required in practice, with 1.5 — 2 mg/kg per 1 mg/kg

Clay-Polymer Systems (Cont)

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To save on space, I have omitted many specific references to the original literature. For these, the interested reader is referred to monographs 1 and 4 in the following list.

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Boiler Corrosion (Cont)

of oxygen being required. Excess hydrazine decomposes in the boiler to form ammonia and nitrogen, the ammonia being alkaline does not attack steel but may cause damage to brass and copper fittings.

Boiler Shut Down

Correctly initiated the steps above will cure the problems associated with on line oxygen corrosion.

However, most catastrophic corrosion in boiler plant occurs during shut down. Why? Simply, lack of understanding of the potential problems by the personnel designing the plant or those responsible for its installation.

Consider a tyre retread plant. Steam at operating pressure is required at 8 am, this means the boiler must start at 6.30 or 7 am. To save an operator having to arrive at this time to start the boiler it would seem logical to start the boiler with a time clock. This time clock would also turn the boiler off — PROBLEM!!!

The steam stop valve is open, as is the feed check valve. As the boiler cools down air is drawn into the steam lines and subsequently into the boiler. Similarly as the water level drops, water which is also cooling down in the feed tank is made up into the boiler — this water continually absorbs oxygen as the temperature drops. Oxygen entering the boiler during shut down causes tube failure.

Quite obviously a time clock is unsatisfactory and unless a suitable electro-mechanical shut down system is installed there is no alternative but to have the operator ensure that the boiler is shut down i.e. feed check and steam stop are closed and that the feed check is again opened prior to start up.

To ensure that any oxygen which enters the boiler during this shut down cycle is adequately scavenged, the addition of some catalysed sodium sulphite is recommended. Ensuring that there is an adequate reserve of sulphite at the end of the shut down cycle will confirm that there is no free oxygen within the boiler and that the investment is being protected.

Carbon Dioxide

Referring to Fig. 1 again it will be noted that carbon dioxide is very soluble in water, dissolving to form carbonic acid

$$CO_2 + H_2O \rightarrow H^+ + HCO_3^-$$

Carbonic acid is aggressive to steel and will dissolve steel pipes rapidly.

Consider feed water which contains an appreciable amount of natural alkalinity — typically 30 mg/kg as HCO_3^- for Auckland water and 60 mg/kg for Onehunga water. When used as boiler feed the bicarbonate ions in the water dissociate at the high temperatures and pressures (typically 10 Bar and 180°C) to produce hydroxyl ions and carbon dioxide.

$$HCO_3^- \rightarrow \overset{\uparrow}{CO_2} + OH^-$$

The carbon dioxide leaves the boiler with the steam, as the steam condenses and gives off its heat the carbon dioxide is dissolved in the condensate. The carbonic acid produced is very aggressive to the steel pipework. Condensate lines should be designed with sufficient fall to reduce the possibility of condensate being retained in the system.

The iron pipe work dissolves to form ferrous carbonate which is soluble, and is therefore returned to the boiler with the condensate via the feed tank.

Once in the boiler the ferrous carbonate reacts to form ferric hydroxide and carbon dioxide. The ferric hydroxide appears as a brown precipitate in the boiler water, whilst the carbon dioxide again enters the condensate system via the steam lines.

There are three approaches to solving the problem.

1) Accept the corrosion and replace the condensate lines when they start to leak. Many plants opt for this as the pipe work is relatively inexpensive to repair.

2) Introduce a neutralizing amine, such as morpholine — this compound is added to the boiler where it is volatilized off with the steam. Control is effected by monitoring the pH of the condensate which is maintained at 8.5 — 9.0, thus corrosion is prevented.

3) In some plants volatile amines are unacceptable as some of the steam may be used for food processing or sterilizing. In such cases, dealkalizing of the boiler make up should be considered. Because dealkalizing is a little beyond the scope of this discussion, only 2 of the various methods used will be mentioned.

a) Addition of acid (generally sulphuric as it is readily available and very economical).

Sulphuric acid is added to the water to react with the bicarbonate, the water is then aerated to remove the carbon dioxide that is formed.

b) By using ion exchange resins — sodium/hydrogen cycle split stream. The

Control Of Industrial Cooling Systems

J.M. Heng, Portals Water Treatment (NZ) Ltd and W. Pugh, Houseman (Burnham) Ltd.

The cost of water to NZ industry continues to rise and at present the Auckland industrial user is paying 25.53c/m³ ($1.02/1000gal.) This is only the supply cost and disposal through trades waste is far in excess of this figure. The incentive for industrialists to save water is therefore considerable. This article discusses savings which may be made in the quantity bought and in the treatment of it in open cooling systems.

The average cost for metered water in Auckland in 1977 was 15.86c/m³ (62.4c/1000gal.) compared to the 1980 price, which has increased 62.12%. It is expected, furthermore, that the price of metered water will continue to rise at a rate higher than that of inflation if previous trends are followed.

A high percentage of the water used within NZ is used by industry and of that water, the majority is used for cooling and steam-raising. The quantity actually consumed in industrial processes is surprisingly low. In many industries the proportion used for cooling and steam plant may be as high as 90%.

Open Cooling Systems

Of the cooling processes, the biggest single user is the industrial open cooling system and it's here quite naturally that industrialists must look for significant savings. As our industrial processes become more sophisticated, then cooling towers increase in number and size and in consequence the need for water increases.

This increased need for cooling related to the increase in costs pro-rata for water necessitates its more efficient use, not only as a responsible attitude towards the availability of water on a national basis but also from the point of view of controlling product costs. The re-use of water is therefore essential and the correct management of cooling systems increasingly important.

Water saving by efficient management of cooling system can be achieved in a number of ways, or by combination of a number of ways, each of which varies in importance related to the local water quality, ambient conditions and also to the purpose for which the cooling water is being put. R Swift (Chartered Mechanical Engineer, April 1977) explained how clean surfaces are paramount in achieving the desired efficiency. Subsequently the cooling tower, heat exchanger surfaces and pipework must be kept clean. Deposits of any type or origin will decrease the efficiency of the cooling system and increase costs.

The open cooling system relies upon evaporation, ie, pure water loss as water vapour, to take the heat from the recirculating water. This water is carrying heat from a heat exchanger. The heat exchanger will be related to a process or some form of machinery which generates heat to do its work and so on.

Water, being a very good solvent, many substances will be carried in a dissolved form. The quantity and variety of these compounds varies from location to location. As pure water is lost by evaporation then the concentration of these dissolved compounds will increase and fresh water being admitted to the system to compensate for evaporation losses will continue to bring a proportional increase of these compounds. Unless some measures of control are imposed the compounds will eventually exceed their solubility and deposits will occur. To ensure that this does not happen, the system must be purged or bled in order to maintain concentration of salts below levels at which they will deposit. This means water usage at a high level unless some form of water treatment is applied.

The problem of deposition at low concentrations is further enhanced by chemical changes in these indigenous water-borne compounds resulting in the production of less soluble materials. If the concentration within the recirculating water can be increased, then water conservation can be achieved.

The water savings which are possible can be shown by the following example:

System details:

Cooling system recirculation rate — 50 m³/h.

Temperature drop across tower — 5°C.

Concentration factor — 2.

Evaporation is a function of the designed recirculation rate and the temperature drop (heat loss) required. Evaporation is normally taken as 1% of the circulation rate per 10°F (≈5.5°C) temperature drop across the cooling tower. Evaporation would therefore drop across the cooling tower. Evaporation would therefore be 0.5 m³/h. The concentration factor is decided upon by the chemical composition of the raw water. If this has a high level of salts, then a concentration of dissolved salts of 2 only may be considered necessary.

To maintain a concentration factor of 2, the system would have to be purged or a bleed installed. This bleed would be calculated by:

$$B = \frac{E}{C-1} - W$$

Where B = Bleed, purge or blowdown; E = Evaporation; C = Concentration; W = Windage or drift loss, usually taken as 0.2% of evaporation.

