

Vol. 55 No.2 May 1991



Chemistry

IN NEW ZEALAND



- NEW FERENZ OXYGEN PLANT
- SOLID-STATE NUCLEAR MAGNETIC RESONANCE
- OXYGEN DELIGNIFICATION AT NZFP

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O₂



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EDITORIAL

This edition of "Chemistry in New Zealand" should appear to be different. You may have noticed that we have a new publisher who already has and will continue to play his part in giving our magazine a "new look". The editor would like to hear from you about any changes that have been made so far.

Editorial policies have not changed. A good mix of notices, news, comment, interest articles and serious papers will continue to be included. Keeping a magazine like "Chemistry in New Zealand" interesting depends on the members to provide suitable material. Neither the editor or the publisher have the time or the resources for seeking out news items.

If you read the fine print in this edition, the bit you never read in any magazine, you will find details about frequency of publication, deadlines for copy and publication dates. Copy deadlines are the dates selected copy is sent for typesetting not the last day for receipt for consideration! There has been a shortage of general interest and serious article copy of late so that the matter of article length has not yet been an editorial problem. However as a generalisation if an article is going to fill more than three or four pages it is getting a bit long, possible warranting a Part 1 and Part 2 if the topic is gripping! To ensure that people read it at all and understand the authors message an article needs to be succinct, enhanced with several good pictures or tables or graphs or diagrams which tell a lot of the story and be written to be understandable at the 6th or 7th form level.

One of the major problems that a magazine typesetter faces (and the editor when proofreading) is having to cope with unfamiliar words and symbols. You will note from the fine print that authors who have the facilities can now submit a supporting computer disc of their article (together with finished copy of course). This should speed typesetting and avoid the justified fury of authors having their work ruined by inadvertent typesetting errors. Both the new publisher and the editor will welcome comment from readers about this new look "Chemistry in New Zealand".
R.B. Hall, Editor

NOMINATIONS FOR COUNCIL

REMINDER TO ALL MEMBERS

Rule 16.2 "The President, Vice-Presidents, Honorary General Secretary and Honorary Treasurer shall be elected annually from nominations made by Branches, or by any six corporate members, and forwarded to the Executive Officer by June 30th." The Council manages your Institute Before the council elections make sure you have nominated the best candidates.

EXERCISE YOUR RIGHT
GET THE COUNCIL YOU WANT
For Council A.A. Turner
Hon. General Secretary

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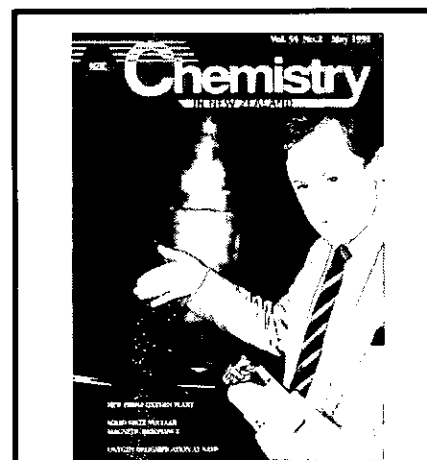
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Editorial: Technical and scientific articles should be submitted to the editor no later than 1st of the month of publication. The editor will always welcome commercial and industrial news on product design, development and testing, processing techniques, company and personal news etc.



THE COVER

The Honourable Simon Upton Minister for Science and Technology and for the Environment pictured getting hands on experience at the opening ceremony of the new FERNZ Oxygen Plant at Kinleith (see story later in this issue). As Minister in a time of great change for research, development and industry, Simon Upton will be an important force in shaping the future of chemistry in New Zealand.

FROM THE PRESIDENT

On 20 February, Council held its first telephone Conference as a full Council Meeting. It successfully, I believe, dealt with Council business in two 2 hour sessions. This cost efficient method will be used again for an appropriate proportion of future Council meetings.

A number of items of interest to the wider membership were discussed at this Council Meeting and are reported on in Council News on this issue of the Journal. I would, however, like to make some additional, personal, comments on some of these items.

Our general financial situation which looked somewhat bleak last year and necessitated a rise in subscription from the year before has now stabilised to the extent that subscription rates will stay as they are for the 1991/92 financial year. This is good news and has been achieved by close control over expenditure and improvements in income other than from subscriptions.

Membership has been static or declining in the last few years and Council is now wishing to widen membership of NZIC, and therefore its financial base without compromising current standards of entry. Council proposes to introduce an affiliate grade for those interested in chemistry but not eligible for the grades that require particular qualifications. This will replace the 'local member' category that Branches currently administer. In addition Council will be investigating the possibility of corporate membership for organisations interested in chemistry.

Several of the Council Committees have been reconstituted in membership and in

some cases are now hosted by a different Branch. Council and myself thank those previously serving on the Public Affairs and Science policy Committee in the Manawatu Branch (now hosted by the Wellington Branch under the convenorship of Mr Walter Freitag), the Chemical Education Committee in the Canterbury Branch (now hosted by the Auckland Branch, convenor Professor John Packer), and the Environmental and Hazardous Chemicals Committees in the Otago and Canterbury Branches respectively (now merged into one Environmental Committee, hosted by the Auckland Branch, convenor Mr Norman Thom). Such reconstitutions of Council Committees from time to time are a good way of spreading the work load of the Institute in its public activity role. The new Public Affairs and Science Policy Committee has already started its work by providing a submission to the Task Force on Crown Research Institutes and also a response to the Task Force's Interim Report.

There was a considerable debate in Council about the future of the NZIC Annual Conference. The 1991 60th Jubilee Conference being held in Christchurch is presently being organised but no Branch is in a position to host the 1992 Conference. Also, the NZ Biochemical Society would not be a co-sponsor in 1992 as it intends to join in with another Society for a Confer-

ence. Therefore, the options for 1992 are for some or all of the Specialist Groups to hold their own Conference in that year and/or to encourage NZIC members to attend the Ninth National Convention of the RACI being held at Monash University, Clayton, Victoria, 28 September - 2 October 1992. These options are being pursued further.

NZIC has recently learnt that we are likely to be invited to be one of the sponsoring societies for the next PACIFICHEM Congress to be held in 1995 in Hawaii. This is quite a coup for New Zealand chemistry as previous PACIFICHEM organisation has been entirely organised by the USA, Japan and Canada. My thanks for the valuable groundwork of Dr Brian Halton, Wellington who is continuing to act as NZIC representative for PACIFICHEM activities.

In my last two letters I have referred to FOSTS (Federation of Scientific and Technological Societies). The first FOSTS Newsletter is being circulated to members by the Royal Society of New Zealand. This Newsletter profiles Council Members and gives information on the role and goals of FOSTS. I have found that FOSTS Councilors are very willing to action their "portfolios" and this bodes well for the future effectiveness of FOSTS. NZIC members, along with members of other organisations affiliated to the Royal Society of New Zealand, will soon be asked to participate in a survey of Royal Society membership for information that will be included in a Directory of Members. The first version of this Directory is scheduled to be published about the end of November this year.

Regards
Harry Percival
President

FIRMS SURVIVE WITH SCIENCE

Companies surviving the tough economic conditions are those which have embraced science and technology,

A public meeting of scientists was told in Palmerston North on 14th of March. David Munro, the technical manager of dairy company Bay Milk Products, said these companies were no longer run by lawyers and accountants.

Companies now needed informed engineers and technologists to become more efficient. Mr Munro was one of four speakers at a public meeting held by the Institute of Chemistry's Manawatu branch.

The DSIR seminar room was filled with scientists seeking more information about the government's proposed Crown Research Institutes from ministry representatives and the Foundation for Research, Science and Technology.

A theme which emerged was the need for better communication between industry and scientists.

Mr Munro said he despaired of scientists who isolated themselves from industry, but he said industry also had to invest more in research. "Our industry is desper-

ately short of scientific and technological people if we want to survive and prosper."

Science review manager for the ministry Margriet Theron said the new research institutes were a logical conclusion following the restructuring of science.

They would work in a more commercial environment and be able to enter into joint ventures with industry. Such ventures are not possible for DSIR and MAF under the present law.

The Crown would remain the sole shareholders and not expect the institutes to make a profit. Their prime role would be research.

Geoff Page, member of the Ministerial Science Task Force looking into CRIs and Massey University assistant vice-chancellor Ian Watson also spoke. Prof Watson is a member of the foundation's board.

by Kamala Hayman
Manawatu Evening Standard - 14 March

COUNCIL NEWS

For the first time, Council met by conference telephone calls on Wednesday 20th February. The meeting was held in two 2 hour sessions, one in the morning and one in the afternoon. The meeting could be regarded as highly successful with a full attendance at a fraction of the cost that would have been involved had members travelled. The personal costs of time and inconvenience involved in meeting at one location were also avoided. The business of the meeting proceeded without difficulty with Harry Percival holding people to the business in hand as though this was a normal method of holding a meeting!

It was agreed that there should be at least one physical gathering of Council per year. The August meeting of Council will therefore be held in Christchurch immediately prior to the 1991 Conference on Saturday/Sunday 24/25 August 1991.

The Council considered a number of membership matters particularly the decline in membership. An analysis of the reasons for the last 65 resignations show that they fall into the following broad categories:-

- **Now overseas** 9 have lost association with New Zealand.
- **With reluctance** 34 have generally moved away from Chemistry.
- **Were life members** 2 No longer any interest and have not attended meetings for a very long time.
- **Students** 5 Have not pursued a chemistry career.
- **Unemployed** 1 Cannot afford subscription.
- **Self-Serving** 6 Feel that the Institute has nothing to offer them for the high level of subscription.
- **Others** 8 Generally, gone no address.

TOTAL 65

It was agreed that a current list of members would be prepared and sent out as an insert in the Journal.

Other matters discussed in Council have been commented on very fully by Harry Percival in his newsletter.

CONFERENCE NOTICES

FIRST ANNOUNCEMENT

3rd EurAsia Conference on Chemical Sciences Bangkok, Thailand December 14-18, 1992

AIM OF THE CONFERENCE

The Eurasia Conferences on Chemistry, held in Bangkok and Seoul in 1988 and 1990, have been organized to bring scientists from the Supercontinent of Eurasia together for an improvement of mutual

relations as well as an enhancement of scientific cooperation in the field of chemical research. The success of this attempt has been culminated by the participation of a large number of distinguished chemists not only from the Supercontinent but also from other continents. At the third Eurasia Conference on Chemical Sciences in Bangkok, the same aim of the conference will be honoured and carried through. Special effort will be made to allow also university students of the region to participate.

SPONSORS

Ministry University Affairs, Chulalongkorn University, Forum of Theoretical Science

SCIENTIFIC PROGRAM

The scientific program will include plenary lectures, invited session lectures, oral contributions and posters in the following fields.

- Biochemistry
- Computer Applications in Chemistry
- Coordination Chemistry
- Environmental Chemistry
- Natural Product Chemistry
- Solid State Chemistry
- Solution Chemistry
- Pharmaceutical Chemistry

All correspondence should be addressed to: Assoc. Prof Dr. Sirirat Kokpol Secretary, EuAsC2S-1992 Dept of Chemistry, Chulalongkorn University Bangkok 10330 THAILAND Tel : (66)-(2)-2521730, (66)-(2)-2527019 (66)-(2)-2501127

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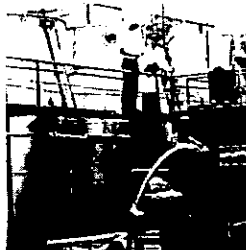
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Conference notice continued page 30

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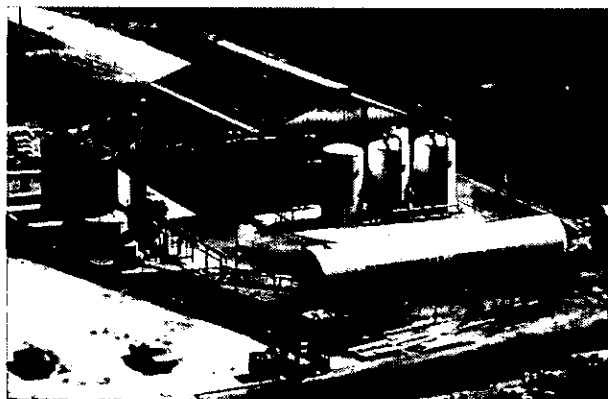
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NEW FERNZ OXYGEN PLANT RUNNING AT KINLIETH

Roger Whiting Auckland Institute of Technology

On 15th March this year FERNZ Industrial Chemicals opened their new oxygen plant at Kinleith. The opening ceremony was officiated by the Honourable Simon Upton, Minister for Science and Technology and for the Environment.



The new FERNZ plant produces oxygen by the PSA (Pressure Swing Adsorption) method. With a capacity of 38 tonnes per day this plant is the biggest of its type in the world. The PSA technology was developed by Air Sep Corp. Air Sep Corp of Buffalo New York have the most advanced technology in this field exploiting the Zeolite Technology developed by Union Carbide in the late 1950's.

The plant is sited next to the New Zealand Forest Products Kinleith kraft mill and supplies the mill with oxygen. The installation of the new plant is part of an upgrade of the pulp mill which has been underway since the middle of 1990. The oxygen is used for bleaching of Kraft pulp. New Zealand Forest Products have moved to using oxygen for part of their pulp bleaching process to eliminate the minute traces of chlorinated species found in the resulting products. Although evidence suggests that the levels found have in fact been below safe limits the mood of the consumer has been to demand total elimination of

these species. This new plant represents a step to this goal.

The plant represents a new approach to plant operation in that FERNZ have built a dedicated plant to supply the NZ Forest Products mill. This leaves NZFP free to concentrate on their primary business of producing pulp and paper while FERNZ are developing their expertise in oxygen supply. FERNZ's Development Manager

Ron Moon feels this will be a growth area as more and more plants follow the NZFP lead and eliminate chlorine bleaching from their processes.

The plant was supplied by Air Separation NZ Ltd. FERNZ engaged Babbage and Partners to oversee the project. The pressure vessels were built in New Zealand by Fitzroy Engineering of New Plymouth. The total cost of the project was NZ \$4M of which \$1.6M paid to New Zealand contractors. The remainder was spent overseas primarily on the compressors, pumps and the Zeolite material itself. The entire project took 9 months from signing the agreement to the opening ceremonies.

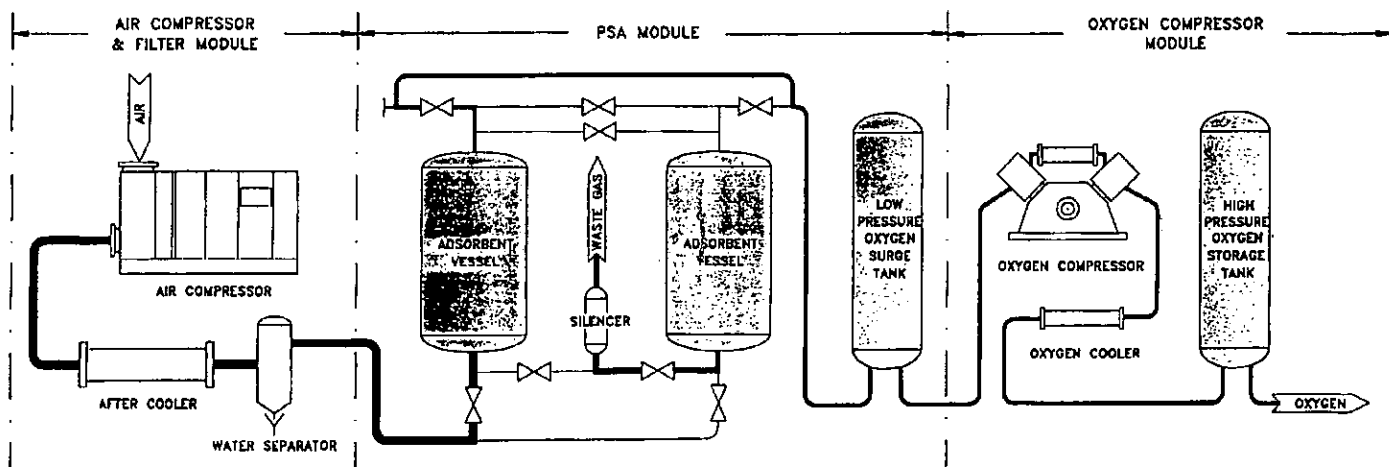
The process is based on the preferential adsorption of nitrogen by a synthetic zeolite. Air is drawn in and compressed. Oil and water are removed as these are irreversibly adsorbed by the zeolite and would slowly build up and render the bed unusable. The system operates at a much lower pressure than the cryogenic process. The compressed air is passed through one of