Bleed in this example would therefore be almost 0.5m³/h. Make-up would be 1 m³/h. Some extra losses from leakages in the system may also occur.

It will be seen therefore that any increase in concentrations will save water. Supposing that the concentration could be increased to 6, then the make-up would be reduced to 0.6 m³/h. For a cooling tower operating 24 h/day the water saved would represent a cost saving of almost $1329 per year at present metered water prices.

High Concentrations

The most common occurrence leading to depositis relates to the deposition of calcium carbonate or hard water scale. Raw water commonly contains calcium bicarbonate which is freely soluble. Unfortunately when water is heated as in cooling systems the bicarbonate converts to carbonate with loss of carbon dioxide. The calcium carbonate is very sparingly soluble and unless measures are taken, scale will deposit. One measure would be not to let concentrations within the system exceed the level where calcium carbonate solubility is exceeded and this of course means high water usage.

Alternatively methods may be used to prevent deposition of these insoluble calcium carbonate particles in a form that will produce hard scale. Two main methods are available:

1. Pre-treatment methods to change the quality of the water.
2. Chemical methods to convert the offending precipitates to a manageable form.

Pre-treatment methods: In the main, the process adopted is base exchange softening. In this process the water is passed through an ion exchange column prior to use within the industrial cooling system. The column consists of a vessel charged with base exchange resin. As the water is passed through the ion exchange column calcium and magnesium cations are exchanged for sodium ions. In consequence the calcium and magnesium salts of the raw water are converted to sodium salts which have a much higher solubility. The cooling system may then be run at much higher concentrations before deposition of salts will occur.

Whether or not pre-treatment of this type is selected as a viable proposition depends upon the system size and design parameters. Where the hardness salts within the raw water are very high and the system design is suitable, base exchange softening will be used. On other systems alternative methods of scale inhibition will be utilised on economic and other grounds.

Unfortunately base exchange water is corrosive so corrosion inhibitors will also need to be added to the circulating water and there comes a point where the savings made by being able to run the system at higher concentrations (say 5 instead of 2.5) are not sufficient to offset the cost of softening plus a corrosion inhibitor as opposed to other forms of treatment. Base exchange softened water is also alkaline which on concentration produces a high cooling water pH which is undesirable and

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Boiler Corrosion (Cont)

free acidity from the hydrogen form resin is neutralised with sodium bicarbonate from the sodium form resin. This produces carbonic acid which is removed in an aeration tower. The alkalinity is controlled by varying the ratio of R.Na to R.H.

Hopefully, this discussion has shown how an understanding of the chemical factors involved in boiler corrosion can be applied to the design, operation and maintenance of steam raising plant.

Cooling Systems Control (Cont)

unless controlled will lead to delignification of wood used in the cooling tower and will also attack any galvanising and aluminium in the system.

An alternative form of pre-treatment is by the use of a dealkalisation plant. This equipment is more sophisticated than the base exchange unit. The process is of the ion exchange type, but in this case the resin bed is designed to exchange the calcium and magnesium ions associated with the bicarbonate. The carbonic acid produced is passed through a degasser where it breaks down to release carbon dioxide, which is then removed thereby reducing the corrosion potential of the resultant water. Very good quality water is produced by the dealkalisation plant and greater concentration of the cooling water can be made with relative savings in water and treatment chemicals. The initial cost of the dealkalisation plant plus the running costs must be appraised against the water savings to determine whether this plant is economically advantageous.

In many cases pre-treatment by softening or by dealkalisation proves cost effective. In many others it does not and various chemical scale inhibitor treatments are used.

Chemical scale inhibitor treatments: The most obvious form of treatment is acid dosing to convert the bicarbonate to the sulphate or chloride dependant on which acid is used. Sulphuric acid is the most common choice in view of its cheapness. With acid dosing, reliable pH control equipment must be installed to call for sufficient acid only to keep the pH in the system to between 6 and 7. Acid dosing is therefore quite widely used where site supervision is adequate. On many sites however the handling of concentrated acid is hazardous and the dangers of overdosing is also very likely with disastrous consequences.

A further hazard is that with insufficient control, sulphates may deposit when using sulphuric acid. Quite naturally, research work has proceeded for a long time into alternative, more convenient, less hazardous, inexpensive ways of scale inhibition by chemical additives.

The earliest successes were achieved with polyphosphates. These compounds were found at low concentration (1—10 ppm) to interfere with the crystal growth of calcium carbonate and inhibit the formation of scale deposition. By the inhibition of growth the particles stay longer in suspension and the system can run with a super-saturated solution. Even if the particles do settle, they form in an easily dispersible form and can be removed by blowdown. This form of treatment is popularly called 'the threshold treatment', and is still used on small systems with a low heat load. Unfortunately where there is a high heat load, conversion of the polyphosphate to orthophosphate occurs. When this happens the phosphate no longer acts as a scale inhibitor but deposits as insoluble calcium orthophosphate.

Research workers then began to look for new compounds which would promote the threshold phenomena but which would not have the disadvantages shown by the phosphates. The organophosphorus compounds were found to satisfy these requirements. The most widely used of these are the organo phosphonates.

These materials function by absorption onto the crystal surfaces of the calcium carbonate or indeed other materials such as calcium sulphate as they are forming and distort the crystal structure, slowing down growth and allow a super-saturated solution to develop. This in turn inhibits deposition of scale onto heat transfer and other surfaces.

Another modern group of materials that similarly are seen to act in the threshold way, viz, small, non stoichimetric quantities exerting an extensive effect are the acrylate and methacrylate polymers and copolymers.

Corrosion In The System

As shown above, there are a number of ways and materials that will inhibit scale production within water systems and which therefore permit greater concentration of the circulating water and effect considerable saving of water. Unfortunately as the concentrations are increased so is the level of total dissolved solids within the water. This means that the conductivity of the water is increased and hence the corrosion potential.

Corrosion is an electro-chemical process where metal goes into solution at the anode, electrons are transferred through the metal or the solution to the cathode where they are involved in a number of reactions. The commonest of these in cooling water is the formation of hydroxyl ions:

$$Fe^{++} \longrightarrow Fe + 2e \text{ (Anode)}$$

$$O_2 + 4e + H_2O \longrightarrow 4OH^- \text{ (Cathode)}$$

The hydroxyl ions in turn will combine with metal ions to form an unstable metal hydroxide which breaks down:

$$Fe^{++} + 2OH^- \rightarrow Fe(OH)_2 \rightarrow Fe_2O_3/Fe_3O_4$$

In acid solution a slightly different process occurs:

$$Fe^{++} \longrightarrow Fe + 2e \text{ (Anode)}$$

$$2H^{++} + 2e \longrightarrow H_2 \text{ (Cathode)}$$

In this case the metal ions will no longer form insoluble hydroxide but will remain in solution. Where hydroxides are formed the process of corrosion will be slower as these hydroxides will themselves eventually tend to afford some protection to the metal and screen it from the corrosive environment. Under acid conditions no such protection is given and corrosion will be more rapid and severe.

It follows therefore, that some form of corrosion inhibition must be practiced and the logical approach is to stifle one of the reactions at the cathode or anode. An anodic inhibitor is one which will control the reaction at the anode and prevent metal ions going into solution. This is achieved by reacting the metal ions with the inhibitor to form an insoluble material at this site. This film of substance must be very thin and not reduce heat transfer. Cathodic inhibitors act similarly by stifling the reaction at the cathode. It follows that a combination of both is the most effective.