two beds of zeolite pellets (2 - 3 mm diam) which adsorb the nitrogen and a very small amount of the oxygen from the air. The out flow from the bed is Oxygen 93 - 95.5% with the remainder being argon and traces of nitrogen. The exact composition depends on how flow velocities through the zeolite. At a production rate of 44 tonnes a day the traces of nitrogen appear and the purity to less than 93%. However at the contracted production rate of 38 tonnes per day the purity is more than 93%. From the zeolite bed the oxygen is compressed again and stored in a holding tank ready for use. When the zeolite bed has been used for some time it becomes saturated with nitrogen and the gas flow is switched to the second bed. While the second bed is in use the first is vented to the air and the nitrogen desorbed. The first bed is now ready for use again but first it is flushed with oxygen to ensure that no nitrogen is carried through to the holding tank as the gas initially flows into the bed.

This entire process is computer controlled on the time cycle basis so that human operators have little to do with the minute by minute operation. In the event of a malfunction the entire plant can be controlled and reprogrammed by the parent company suppliers Air Sep Corp in Buffalo, New York.

The advantage of the PSA method for producing oxygen is that the only energy required is that to compress the air and then the oxygen up to the desired application pressure in this case 1500kPa. The only effluent is nitrogen which can be harmlessly vented to the air. This environmental advantage also applies to the bleaching process using oxygen. There are no chlorinated species or hazardous materials needed so that the risk of environmental damage is much reduced.

This represents an overall approach to environmental issues which has become much more the hallmark of large responsible corporations. In this case the comparison of the use of oxygen produced by the pressure swing adsorption method to bleach pulp compared to using chlorine produced electrolytically to has advantages in terms of reduced risk of chlorinated species in the product and in the effluent, reduced energy usage in the production of the raw material and less hazardous plant operation.



HOW TO MAKE OXYGEN

A quick look through a high school chemistry text or undergraduate text will indicate that oxygen can be made by decomposing potassium chlorate in the presence of manganese dioxide. However this method was never used industrially.

The Brin Method¹

The earliest industrial method for making oxygen was the Brin process. This involved heating Barium oxide in compressed air to produce barium peroxide and the heating the barium peroxide which decomposed to give oxygen and barium oxide.

The Joule - Thompson Method (Cryogenic oxygen)²

For a long time the main process for producing oxygen was based on the Joule - Thompson method. In the Joule Thompson method for the production of oxygen air is first compressed (to approx 13,000 kPa). It is then cooled using a water cooled heat exchanger where water is removed. After this it is cooled by the cold waste stream from the final stage of the process which takes the temperature down to ca -130°C. The cold compressed gas is passed through an expansion valve to ca 400 kPa where it cools further as it expands and some condenses as a liquid. This liquid contains about 32% oxygen and is fractionally distilled at 400 kPa to give liquid nitrogen. It is then expanded further and fractionally distilled again to give liquid oxygen and neon gas.

The purity of the products from the Joule - Thompson method in its modern form is high - in the region of 99%. Refinements to the process include with counter current heat exchangers using the cold waste gas from the fractional distillation and booster compressors using the expansion of the gas on cooling to increase the compression of the incoming gas. Even with these refinements the process is energy intensive.

The Pressure Swing Adsorption (PSA) Method^{3,4}

The key to the PSA method for the production of oxygen is the zeolite bed through which the air is passed.

Zeolites are Aluminosilicate minerals with a complex crystal structure made up of interlocking rings of silicon aluminium and oxygen ions. Naturally occurring Zeolites which released water on heating and reabsorbed it on cooling were first noted two centuries ago. The ability of these material to selectively

adsorb molecules other than water was not recorded until the 1920's. By the early 1930's, X ray diffraction studies were revealing the zeolites as crystalline materials having within each crystal a system of precisely arrayed cavities and pores. precisely

In 1948, Union Carbide Corporation researchers became interested in the possible use of adsorption for the separation of atmospheric gases and other industrial uses. Natural Zeolites showed a degree of promise but their scarcity and variability made the use of naturally occurring zeolite unattractive. Recognising both the limitation of natural minerals and the potential for of zeolite type materials Union Carbide set up a research programme to synthesise and characterise zeolite materials.

By 1953 over 30 distinct pure zeolite species had been prepared. Some of these were completely novel materials and are now covered by patents. The range of uses to which these materials have been put is very broad from catalysis as in the case of ZSM-5 in the synfuels plant to the more mundane molecular sieves used for drying laboratory reagents.

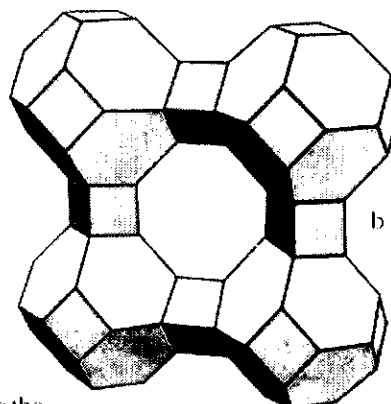
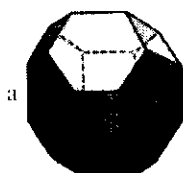
For the separation of oxygen from air there are two possible zeolites used these are the calciumA and calciumX types. The formulae are based on:
 $\text{Na}_{12}[\text{AlO}_2]_{12}[\text{SiO}_2]_{12} \cdot 27\text{H}_2\text{O}$ - sodiumA
 $\text{Na}_{46}[\text{AlO}_2]_{46}[\text{SiO}_2]_{86} \cdot 264\text{H}_2\text{O}$ - sodiumX
some or all of the sodium ions are replaced by calcium ions to form the calciumA and calciumX materials. These are then dehydrated to give a crystal structure with voids and channels through it.

The crystal lattice of is made up of AlO_4 and SiO_4 tetrahedra joined together to give truncated octahedrons joined by rectangular channels

with maximum diameter of 110 nm and a minimum diameter of 42nm. The truncated octahedra themselves enclose a second set of smaller cavities with and internal diameter of 66nm. These are called cages and are connected to the larger cages by means of distorted rings of oxygen atoms with a diameter of 22nm. The calciumX zeolite has a similar basic unit of truncated octahedra so the cages are still present with the diameter of 66nm and an entry ring of 22nm diameter. However the octahedra are arranged differently so that the larger truncated cube octahedral cavities do not form.

The adsorptive powers of these materials are primarily due to the cations which are exposed in the crystal lattice. These will attract polar molecules and hold them in the crystal. The greater the dipole the more strongly bound the molecule will be. In such close proximity to a positive charge even molecules which are non polar can have a dipole induced in them (This is termed a charge induced dipole interaction) and are attracted to the cations. This is similar to attracting pieces of paper to a charged plastic ruler. In this case the adsorption of the molecule will depend on the polarisability of the molecule. The more polarisable the molecule the more strongly it is adsorbed. As nitrogen is more polarisable than oxygen it is more strongly adsorbed. In the case of nitrogen there is also a strong charge - quadrupole interaction contributing to the free energy of adsorption. This is probably due to the triple bond structure of nitrogen.

When the gases are adsorbed into the cavities of the zeolite the process is competitive. This means that as nitrogen is adsorbed that the adsorption of oxygen is decreased thus there is a strong selectivity for nitrogen resulting in only oxygen and trace gases being carried through.



The truncated octahedron (a) and (b) the array of truncated octahedra in the framework of zeolite A. The linkage is shown via the double 4-rings

In the case of the calciumA type Zeolite the lattice forms a truncated cube octahedra with an internal diameter of 110nm. This is a central cavity termed a cage and the way into it is through six (roughly) circular apertures formed by a nearly regular ring of eight oxygen atoms with a free internal diameter of 42nm. These cavities join together to give a three dimensional array forming a system of unduloid-like channels

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1. KM & RA McKay, "Introduction to Modern Inorganic Chemistry", Intertext London
2. Union Carbide "Air Separation Technology"
3. Union Carbide "Molecular Sieves"
4. Donald W Breck, "Zeolites Molecular Sieves" Wiley Interscience 1974 pp689-718.

OXYGEN DELIGNIFICATION OF PAPER PULP AT NZFP

A MAJOR ENVIROMENTAL ADVANCE

Brian Jones - NZFP Pulp & Paper Ltd. Technology Division

In May NZFP Pulp and Paper Limited will commission its new oxygen delignification plant and modernised bleach plant at Kinleith.

It is not often that a pulpmill has the opportunity to make major changes to its process because of the large capital costs involved, but when the opportunity does present itself, a wise company will install not only the most efficient but also the best, environmentally friendly technology possible. NZFP has done this. In fact, NZFP has been much more environmentally proactive than has traditionally been the case with many pulp and paper mills. It has installed not just one, but two oxygen delignification stages, followed by a bleach plant designed to use no molecular chlorine.

Pulp bleaching is a multistage process in which the first two stages involve lignin removal. The final two or three stages bleach or brighten any residual coloured material. It is the effluent from the first two stages, with their loading of chlorinated organics, which has been the main environmental concern for any pulpmill in the past. In particular, the main problem has been the polychlorinated lignins. In recent times it is the family of polychlorinated dibenzodioxins and dibenzofurans, collectively referred to as "dioxin", that has received most attention. The most well known of this family of over 300 members is 2,3,7,8-tetrachlorodibenzo-p-dioxin. While the dioxins may be the pollutants of

most concern, it is desirable that all organochlorine compounds discharged to the environment be reduced to a minimum. This is especially so of the polychlorinated compounds, which tend to be the most persistent and thus potentially the most troublesome. While it is possible to treat the effluent before discharge, and both New Zealand kraft pulpmills have good secondary effluent treatment systems, it is obviously best to avoid making the pollutants in the first place.

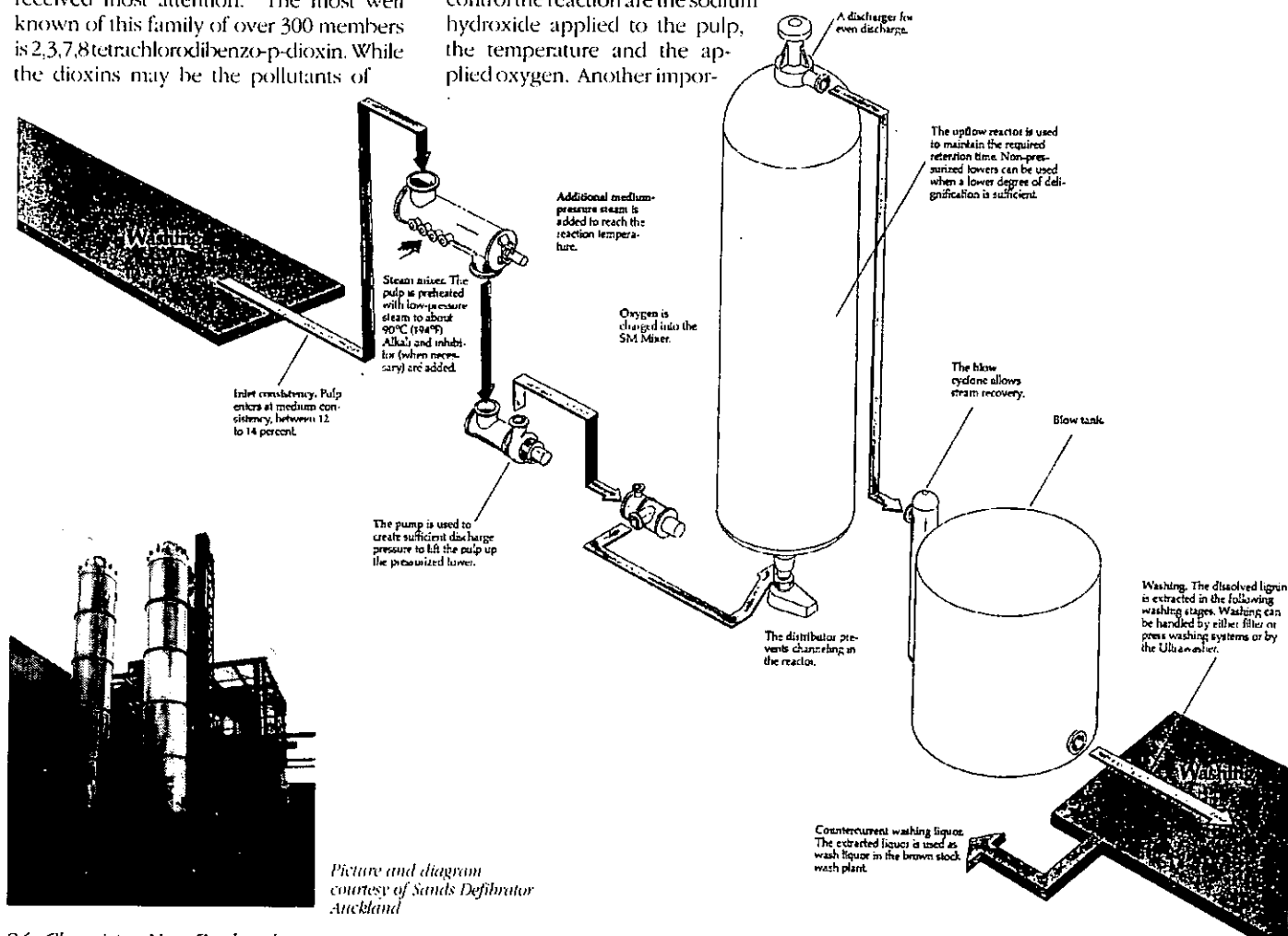
The basic approach is to lower the amount of lignin entering the bleach plant and there reduce the use of molecular chlorine by increasingly substituting it with chlorine dioxide. By adopting these techniques the industry has already shown it can reduce the production of dioxins to non-detectable levels. Analytical techniques now enable dioxin detection down to the parts per quadrillion level.

Increased delignification prior to the bleach plant is usually achieved using a one stage oxygen delignification process. At Kinleith NZFP will use a two stage process to boost the delignification even further, 75% compared to the usual 45%. Each oxygen stage is carried out in a 280 m³ pressurised reactor at 100.C for approximately 1 hour. The parameters which control the reaction are the sodium hydroxide applied to the pulp, the temperature and the applied oxygen. Another impor-