The most well known anodic inhibitors until recent times were the chromates, but these substances are highly pollutant and with the growing concern for environmental safety have virtually now been dropped from use. Phosphates have also been used for some time as anodic inhibitors but as stated earlier suffer the disadvantage of reverting to orthophosphate. Other anodic inhibitors are the tannins and nitrites. Both these compounds are however readily attacked by microbiological growth. Nitrite has been found to be an excellent inhibitor. The tannins however although good in more easily controlled systems such as boilers, are problematic in the variable conditions of the open cooling system and it is difficult to maintain a good film quality without creating a layer of iron tannate that becomes too thick in places and inhibits heat transfer.

With regard to cathodic inhibitors, the best known have been the amines of the filming type, calcium carbonate itself, which is very difficult to control, and the most successful and still widely used zinc salts such as zinc sulphate and zinc chloride. More recently however the introduction of organic phosphonates to water treatment has revolutionalised anti-corrosion treatment. Apart from being excellent scale inhibitors, the phosphonates in combination with other materials such as zinc and calcium salts provide an excellent inhibitory action at both anodic and cathodic sites. Furthermore, both the phosphonate and zinc may be used at low concentration. The natural carbonates in the water are relied upon to provide the third member of a highly successful corrosion inhibition complex.

Phosphonates are also used in low concentrations with nitrites and occasionally chromates as a dianodic corrosion system reinforcing the action of each at the anodic sites. In this way, low concentrations of nitrites and chromates can be used with the relevant advantages that this offers in terms of cost and effluent quality.

The second part of this article will appear in our December, 1980, issue.

Rust Prevention For Motor Vehicles

Corrosion is estimated to cost NZ between $200-$300 million annually (some put it at a higher figure) and among the more expensive items affected are motor vehicles. For the average person, a car is the second most expensive purchase made after a house.

Unfortunately, motor vehicles are, in many cases, rapidly deteriorating assets and rust can reduce their value more quickly and effectively than anything else except, perhaps, an accident.

Rust is caused by the combination of metal with oxygen or carbon dioxide. Moisture acts much like a catalyst to produce the union of iron and oxygen. A chemical reaction takes place by oxygen dissolving in water and this water layer adheres to the surface of the metal in such a manner as to allow the oxygen to remain long enough to cause corrosion.

An even more severe form of corrosion is by exposure of metal to acid fumes. With the addition of moisture, this combination forms hydroxides which finally dehydrate to form rust. If the air and mositure can be prevented from contacting the metal surface, rusting can be prevented or, if it has already started, stopped from spreading.

Valvoline Tectyl rust preventives were first made in 1938 by the Valvoline Oil Co., and are now marketed in over 80 countries throughout the world. More than 30 vehicle manufacturers, including Rolls Royce, Mercedes, BMW and Volvo recommend the product for factory and after market protection against rust.

There are many different grades: those used for car rustproofing are of the petroleum wax based, solvent cut back type and are thixotropic gels. The resilient underbody product that remains pliable is airlessly sprayed on to the whole floor pan of the car and leaves a shiny black film, while a different product is fog sprayed into all sections of the upper body including doors, sills, bonnet, and boot folds, and door pillars and posts under chrome mouldings — in fact anywhere a car will rust.

The preventives contain moisture displacing agents and are reacted or formulated into polar-chemical active compounds and given an electro-chemical affinity for ferrous and non ferrous metals. One end of the molecules of the polar-chemical compounds is strongly attracted to metal — the other end to the petroleum base. When a Tectyl compound is applied, this molecular attraction tightly binds the extremely thin film to the metal surface so that air and moisture are sealed out and corrosion is checked.

The coatings carry up to 6-year guarantees which are underwritten by insurance in NZ. Even vehicles up to 6 years old can qualify for a 2-year guarantee. Guarantees are transferrable from owner to owner.

Complete treatments vary in price from $100 to $147 depending upon the size of the vehicle and how difficult they are to treat. To obtain a guarantee the vehicle must have a complete underbody and upperbody treatment.

ENERGY STRATEGY '79

Issued by the Minister of Energy, Hon. W.F. Birch.

(Government Printer, Wellington, 1979)

pp96, $5.50, paperback

Energy Strategy '79 seeks to place before the general public the energy policy of the Government, together with some of the reasons for that policy. The major problem (our dependence on imported oil), and major hope (development of our own resources, particularly the Maui Gas field), together with the consequent challenges ("The capital investment for development of Maui alone is estimated at $2 billion"), and potential rewards ("such development would save $300 million per annum"), are all enunciated in the introduction. The goals for NZ's strategy are outlined in the second chapter as follows:

1 To reduce NZ's dependence on imported oil.
2 To increase diversity in NZ's Energy Supply System.
3 To ensure that energy is efficiently used.
4 To transfer energy supplies from non-renewable to renewable resources.
5 To establish a framework for energy planning which provides for changing social and economic circumstances.

In the next three chapters, which look at policy for Energy use, Energy pricing, and Energy supply, the first goal is the predominant one. Essentially the aim is, where possible, to switch away from oil, particularly in the industrial, domestic and commercial sector. In the transport sector (which is the major user of oil), the aim is to conserve fuel as much as possible, and to encourage some fuel diversification by using LPG and CNG. Although M15 (15% methanol-petrol blend) is mentioned, it does not seem to be a strong possibility at least in the near future.

The 96-page publication is very attractively presented, and contains a number of tables and graphs, which clearly convey a wealth of information on all aspects of production and utilisation.

While there is little of an explicit nature on the effect of the Government's energy policy on chemical industry in NZ, it is clear that its impact will be considerable. There will be opportunities provided by the existence of methanol and synthetic fuel plants, and by increased use of LPG and CNG. There will be opportunities created by future utilisation of our coal resources. Already both the Coal Board and the Liquid Fuels Trust Board have expressed interest in this area. Finally there will be numerous opportunities in the development and harnessing of biomass. All these should greatly enhance employment prospects of future chemists. Those involved, or considering becoming involved, in research in this area may be interested to learn that the Government increased its allocation by over 50% to $8.5 million last year.

There will be some chemists who find the lack of specific examples of future technology such as the use of hydrogen, development of batteries, photovoltaic effects and solar technology rather frustrating. It is helpful to bear in mind, however, that the document is aimed at a broad audience, and should perhaps by judged accordingly.

I.D. Watson

Dr Watson is Chairman of the Energy and Chemical Materials Resources Committee. He is also Reader in Chemistry at Massey University.

AN INTRODUCTION TO BOILER FEEDWATER TREATMENT

Booklet published by Catoleum

The booklet is recommended for industry as an excellent summary of boiler water problems. It deals with the type of impurities found in feed water, guidelines for the limits of impurities, and suggested methods for their removal. These impurities include calcium carbonate and sulphate, silica, magnesium hydroxide or silicate, iron and copper oxides and possibly calcium and magnesium phosphates.

The measures taken to prevent boiler system corrosion include removing dissolved oxygen, maintaining alkaline conditions and counteracting corrosive gases in steam and condensate systems.

Methods of removing impurities from water are listed which include coagulation and precipitation, ion exchange, deaeration and reverse osmosis.

Finally, details are given of methods of chemical dosage and tests carried out to determine the efficiency of the boiler water treatment. Overall the booklet is an extremely useful information source for the Works Chemist.

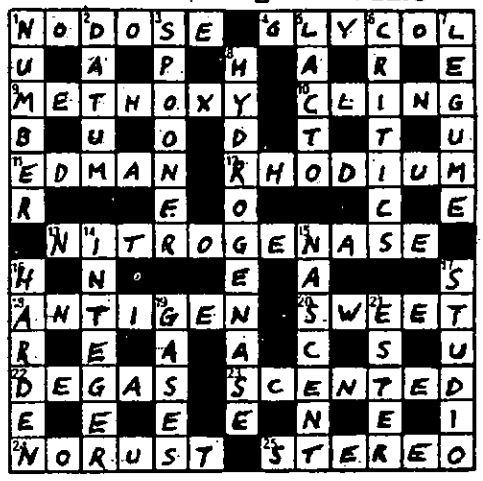
The booklets are available from Catoleum free of charge.