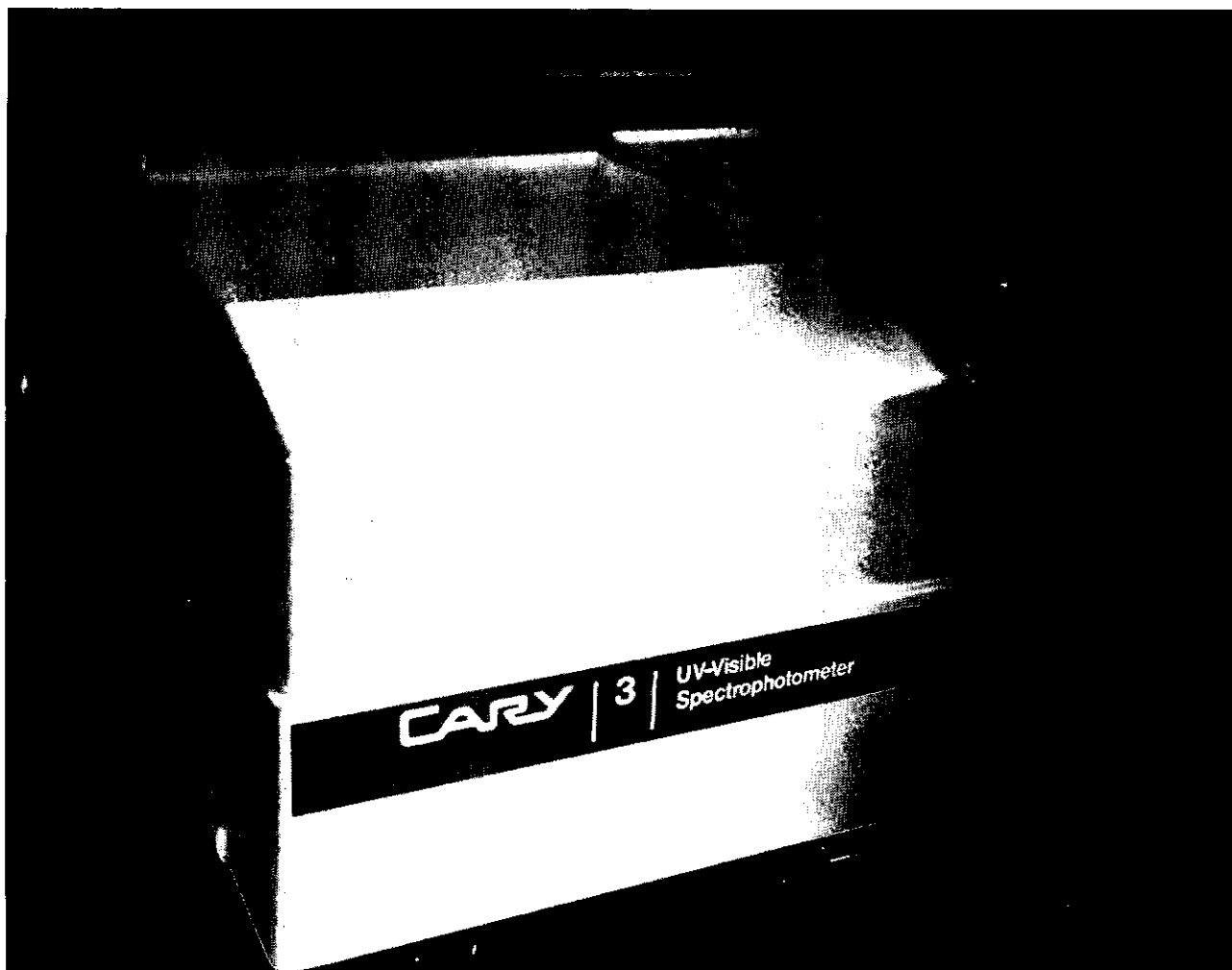
tant factor in reducing the lignin entering the bleach plant is the efficiency of the post oxygen delignification washing. It matters not whether the lignin entering the bleach plant is still bound within the fibre or whether it is dissolved lignin entrained in the pulp due to poor washing. The important factor is the total amount. For this reason NZFP have opted to use three very efficient press washers in the oxygen delignification plant.

Traditionally, the first stage of a bleach plant has used a combination of molecular chlorine and chlorine dioxide. The chlorine is undoubtedly an extremely efficient delignifying agent, but because it both oxidises and participates in substitution reactions significant quantities of chlorolignins are formed. Chlorine dioxide, although more costly and a less efficient delignifier, produces little chlorolignin and virtually none of the polychlorinated material.

Because of the elaborate oxygen delignification process, and to a lesser extent the *Pinus radiata* furnish, NZFP have been able to design a bleach plant which will use no molecular chlorine at all. For this reason the Kinleith bleach plant will have one of the best effluents in the world.



Picture and diagram courtesy of Sands Defibrator Auckland



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JOINT RACI/NZIC INORGANIC CHEMISTRY CONFERENCE, JANUARY 1991

There has always been a strong association between New Zealand and Australian inorganic chemists, with a significant contingent of New Zealanders attending each of the conferences organised by the Inorganic Division of the RACI. This interaction was placed on a more formal footing with the first joint RACI/NZIC Inorganic Conference (COMO 10) which was held in Queenstown in 1981. This pioneering venture was so successful that it was resolved that NZ should take a regular turn, along with the Australian states, in holding the inorganic meetings.

The latest of these gatherings was the Inorganic Chemistry '91 conference which was held at the University of Waikato in January 1991. This was organised under the combined auspices of the RACI and the NZIC by a joint committee of Auckland and Waikato chemists. Because of the distance of Hamilton from an international airport, overseas participants were "aggregated" in Auckland during the preceding weekend and were able to attend a barbecue hosted by the Auckland chemists. Delegates were then transported en masse to Hamilton by bus.

The Conference enjoyed strong support, with over 200 registrants from 10 countries. Every effort was made to minimise the cost for students and as a consequence about half of the people attending were research students from New Zealand and Australia. This augurs well for the future of inorganic chemistry in Australasia.

The scientific programme was strong, with nine one-hour plenary lectures, eleven half-hour session lectures and 154 poster papers, covering all aspects of inorganic chemistry; virtually every element in the periodic table got a mention.

Philip Power (University of California, Davis) explored inorganic analogues of benzene, generated by replacing carbon atoms by alternating group 13/group 15 or group 12/group 16 atoms. Clever synthetic work has provided a number of examples such as $(RZnSR)_3$ or $(RGaPR)_3$. The near-planar geometry of these molecules was established by crystallography and the bonding analysed theoretically. Organic chemists no longer have exclusive rights to aromatic compounds.

Alan Sargeson (ANU) in his plenary lecture and Len Lindoy (James Cook) in the Burrows Lecture covered aspects of traditional coordination chemistry. Australian chemists lead the world in the design of macrocyclic encapsulating ligands and the recent advances made by these two groups demonstrated highly sophisticated ligand preparation. The factors leading to varia-

tions in complex stability were nicely illustrated. These compounds are not only of academic interest. For example, Sargeson showed that the complexes can be used to deliver metal ions to biochemical sites, and that detergent-like molecules can be formed by adding a hydrophobic chain to a neutral encapsulating ligand which then complexes with Co(III) ions to give compounds which are effective agents against tape-worms! The ligands described by Lindoy could be delicately tuned by varying ring-sizes and substitution-patterns to give remarkable selectivity for particular metal ions; this work has obvious applications in the absorption of specific metal ions from solutions for mineralogical or environmental purposes.

Bio-inorganic chemistry was represented by Akira Nakamura (Osaka) and George Christou (Indiana). Nakamura's lecture covered metal complexes formed by thiolate ligands and explored conformational variations. Properties such as redox potentials at the metal centre depend markedly on the conformations and the results were related to the chemistry of metalloproteins with cysteine coordination. Christou described the chemistry of manganese with carboxylate groups, which models the tetra-manganese species identified as the active centre in the water oxidation processes of green plants. The model compounds are providing useful insights into the mechanisms of the biological processes. In parallel, amazing aggregates of up to twelve manganese ions linked by oxo and carboxylate groups have been characterised and found to exhibit unexpected magnetic properties.

Continuing the theme of specially designed ligands, Terry Collins (Carnegie Mellon) described the preparation of chelating ligands which are highly resistant to oxidation, so that they can be used to form stable complexes of metals in very higher oxidation states. This chemistry is leading to species which have applications in catalytic and stoichiometric homogeneous oxidations.

Organometallic chemistry was represented by Gottfried Huttner (Heidelberg) who reviewed the synthesis and characterisation of mixed main group/transition element compounds which have delocalised π -systems. Karin Weiss (Bayreuth) presented an impressive body of data relating to the olefin metathesis reaction. This versatile reaction has now been extended to metathesis and polymerisation of alkynes, heteroalkenes and heteroallenes. She also described anchoring of carbene complexes onto solid supports which gives enhanced

activity for these "heterogenised homogeneous" catalysts.

Ken Wade (Durham) gave a highly entertaining and clear review of the electron-counting/ cluster-structure relationships that are commonly known as Wade's rules. This is now standard material taught in inorganic chemistry and so it was a pleasure to have this recent theoretical advance discussed by the main developer of the theory.

These plenary lectures were well supported by the section presentations. The impressive New Zealand contributions were from Penny Brothers and Warren Roper (Auckland), Dave Weatherburn (Victoria), Ward Robinson (Canterbury) and Tony Wright (now at Nottingham), while the Australian scene was illustrated by stimulating papers from Colin Raston, Danis Dakternieks, Les Field, and Ian Dance. This part of the programme was completed by excellent papers from Dave Curtis (USA) and Akira Yamasaki (Japan).

There were two poster sessions which included over 150 papers, many of them presented by research students. An amazing range of chemistry was described in the presentations and the papers stimulated intense discussions — many new ideas and understandings will have resulted from these conversations.