L. Eyres

L. Eyres is Research & Development Chemist with Abels Ltd, Auckland.

Chemical Crossword

Solution to August Puzzle



1980 AGM Report

The 1980 AGM was held at Massey University on Tuesday, August 19, with **President A.D. Campbell** in the chair.

Minutes of the 1979 AGM, the Annual Report, the 1979/80 Statement of Income and Expenditure and the 1979/80 Balance Sheet were all adopted.

Officers for the 1980/81 term were elected.

President: Dr A.J. Ellis, Assistant Director, DSIR.

First Vice President: Dr W.S. Simpson, Director, WRONZ.

Second Vice President: Dr D.E. Wright, Asst. Director, MAF, Wellington.

After nominations had closed, Mr Fletcher announced he had been appointed Director of the Heavy Engineering Research Association and would not be able to continue as General Secretary. Consequently branches were asked to forward nominations for the position of Acting General Secretary to hold the position until an official election at the next AGM.

Dr Ellis outlined preparations for the Golden Jubilee in 1981. The remit that "A fund be established during the Golden Jubilee year for the purpose of bringing overseas visitors to NZ and to which there shall be an annual addition from council funds. Only in exceptional circumstances shall the fund be used for other purposes" was carried.

Awards and prizes announced were:

Easterfield Award for 1980 to **Dr D.R. Crump** DSIR Chem. Div. Wellington.

ICI Prize to **Dr B. Halton** Chem. Dept. Victoria University.

Industrial Chemistry Prize to **Dr H.P. Rothbaum,** DSIR Chemistry Div., Wellington.

Chemical Essay Prize to **Miss L.M. Ball** Chem. Dept. University of Canterbury.

The prize for the Best Student Paper at the Conference was awarded to **Mr S.J. Henderson** of Victoria University, Wellington.

A remit that "The Rules of the ICI Prize be amended to read inter alia 'that only papers actually published during the 5-year period before the closing date (April 30) be considered as support for the prize" was carried.

The adoption of a logo in addition to the current seal of the Institute was discussed. No consensus of opinion was reached but Dr Halton suggested that any members who were interested could submit designs to the General Secretary for consideration by Council.

Under general business, **Prof Mackay** summarised a survey of employment opportunities for chemists that had been untertaken at Waikato University. Preliminary analysis suggested that there are 2.5 times more vacancies than available chemists. It is hoped to publish details in a future issue of Chemistry in New Zealand. A motion that "A more detailed study of the vacancies for chemists and technicians be undertaken by the NZIC" was carried.

Mr G. Husheer suggested that the Institute consider investigating the possibility of government assistance for firms employing technicians who were undergoing training similar to apprenticeship schemes. Council asked that he forward relevant information.

Dr Shorland raised two points in which he felt he had been unjustly treated by Chemistry in NZ* and by the 1980 Conference Committee. A further comment on the accuracy of Institute records was answered with a request to members that they inform their branch secretaries of the deaths of Institute members. (* In our February, 1980, issue we referred to Dr Shorland as "Mr Shortland". We take this opportunity to apologise to him for our errors).

A remit from the Auckland Branch that "There be a student grade of membership available for students of tertiary institutions" was carried.

August Council Briefs

The emblem of the NZIC again came under discussion, and the need for an additional stylised logo was mooted. Factors such as the relevance and clarity of reproduction of the current emblem and the cost and desirability of a logo were considered. The views of members were forewarded to branch delegates. Opinion was divided and it was resolved to put the matter before the AGM.

Finances were discussed at length, several branches expressing concern that too much money was being promised for undertakings which should pay their own way. Council affirmed that all conferences should be self-supporting.

Subscriptions will be considered at the November Council meeting but it was predicted that with a current rate of inflation nearing 20%, an increase of at least $5 would be necessary.

Dr Eyres reported to Council on the future of "Chemistry in NZ". Current postage rates are 10c per copy within NZ and are scheduled to rise to at least 14c in January. Council discussed ways of reducing costs without sacrificing the high standard.

Dr A.J. Ellis reported on progress for the Golden Jubilee celebrations. In association with the Manawatu Branch, a film on the contributions of chemistry to NZ is in preparation by the DSIR film unit and should be ready by the middle of 1981. The 1981 conference preparations are well advanced, promising a host of prominent overseas speakers. The February 1981 issue of "Chemistry in NZ" will feature the Institute's 50 year history. Council approved money to be set aside for the initiation of Golden Jubilee projects. **Prof A. Campbell** has written to other chemical societies inviting them to send representatives to the conference.

Mr S. Brooker and **Dr Eyres** are sounding out support for an international conference on fats and oils, to be held in NZ possibly in 1983. It was agreed that the event should get NZIC backing.

Dr David Bibby has replaced **Dr John Featherstone** on the Public Affairs Committee.

The following were elected to the Fellowship:

BRODIE Andrew Martin B.Sc (Hons) PhD (Cantuar). Dept. of Chemistry Biochemistry & Biophysics, Massey University (Snr. Lecturer).

Khaik Cheang B.Sc (Hons) Ph.D (Otago). Dept. of Biochemistry, University of Malaya, Kuala Lumpur, Malaysia. (Associate Professor).

Tetrahedron Prize

The editorial board and publishers of Tetrahedron Publications have decided to honour the memory of its founding co-chairmen, **Sir Robert Robinson** and **Prof R B Woodward,** by the creation of a Tetrahedron Prize. This prize will be given biennially for "Creativity in Organic Chemistry". It will consist of an appropriate gold medal and $US10,000. There will be no restrictions whatsoever on the award of this prize, except that it cannot be given to the present members of the editorial board.

Candidates for the first Tetrahedron Prize should be nominated by an appropriate expert with a 2-3 page citation of the creative work involved (with appropriate references) and the names of two referees. Nominations for the 1981 Prize should be sent to:

Prof Sir Derek Barton, FRS, ICSN, CNRS, 91190 Gif-sur-Yvette, France, and must arrive by December 31, 1980.

BOOKS RECEIVED FOR REVIEW

1) "Electronic Structure and the Properties of Solids"
W.A. Harrison
W.H. Freeman & Co.
2) "Kinetics Applied to Organic Reactions"
W. Drenth and H. Kwart
Marcel Dekker (paperback)
3) Soviet Scientific Reviews, Section B Chemistry Reviews
Ed. M.E. Vol'pin
4) "First Year University Chemistry"
J.M. Coxon, J.E. Fergusson and L.A. Phillips
Edward Arnold
5) "Computers in the Curriculum — Chemistry Pack"
R. Lewis
Edward Arnold
6) "Biological Magnetic Resonance" Vol 2
Ed. by L.J. Berliner and J. Reuben
Plenum Press
7) Fibrous Proteins: Scientific, Industrial and Medical Aspects Vols 1 & 2
Ed. by D.A.D. Parry and L.K. Creamer
Academic Press
8) The Nalco Water Handbook.
McGraw Hill.
From Catoleum Pty. Ltd.

BRANCH NEWS

Manawatu

The 1980 Branch Address to the New Plymouth Section was presented by **Mr Stan W. White** at Ivon Watkins-Dow Ltd on July 21. Mr White's subject, "A Chemist in the Freezing Industry"covered beef and sheep processing related to new hygiene requirements, various aspects of plant effluent treatment and modification to a machine that mechanically debones meat. Members are reminded of the Branch AGM to be held on October 13 when Mr White will present a similar address.

An informal meeting of the Hawke's Bay Section is being planned for later this year. Members requiring further information or wishing to attend this meeting are asked to contact either **Peter Dawson** (Napier 446-323) or **Ted Fletcher** (Napier 777-769) in the evenings or weekends or **Godfrey Husheer** or **Barry Streeter** (Napier 439-218) during business hours.

Wellington

The July meeting took the form of an Education Symposium (and public meeting) concerned with the subject "Is Inadequate Funding Jeopardizing our Agricultural Future, (or Can We Produce Sufficient Numbers of Well-trained Chemists)". Three speakers, **Mr Rod Julian** (Newlands College), **Mr John Offenberger** (Wellington Polytechnic), and **Prof John Tomlinson** (Victoria University) discussed the difficulties faced by the education system in producing chemists trained to a modern international standard.

Dr Brian Halton gave the Branch Chairman's Address "Stress and Strain: A century of Closed Carbon Chains" to the Nelson members in early August. The meeting was held jointly with the Nelson Branch of the Royal Society. This address will also be given in Wellington in September but will now be the 1980 ICI lecture and Branch Chairman's Address following Dr Halton's success in obtaining the ICI prize.

Later in August a Branch meeting held jointly with the Biochemical Society was addressed by **Dr David Ellerton,** Biochemistry Department, Victoria University on the subject "Invertebrate Respiratory Proteins". These metalloproteins serve as oxygen carriers and Dr Ellerton reviewed recent developments in the elucidation of the structures of erythrocruorins and hemocyanins.

Mr D. Howell of Unilever (NZ) Ltd is the convener for the local Jubilee Committee set up to co-ordinate and organise Branch activities in 1981 for celebrating the Institute's Jubilee. Mr Howell welcomes any ideas or offers of assistance.

Otago

In July a joint meeting was held with the Otago Branch of the NZIE. At this meeting **Prof G. Williamson,** Chemical Engineering Dept., of the University of Canterbury gave a very interesting talk entitled "Solar Thermal Energy Recovery". In this talk he described the work his department has carried out in developing a high efficiency solar heating panel for domestic and commercial applications.

In August the annual social function was held at the new Otago University Senior Common Room. **Prof F. Fastier** gave an after dinner speech and everyone enjoyed the evening.

University News

Auckland

Chemistry Dept: Dr G.A. Wright is at present spending a period of leave at the Wolfson Centre for Electrochemical Science at Southhampton University.

Dr M.J. Taylor recently returned from leave spent partly in Oxford and partly at the University of Windsor, Ontario. Activities included the completion of a review on I.r. and Ramon Spectroscopy of Organometallic Compounds.

Massey

The University was the venue for a number of important meetings during August, including the combined Institute of Chemistry — Biochemical Society Conference. Two meetings of particular interest to Institute members were the NELCON electronics conference and the "Sciences for Industry" course. The course, designed for sixth and seventh form students from the lower half of the North Island, provided an introduction to the place of the manufacturing and processing industries in the NZ industrial scene. It showed how school studies in science formed the basis of much of the work in a B. Tech degree.

Prof R. Hodges of the Department of Chemistry, Biochemistry and Biophysics was recently appointed Director of the Computer Centre. **Dr E.N. (Ted) Baker** of this Department was recently promoted to Reader and **Drs Ian G. Andrew, Gavin R. Hedwig, T.M. Kitson** and **Paul T. Callaghan** were promoted to senior lecturers.

Prof R.L. Earle and **Dr V.F. Larsen** (Biotechnology Department) recently received grants from the NZ Forest Service, BP Chemicals Ltd and the NZ Energy Research and Development Committee to undertake work on the production of liquid fuels by the fermentation of various plant-produced substrates.

Dr John D. Brooks (Department of Food Technology) and **Dr Ian S. Maddox** (Biotechnology Department) were awarded a research grant from the Ministry of Foreign Affairs to support an overseas PhD student's work on the production of citric acid from dairy whey by fermentation.

Victoria

Recent visitors to the Chemistry Department have included **Prof G.O. Aspinall** (Ontario, Canada) and **C Reed** (UCLA) who provided research seminars. **Prof R. Ferrier** of the Department also gave a seminar "Survey of Research at VUW on Carbohydrates and Prostoglandins".

Dr S.I. Smedley attended the Corrosion Conference in Perth, and **Mr D.L. Officer** the RACI National Organic Meeting in Melbourne in August, the latter sponsored by the Royal Society Young Scientist Fund. Both gave papers on their research work. **Mr D. Nelson** attended the Australasian Foundation for Dental Research conference in Adelaide by virtue of his winning paper at the anologous NZ meeting earlier in the year.

New proton and carbon-13 NMR facilities have been installed in the Department with the aid of grants from the University Grants Committee research committee and the NZ Lotteries Board.

Dr A.G. Grant, of the Biochemistry Department, left in August for 8 months' refresher leave. He has been awarded a Fulbright Travel Grant to visit the State University of North Carolina, Raleigh, NC to pursue his studies into the role of the glutathione S-transferase enzymes in creating insecticide resistance. Prior to this, he will be visiting the University of Surrey, Guildford, and the Courtauld Institute of Biochemistry, London.

Otago

Nutrition Dept: Dr L. Melton presented a paper at the 10th International Symposium on Carbohydrate Chemistry in Sydney in July. **Dr Joan McKenzie** has just returned from 8 months sabbatical leave at the Rowett Institute, Aberdeen, Scotland.

Pharmacy Dept: John Whitlam from the Sydney University, Pharmacy Dept. has just joined the staff as a lecturer at Otago.

Chemistry Dept: Visiting lecturer **Dr R.J. Sturgeon,** a carbohydrate chemist from Heriot-Watt University, gave a seminar in the department. **Dr R.A. Matheson** attended the RACI Electrochemistry Conference in Perth and **Drs M.R. Grimmett** and **R.A.J. Smith** attended the RACI Organic Symposium in Melbourne.

*

Dr L.H. Princen, chief, Horticultural and Special Crops Research Laboratories, USDA Northern Regional Research Laboratory, Peoria, USA, will visit NZ in November and will present a siminar on the work of his organisation at DSIR, Mt. Albert, Auckland, on November 10. For more details contact Dr L. Eyres, Abels Ltd. (Ph. (9) 548-145).

*

News From Govt. Departments

DSIR — Chemistry Division: Dr K.J.D. Mackenzie has been awarded Fellowships with both the Royal Society of Chemistry and the Institute of Ceramics in UK. Recent seminars organised by the Division have included "Developments in Cement Displacement Research" by **Lucille H Novak,** Exxon Production Research Company, Houston, Texas; "Cadmium in the Environment" by **Dr T Kjellstrom,** MRC Senior Research Fellow, School of Medicine, Auckland University; and "Could Electric Cars Help Ease NZ's Transport Problems" by **Dr S K Fellows,** Chemistry Division.

DSIR — Institute of Nuclear Science: During July **Dr Scott Whineray** of the Department of Chemistry, Biochemistry and Biophysics, Massey University, gave a seminar entitled "The Determination of Elemental Concentrations in Animal Tissue by **In vivo** Neutron Activation Analysis".

Central Institute of Technology: A series of seminars has recently been held at the School of Pharmacy on a variety of topics: The Role of the Analyst in Pharmaceutical Preformulation Studies **(Dr C G Hughes).**
Stability Studies of Acetaminophen-Peg-6000, solid dispersions **(Mr K Kumar).**
Glutathione-5-transferase in Galleria Mellonella (The Greater Wax Moth) **(Mr N Carroll).**
Aspects of the Toxicology of 1080 **(Dr J P Fawcett).**

Cawthron Institute, Nelson: Dr Don Grant has left for a 3-month visit to USA and UK. He will be working at the Glasshouse Crops Research Institute in Littlehampton, West Sussex and will be attending the 2nd Microbial Ecology Symposium at the University of Warwick, Coventry. He also hopes to attend the Biotechnology School — Queen Elizabeth College, London. **Miss Pat Johnstone** has left the Institute and has gone to Australia.