A full social programme ensured that the chemistry discussions continued well into the nights — some Australian students learned for the first time that Fosters is not the only beer in the world. On the one spare afternoon, bus trips to Rotorua and to the Waitomo caves were organised. The conference dinner showed the overseas visitors that New Zealand food and wines are beyond comparison and the evening ended on a traditional note with a recitation by Derek Smith of selected works of the great poet McGonagall.

The conference was a success on every level. There has been a lot of discussion lately on the possibility of closer ties between the NZIC and RACI. The New Zealand chemical community is too small to support regular specialist group conferences in isolation but our experience shows that cooperation at specialist-group level with the corresponding division of RACI can be highly beneficial; the larger population base provides a wider range of chemistry which helps guard against local "in-breeding" of ideas. It should be noted that the combined conferences are not necessarily an expensive option, with cross-Tasman air-fares cheaper than those for Auckland-Dunedin or Sydney-Perth flights. We would be pleased to give advice to any other specialist groups who would like to organise a combined conference in New Zealand.

For anyone who is already looking forward to the next meeting of the Inorganic groups we can report that organisation of IC'2001 is already under way at Canterbury.

Ken Mackay,
Brian Nicholson,
Derek Smith,
University of Waikato.

NEW ZEALAND INSTITUTE OF CHEMISTRY INC SENDS 150TH ANNIVERSARY GREETING TO THE ROYAL SOCIETY OF CHEMISTRY

*On the occasion of the royal society of chemistry's 150th anniversary
annual chemical congress*

Over a year ago the RSC wrote informing me of plans to hold a meeting of overseas secretaries (and "local members") on the Friday following their 150th anniversary annual congress, 8- 11th April 1991 and suggesting organisations I should approach for financial help. When late last year no support had been forthcoming I informed the RSC I would be unable to attend. On Friday 22nd March I received a fax saying "Sorry you cannot come - would £500 make any difference?". It did! So with rapid planning and rearranging of teaching commitments I left for London on 6th April and arrived at Heathrow late Sunday afternoon in spite of an unscheduled 11 hour stopover in Bangkok due to engine problems.

The Congress, held at Imperial College, was a memorable occasion. I took with me a scroll of congratulations and best wishes from the NZIC and presented this to the RSC President, Sir Rex Richards, at a special function for the handing over of gifts and congratulations from a number of scientific bodies held immediately after the impressive opening ceremony on Monday afternoon. In the evening there was a splendid reception for all participants held amongst the space exhibits on the ground floor of the Science Museum.

An exciting and varied programme of lectures and seminars was held over the next three days, with up to eleven sessions running concurrently. No doubt the most

frustrating aspect of the Congress was the numerous sessions one would like to have attended out of general interest, but couldn't, and one often wondered if the right choice had been made. I certainly had no regrets at hearing Sir John Cadogan, BP, Professor Howard Purnell, Swansea and Professor John Thomas, Royal Institution, present their visions of our likely major sources of energy in the year 2001 in a session titled "Three Welshmen in a Balloon". In addition to these programmes of the Education, Perkin, Dalton, Faraday and Analytical Divisions, the Industrial Division had three programmes running concurrently, while, as was fitting for the occasion, the Historical section ran a full programme. On top of this welter of chemistry, two other occasions made my trip truly memorable. The first was a reception on Tuesday night at the Royal Institution where the Director, Professor J.M. Thomas, gave a magnificent lecture on "The Genius of Faraday", illustrated with experiments using much of the original equipment of Faraday himself. Just to be seated in that famous lecture theatre was an experience in itself. The second was the Congress Banquet in Guildhall on Thursday evening when the guest of honour, listed as Lady Blinge on the top table seating plan on display during the congress, turned out to be Mrs Thatcher.

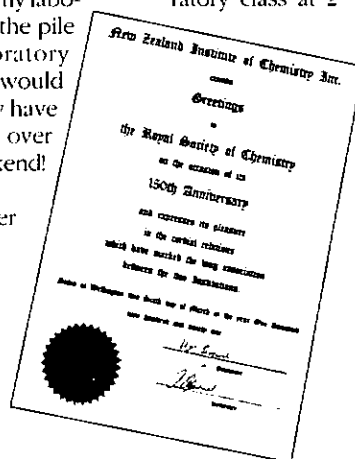
This second meeting of overseas secretaries proved less interesting me than the first in Manchester in 1985, but what was

valuable was the opportunity to meet and talk (Both at Burlington house and at the Congress) to many officers of the Society including the President, Sir Rex Richards, and the General-Secretary, Dr J.S. Gow. Very useful contacts were made with Tony Ashmore and Neville Reed of the Education Division and at the request of our secretary, Alan Turner, I was able to explore possible ways in which we could benefit more from the excellent educational material they produce.

Of approximately 1600 people registered for the Congress I believe I was the only resident New Zealander present, although our two Professors at University College London, Robin Clark and David Williams, both delivered papers, as did resident Australians, Alan Bond and Ben Selinger. Over all six days I was in London we had idyllic weather, warm, still and sunny, with the daffodils still in bloom, bluebells beginning to appear, blossom at its best and the trees coming into leaf - that wonderful feeling of Spring that we in New Zealand never experience. I arrived back on the direct flight from London at 7.30 on the following Monday morning in good time for my laboratory class at 2

pm and the pile of laboratory books I would normally have marked over the weekend!

J.E.Packer



QUALITY ASSURANCE

ICI Paints wins inaugural quality prize

The first ever New Zealand Quality Prize was awarded to ICI Paints of Lower Hutt. The prize presented during the Asia Pacific Quality Conference was made in recognition of the company's quality improvements through its application of quality management techniques.

ICI Paints will receive a package of benefits and services from the prize sponsors, TELARC New Zealand and the New Zealand Organisation for Quality (NZOQ), but the sponsors believe that the public recognition of ICI Paints as a company with a disciplined commitment to quality improvement will be the winner's greatest reward.

"Quite apart from any dollar value attached to winning this prize, I would expect that ICI Paints will capitalise on the intangible benefits," said Roger Atkinson, President NZOQ. "Those benefits will include a marketing edge, as well as enhanced internal team motivation".

The prize which has been in the planning stages for two years was created to

recognise the efforts of companies in New Zealand who are making significant progress in quality.

"We're very pleased with both the response and the quality of the applicants," said Atkinson. "We're hoping this prize will stimulate a lot more interest within New Zealand industry, providing both an incentive to entrants and an example to their competitors."

"Similar awards are already established overseas and are keenly sought by major corporations and have resulted in significant lifting of quality performances in both the winning company and its competitors."

Seven companies were entrants for the prize, having submitted details of recent projects they had undertaken to improve product or service quality. The applications were evaluated by a panel of five judges, including an independent chairperson, who selected two for more detailed investigation before the final prize winner was determined.

"The ICI Paints "In Full-On Time" project

set out to improve the company's performance in completing customer orders in full and on time. At the beginning of the project in early 1989 as few as 40% of orders met the "full-on time" requirement, by the end of 1990 ICI performance had been increased to over about 90% of customer orders," says Malcolm Bell, Deputy Director TELARC and co-ordinator of the 1990 Prize Programme.

"During this period there was no loss of product quality due to the increased focus on delivery."

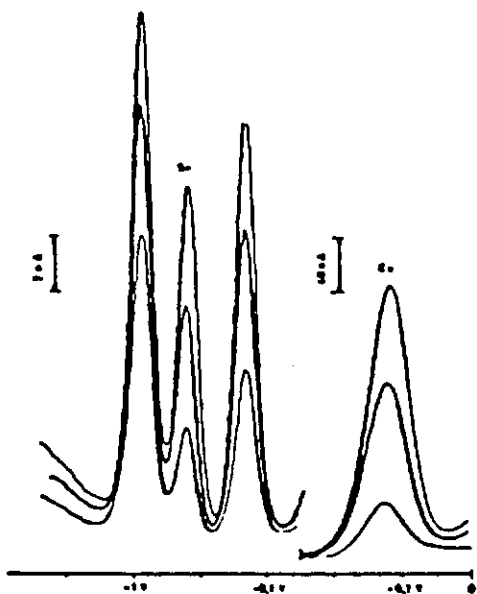
New Zealand's largest dairy company, the Tirau plant of Anchor Products Limited, was runner-up for the prize and awarded a Highly Commended citation for its quality project.