Invermay: Building is about to commence on the erection of new offices and laboratory facilities for the animal nutrition unit. **Dr David Stewart** and his staff will also be housed in these buildings. There will also be an abattoir built with these buildings. Permission has been received to relocate the rest of Invermay at Puddle Alley. This will take several years to complete.

Dairy Research Institute: Following a visit earlier this year to Australia, USA and Canada, **Dr Peter S. Robertson** recently travelled to Japan and Europe to complete his programme of visits to dairy processing and research establishments as part of a familiarization with the world diarying scene since his appointment as Director. While in UK, he attended the Annual Sessions of the International Dairy Federation (IDF) in Bristol.

Dr Wayne B. Sanderson recently headed NZ's delegation to the IDF Annual Sessions in Bristol. He also visited a number of dairy processing and research establishments in Europe before returning as a participant at an IDF Seminar in Singapore on "Recombined Milk and Milk Products". **Dr David F. Newstead** and **Mr John Gilles** also attended this seminar.

Mrs Helan R. Cleland recently joined the Whey Products Section. **Mr Brian P. Robinson** has resigned to take up an appointment as Senior Technical Officer with the Manawatu Co-op Dairy Co. **Dr Neil J. Walker,** who was seconded to NZ Milk Products Inc. in Chicago in 1977, has also recently resigned from the Institute to take up a permanent appointment in that company.

Dr L.K. Creamer is at present working in the Dept. of Food Science, University of Wisconsin, Madison, USA, where he has the status of Visiting Professor.

DSIR — Applied Biochemistry Division: The Director, **Dr Ray W. Bailey,** attended the General Assembly of the International Council of Scientific Unions in Amsterdam (6-12 September) and then spent 4 weeks at the Grasslands Research Institute at Hurley, UK. On his way home he will visit Peking for a week on behalf of Foreign Affairs scientific exchange between China and NZ.

On 26 August, **Dr Eric E. Conn** (Department of Biochemistry and Biophysics, University of California, Davis) presented a seminar entitled "Cyanogenesis — the production of HCN — in Plants and Animals". Dr Conn discussed various aspects of cyanogenic compounds, including glycosides and lipids, produced by some species of plants, bacteria and insects. Many of the toxic plants with which he illustrated his talk, were common ornamental varieties of shrubs and trees. Dr Conn paid tribute to the contributions of many people, in particular **Drs Graham W. Butler, Peter F. Reay** and **Brian A. Tapper,** who have investigated the biosynthesis of cyanoglucosides from amino acids. Although the pathway is not complicated, problems arose in these investigations because the enzymes involved in the various transformations are membrane-bound. Also, the metabolites are channelled and thus are not released in a free state and do not exchange with added labelled materials.

On "Open Day" for research workers in the Palmerston North area was held recently at the electron microscope facility. **Mr Keith I. Williamson** opened the demonstration by briefly describing the operating principles of electron microscopy in relation to both conventional transmitting (TEM) and scanning (SEM) modes of operation. Examples of studies were shown in which the Division's Phillips Models EM—200 (purchased in 1965) and EM-201C (1979) as well as the Cwikscan 100 Field Emission SEM (1973) were used.

Mr Michael J. Evers joined the Division on September 1 from NZ Forest Products Ltd, Auckland. Mr Evers has been appointed to set up, operate and develop the National Biochemical Engineering Unit. This unit is a joint operation between the Division and the Department of Chemistry, Biochemistry and Biophysics, and Biotechnology Department of Massey University.

Meetings And Conferences

The Second Circular about the Golden Jubilee Celebrations of the NZIC, particularly the Conference in Auckland next August, is now available; and members should receive it through their local branch mail. Through the generosity of 17 (at the time of writing) firms in NZ, and the personal contacts of the Chairman of the Conference Committee, **Mr Alan Mackney,** a glittering array of chemical leaders has been arranged, which can probably equal any group previously seen in Australasia. Spare copies are available from the Conference Secretary, Chemistry Dept, University of Auckland.

* * *

The Auckland Branch of the NZIC has arranged a 2-day symposium on 'Modern Laboratory Practice' to be held at the Secondary Teachers' Training College, Epsom, Auckland, on 21-22 October. A very good programme has been arranged, including a social evening and dinner. Overnight accommodation is available for attendees from out of town. Registration is $10, with extra for meals. Enquiries and registration to **Ian Scoltock,**c/- Abels Ltd., Box 9573, Auckland (Phone 548-145).

* * *

The Polymer Division of the Royal Australian Chemical Institute is holding two meetings of interest to us. On December 2-3, there will be a symposium on Adhesion Technology at the Caulfield Institute of Technology, Melbourne, where the main speaker will be **Prof Alan Gent** of the University of Akron, U.S.A. Enquiries to **Dr G B Guise,** CSIRO Division of Textile Industry, Box 21, Belmont, Victoria, 3216. The 12th Australian Polymer Symposium will be held at the Redleaf Lodge Motel, Blackheath (in the Blue Mountains of New South Wales.) Enquiries and offers of papers to **Dr David Sangster,** AAECRE, Sutherland, NSW 2232. Guest speakers will be **Prof C H Bamford,** FRS, of Liverpool, and **Prof J Guillet** of Toronto.

* * *

The Auckland Branch of the Oil and Colour Chemists' Association is having a one-day symposium on 'New Technology in the 80's' at Trillo's Downtown, Auckland on November 10. Enquiries to **R Spargo** Box 5192, Auckland.

* * *

The Canterbury Branch of the NZIC's July meeting consisted of a guided tour of the Chemical Engineering Dept of the University. The August meeting heard the President's address on analytical chemistry, which was preceded by a smorgasbord and an informal meeting. On the occasion of **Prof Campbell's** visit, opportunity was taken for the local Atomic Absorption Group to have its first meeting, when he spoke on selenium analysis by AA, and **Daphne Hinton** of Princess Margaret Hospital dealt with monitoring of industrial health. The Branch is planning a one-day symposium on chromatography as its activity for November. Sessions on HPLC and GLC techniques will be included. Further inquiries may be directed to **Dr Kip Powell,**

The Fletcher Memorandum

Meetings (Cont)

Chemistry Dept., University of Canterbury.

★ ★ ★

A seminar will be held in Hamilton, November 25-26, 1980, on oxygen in river estuaries and lakes. The proposed programme will include the following topics: Significance of oxygen in natural waters; Measurement of oxygen demand; Characteristics of sources of demand (meat, dairy, sewage, pulp and paper, effluents, etc); Sources and sinks of aquatic oxygen. Further details from: Scientist-in-Charge, Hamilton Science Centre, MWD, Private Bag, Hamilton.

★ ★ ★

An International Symposium on "Trace Analysis And Technological Development" is to be held at the Bhabha Atomic Research Centre, Bombay on December 15-18, 1980, or February 16-19, 1981. It is sponsored by the Indian National Science Academy.

Contact: **Dr M. Sankar Das,** Convener, International Symposium on Trace Analysis and Technological Development, Analytical Chemistry Division, Bhabha Atomic Research Centre, Trombay, Bombay 400 085, India.

Dr Roger Reeves and the Manawatu members worked hard for a successful Conference — and succeeded in every domain. Visitors to the Massey campus were impressed both by its physical and chemical maturity. With the strong Applied Biochemistry Division of DSIR and the Dairy Research Institute over the road, it seems set to become a great centre of scientific excellence. (Who says it wasn't one already!). We all enjoyed the 1980 Conference and express our gratitude to those who prepared it.

★ ★ ★

The Institute has a group of committees which are appointed by council (Branch committees bring forward nominations) at the November Council meeting. At present there are the following:—

Energy & Chemical Materials
Chairman: Dr G.J. Wright

Hazardous Chemicals
Chairman: Mr A.C. Kennett

Publications
Chairman: Dr L. Eyres

Public Affairs
Chairman: Dr M. Kingsford

to which has now been added:

Environmental
Chairman: Prof. R. Laverty, Dept. of Pharmacology, University of Otago

Any member wishing to "have a go" should write to the appropriate chairman.