The prize will be an annual event awarded every May, brought forward this year to tie in with the Asia Pacific Quality Conference which was held in Auckland.

"It seemed appropriate to launch such a special prize as a prestigious international event," said Malcolm Bell. "Over 500 conference participants from 17 countries now know about ICI Paints," he says.

Manufacturers can expect the next prize to be presented in May 1992 at the NZOQ Annual Conference.

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SOLID-STATE NUCLEAR MAGNETIC RESONANCE-NEW WAYS OF LOOKING AT AGE-OLD MATERIALS

K J D MacKenzie Winner of the ICI Prize 1990, DSIR Chemistry, Private Bag, Petone.

Ceramics made from clays are as old as the hills. This is literally true, because the substance we call 'clay' is also the substance from which the hills and other geological features are composed, at least as far as the outer, weathered layers are concerned.

Clays are silicates of aluminium or magnesium, and commonly contain other elements such as iron or alkalis, and so, if we consider the composition of the earth's crust, (Fig. 1), it is clear that we are sitting on vast quantities of potential ceramics.

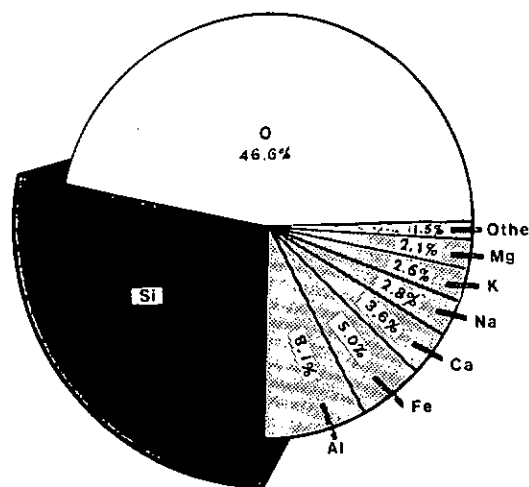


Fig. 1. Elemental composition of the earth's crust.

Some time back in the palaeolithic age, homosapiens discovered the most useful properties of clay - its ability to be moulded and then hardened by drying in the sun or baking in a fire. Over the centuries, these properties were put to good use, for making bricks for houses and other buildings, and pots for storage or cooking. In ancient Sumer, the palace of Kish, built 6,500 years ago, contained millions of sun-dried bricks in its walls. The harder, fired bricks were used for cladding and paving - they were more expensive to make, and had to be conserved.

Ancient pottery also goes back a long way. This technology received its biggest boost with the probably 'accidental' discovery of glazing, which had the effect of covering the pot with a thin layer of glass to make it waterproof. It was not long before these purely functional objects began to be decorated, being thus elevated to objects of beauty as well as usefulness.

Another huge step forward was the Chinese discovery of porcelain. This resulted from a fortuitous combination of the right raw material, a naturally occurring mixture of white clay, feldspar and silica called 'Chinastone', and advanced kiln-technology, which enabled the Chinese potters to routinely attain 1200-1300°C. Chinese porcelain was brought to Europe by Marco Polo in 1295, and from then on, Italian, German and French ceramists devoted countless hours of trial and error to reproducing the product (1). There were some partial successes - the Medici porcelain produced in 1575, the French soft paste porcelain produced in 1698 after 25 years of experimentation, and the Meissen ware of 1708. None of these materials had compositions anything like the Chinese porcelain, and had those early ceramists

had access to even rudimentary phase diagrams, they would have been spared years of trial and error. But, for the first 28,000 years its history, ceramics was solely an experimental technology. The scientific understanding of the chemical and physical processes involved began only very recently in the long history of ceramics. In fact, the first real efforts to understand the true nature of clay minerals date back to 1887, when Le Chatelier, who is better known for his principle of chemical equilibrium, embedded a thermocouple in a lump of clay, and observed temperature changes resulting from endothermic and exothermic reactions as he heated it up in a furnace at a rate of 100°C per minute (2). The thermocouple was connected to a galvanometer, and the mirror of the galvanometer reflected onto a photographic plate a series of flashes from an induction coil set to spark at 2-second intervals (Fig. 2). With the primitive timing and recording device, Le Chatelier could detect when the temperature of the sample was changing more rapidly than that of the furnace. This detection of endothermic and exothermic reactions was the first indication the firing of clays was doing more than just drying them, but this is a common misconception even today.

The next big step forward came with ability to determine the crystal structures of clays and the fired products of clays. Quite good chemical analyses of most minerals, including clays, had been available for some decades before Le Chatelier, but these were expressed in terms of oxides, and gave no hint as to how the elements were combined into a structure. The suggestion made in 1912 by Max Von Laue that the magic rays discovered in 1895 by his countryman, Wilhelm Roentgen, were of a suitable wavelength to be diffracted by atomic planes in a crystal was a big step forward, but it fell to the English father and son partnership, William and Lawrence Bragg, to make the first practical structure determinations. In 1915, Bragg Jr. won the Nobel Prize for his determination of the structure of cubic sodium chloride. However, the structures of the clay minerals were an entirely different matter, and it was not until the early 1930s that crystallographers such as Sterling Hendricks at the US Department of Agriculture, and John Gruner, at the

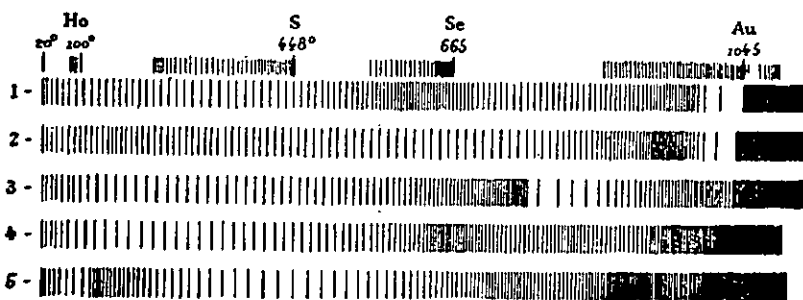


Fig. 2. Original heating curves of Le Chatelier (ref. 2) for: 1-halloysite, 2-allophane, 3-kaolinite, 4-pyrophyllite, 5-montmorillonite. The calibration points are the boiling points of water (Ho), sulphur (S), and selenium (Se) and the melting point of gold (Au).

University of Minnesota began to work out the basic structures (3,4), with the assistance of Linus Pauling's suggestions (5). About the same time, other crystallographers, notably William Taylor from Manchester University, were working out the structural details of the aluminosilicate minerals sillimate and mullite (6), which turned out to be the main compounds formed when clay minerals were heated to high temperatures, as in a potters' kiln.

And so, in the 1930s, all the strands were coming together for a speedy solution to the high temperature reaction sequence of clay minerals, or so one might have thought. In fact, things turned out not to be quite so straight forward as that, and it was another fifty years or so before the loose ends were finally tidied up.

Let us now summarise the state of knowledge in the subject by the late 1930s. By that stage, it was well understood that the clay which formed the ceramist's raw material could in fact, be a mixture of a number of different clay minerals. The structural principles of these had been well established, and many of the details of the individual clay minerals had been worked out. For example, it was known that these minerals have layer structures composed of silicon-oxygen tetrahedral sheets and aluminium-oxygen or magnesium-oxygen octahedral sheets (Fig. 3.)

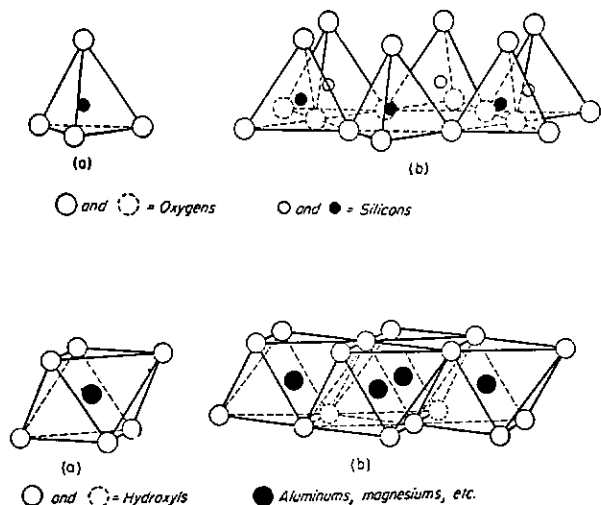


Fig.3. Diagrammatic sketch showing:-
top - single silica tetrahedron and sheet structure of silica tetrahedra arranged in a hexagonal network;
bottom - single octahedral unit and sheet structure of octahedral units.