In addition, on the Administrative side, we have

Honours Committee — to consider recommendations for Hon. Fellowships, nominations to ANZAAS, RSNZ etc.

Standing Committee — an executive committee to act on Council's behalf between meetings.

Membership Committee — to consider and recommend on membership applications.

I have long thought we should have some more, like

Finance Committee — to ensure we're doing the right things with our income.

Professional Committee — to ensure members keep to the Institute's code of ethics etc.

Continuing Professional Education Committee — to assist Branches and to update members' professional knowledge in chemical science. (NZIE has a new "Structured Continuing Education Course").

★ ★ ★

Question from a member recently. Where (how?) do I dispose of 2 x 200 litre drums of flammable solvent wastes (legally)? Can you help him?

★ ★ ★

The National Research Advisory Council has just released "Research Evaluation & Review Working Party Report" for comment. This report reviews management techniques used in Government-funded research organisations and makes recommendations on how these can be improved. Anyone wishing to comment on the report should contact me.

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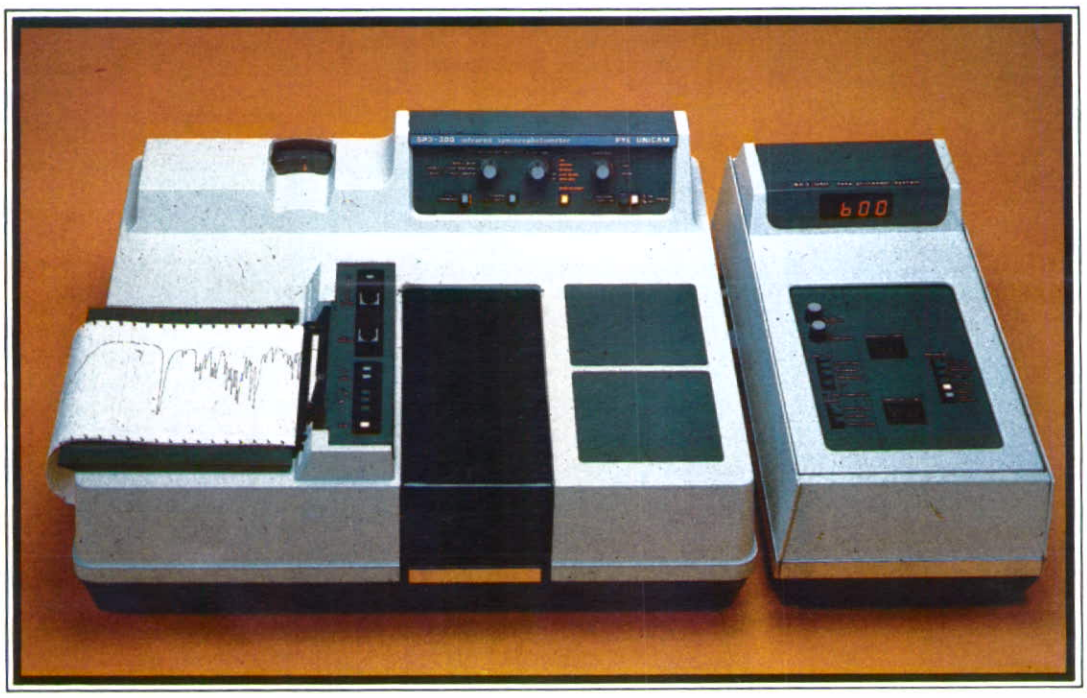

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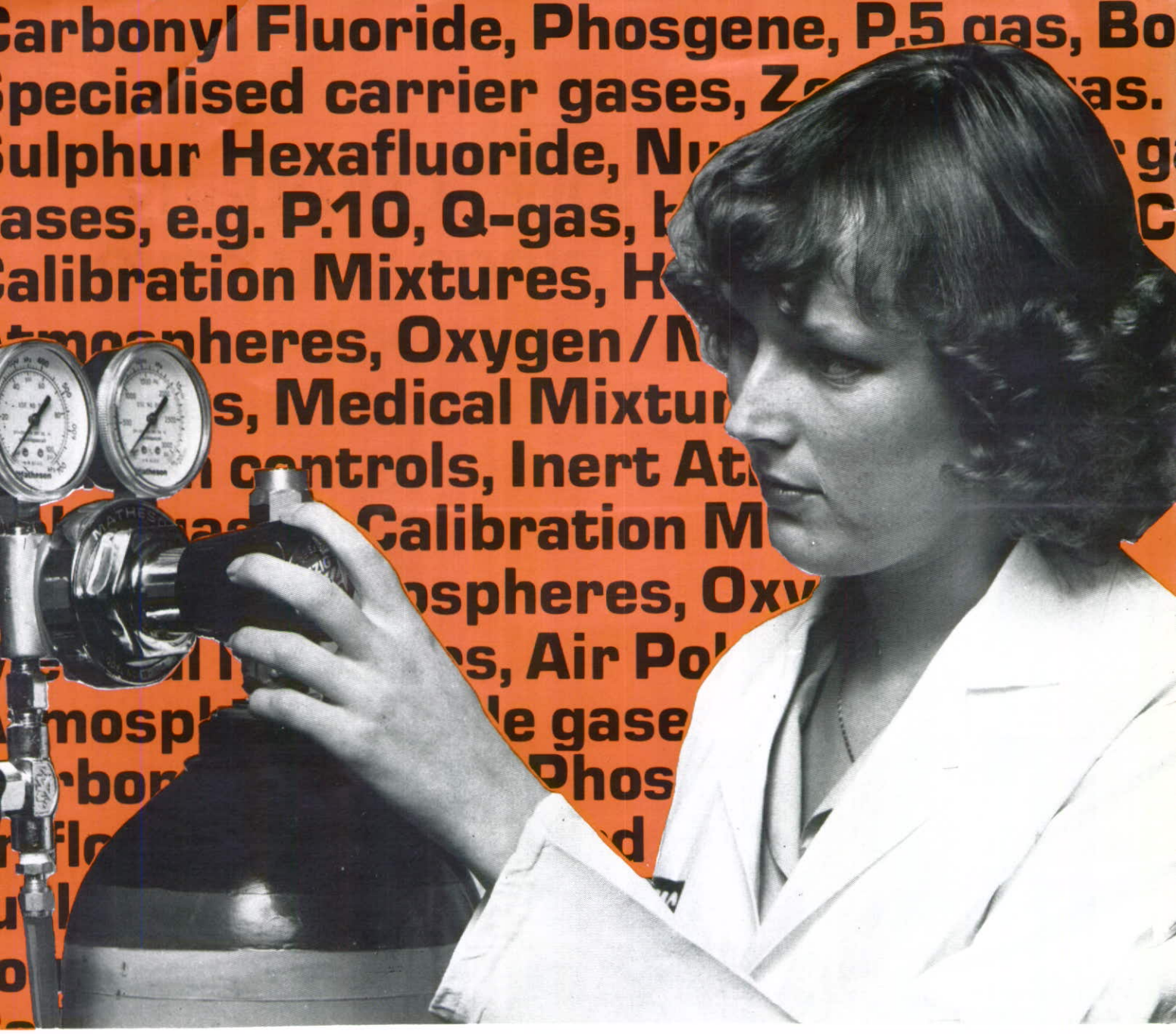

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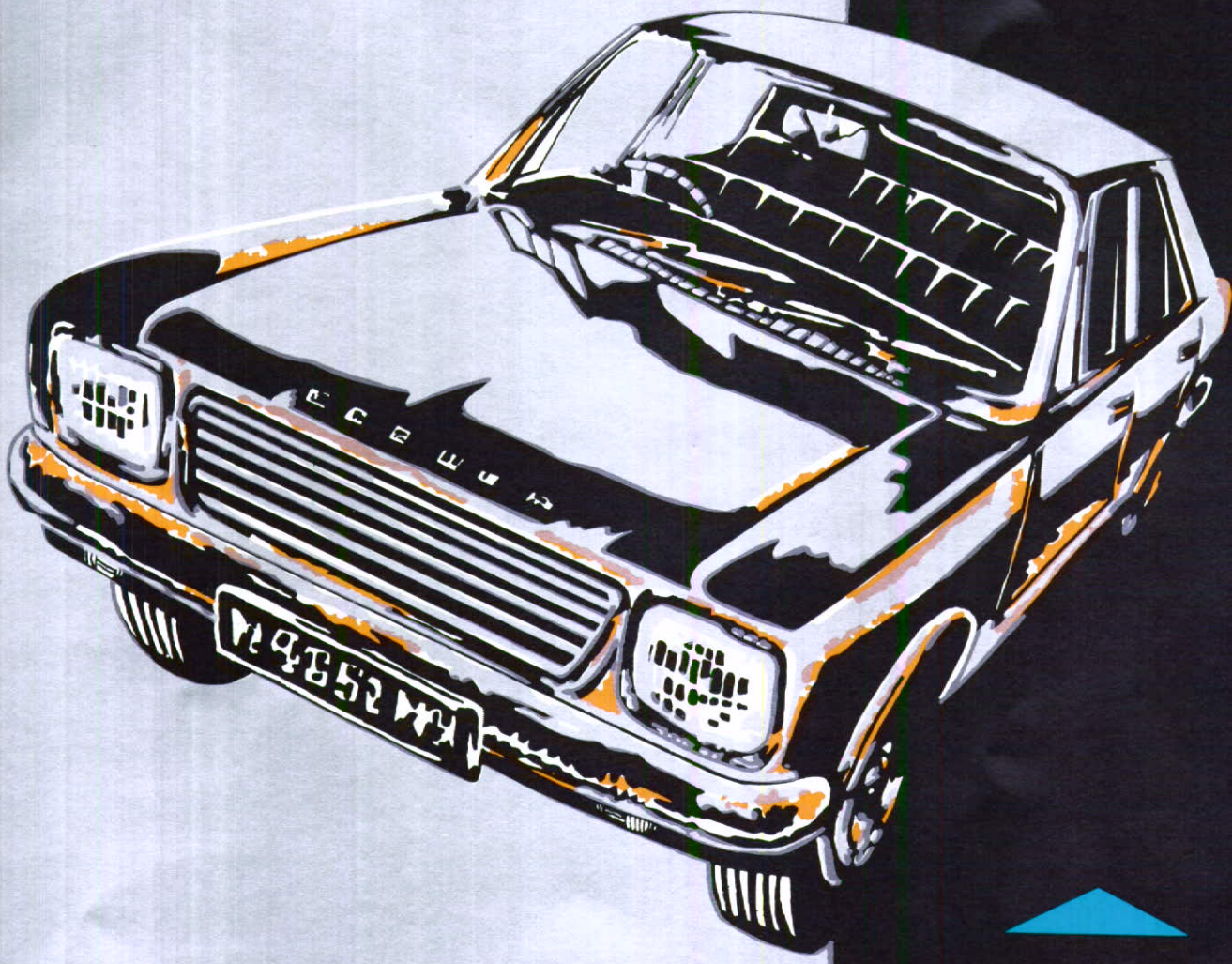

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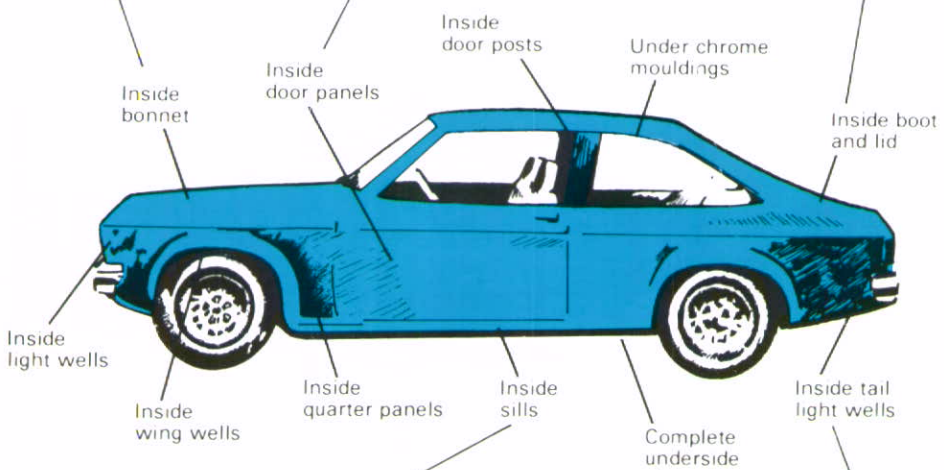

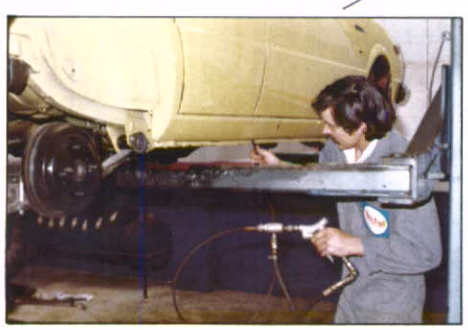

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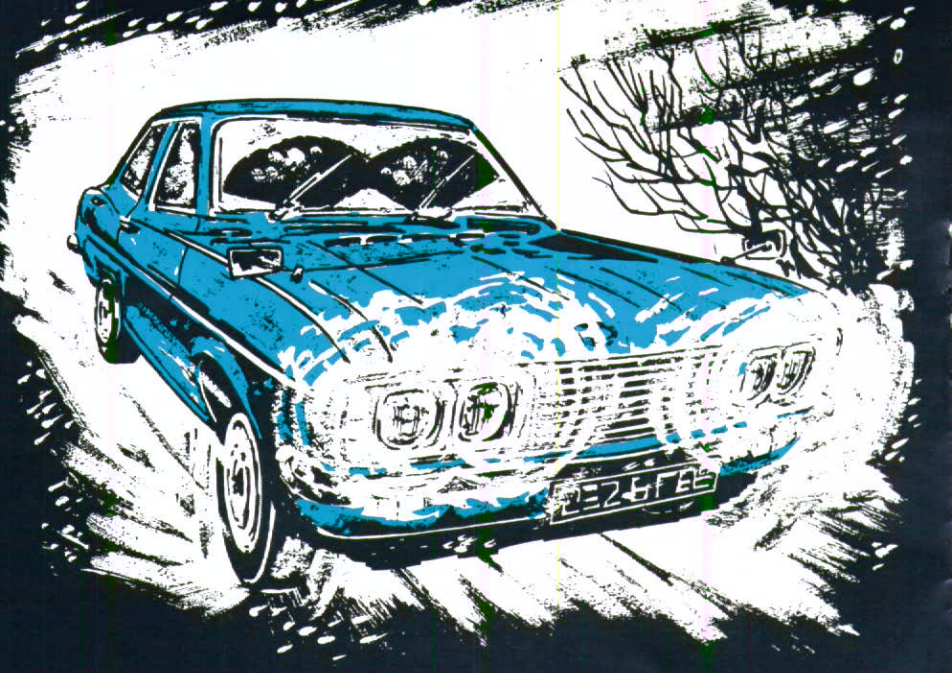

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how long does it take

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ENTER REFERENCE NUMBER OF PRODUCTS FOR FURTHER INFORMATION

NAME ..... POSITION .....

COMPANY .....

ADDRESS .....

PRINT PLEASE

Main Company Activity | | Number of employees | |

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NAME ..... POSITION .....

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Main Company Activity | | Number of employees | |

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