Some of the oxygen atoms in those sheets are replaced by hydroxyls, giving structures such as that of kaolinite, the most common ceramic clay mineral (Fig.4A).

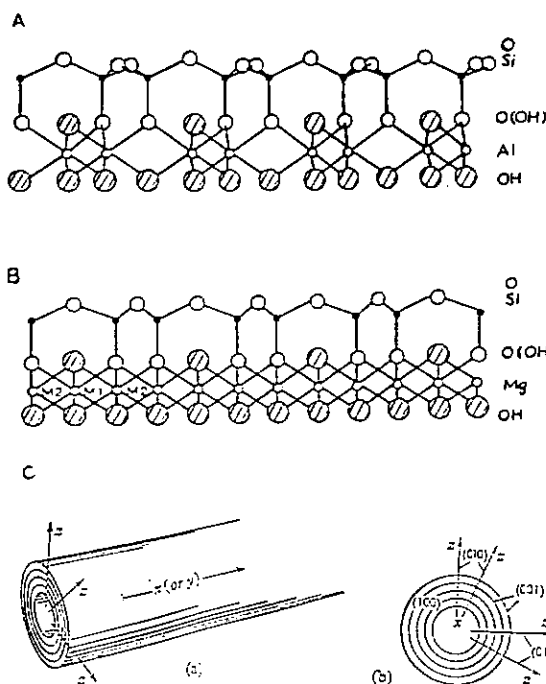


Fig.4. A Crystal structure of kaolinite, viewed along the *a*-axis.
B Crystal structure of serpentine, viewed along the *a*-axis.
C Tubular structure of halloysite, in perspective and in cross-section.

Sometimes the kaolinite sheets can be rolled up into tubes like cigarettes, in which the place of the tobacco is taken by water molecules (Fig.4C). This mineral, called halloysite, is common in the volcanic regions of New Zealand and Japan.

The magnesium-containing material analogous to kaolinite is serpentine, which occurs in several forms, including a fibrous form which is white asbestos (Fig.4B). Kaolinite and serpentine are both 1:1 layer silicates because the periodicity of their stacking is 1. There are also 2:1 layer silicates in which the octahedral layer is

sandwiched between two tetrahedral layers. Examples of these are the mineral pyrophyllite, muscovite mica and montmorillonite, of which the bentonite drilling muds are well-known examples.

By the 1930s, it was also known that when clay minerals are heated, they undergo chemical reactions which can be either endothermic or exothermic (Fig.5)

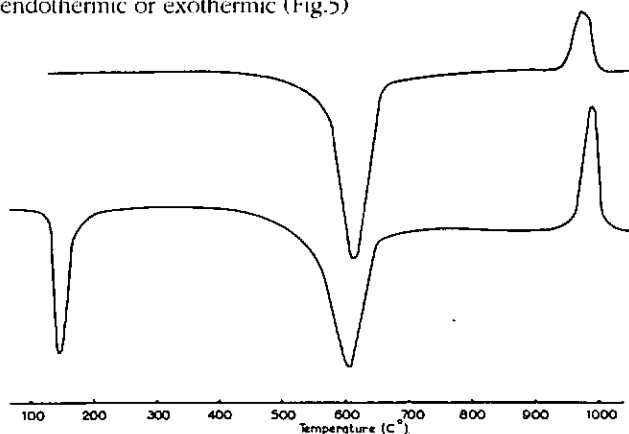


Fig.5. Differential thermal analysis traces of: A. kaolinite, B. halloysite. Size fraction 0.5-2.0µm ESD. Heating rate 10.°C/min. in air.

Le Chatelier's experiments were developed into the technique of differential thermal analysis or DTA, which indicates these different reactions quite clearly, for example in kaolinite. Here, the endotherm at 550°C results from the loss of the hydroxyl water, to form a material called metakaolinite, and the exothermic reaction at 980°C is the formation of new mineral products, including mullite and cristobalite, one of the crystalline forms of silica. In the late 1930s, the elements of these crystal structures were also established. But what was not understood was the nature of metakaolinite nor the process by which it formed, nor the exact nature of the exothermic reactions at 980°C in kaolinite. There was even less information about the thermal reactions of the other clay minerals. The reason for the gap in knowledge was that the phases formed as a result of dehydroxylation tend to lack the short-range atomic ordering needed to give an x-ray diffraction pattern. Furthermore, in the case of kaolinite, the high temperature exothermic reactions do not immediately result in the appearance of new compounds which are readily identifiable by x-ray diffraction. This made it necessary to try to deduce the probable course of events between 500°C and 1000°C from less direct evidence such as density measurements, changes in the cation exchange capacity, solubility in acid or alkali, and so on.

One of the first groups of workers to speculate on a crystal structure for metakaolinite was Tschischwili, Bussem and Weyl (7), but their work was published in German in 1939. Because the attention of the world was focused on the War, this contribution did not attract much attention, even though it recognised the important fact that when 6-coordinated aluminium atoms are dehydroxylated, they must become 4-coordinate (Fig.6A)

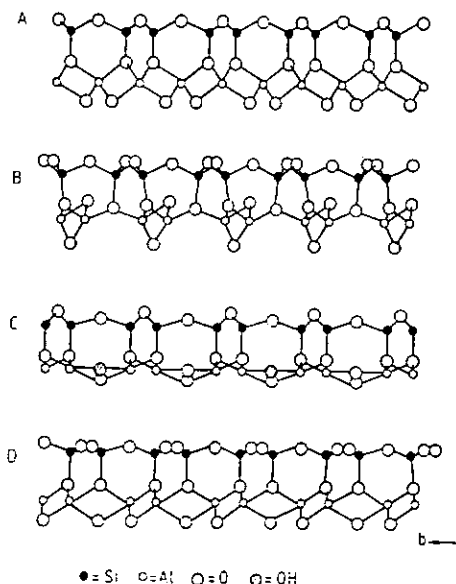


Fig.6. Computer-generated views along the *a*-axis of previously-proposed metakaolinite structures.

A Structure of Tschischwili et al., 1939. (ref.7).

B Structure of Brindley and Nakubira, 1959. (ref.8).

C Structure of Pampuch, 1965. (ref.9).

D Structure of Iwai et al., 1971. (ref.10).

Other suggestions about the structure of metakaolinite followed at regular intervals, from Brindley and Nakahira (8) in America in 1959 (Fig.6B), from Pampuch (9) in Czechoslovakia in 1965 (Fig 6C), and from Iwai, Tagai and Shimamune (10) in Japan in 1971 (Fig 6D). Of all these, the contribution of George Brindley from Pennsylvania State University attracted the most interest, partly because of his standing as a clay mineralogist and crystallographer, and partly because he had thought through the complete sequence, and his concept of structural continuity was very elegant. Brindley and Nakahira proposed that the loss of hydroxyl water at 550°C leads to a structure in which the a- and b-dimensions are similar to the starting material (8).

They calculated a new c-dimension from very old density measurements which subsequently proved to be wrong. another problem with their metakaolinite structure was that it was totally anhydrous, and took no account of the 12% residual hydroxyl water which remains right up to the 980°C reactions. With hindsight, too, their interatomic bond distances do not agree with measurements made by radial electron distribution methods (11), although, in fairness, these were not available in 1959.

The elegant thing about the Brindley metakaolinite structure was that it will decompose at higher temperatures to a compound with a cubic spinel structure which contains both aluminium and silicon. One of the compounds sometimes observed by x-ray at this stage was known to be a cubic spinel, which had a cell parameter like that of γ -alumina, but since the final product contains mullite, (an aluminosilicate), Brindley and Nakahira's suggestion that the preceding compound, the spinel, contains both silicon and aluminium is attractive.

Their proposed reaction sequence can be summarised by the following equation (Fig.7) which was the generally accepted view right up until 1985, when a totally new investigative technique was brought to bear on the problem.

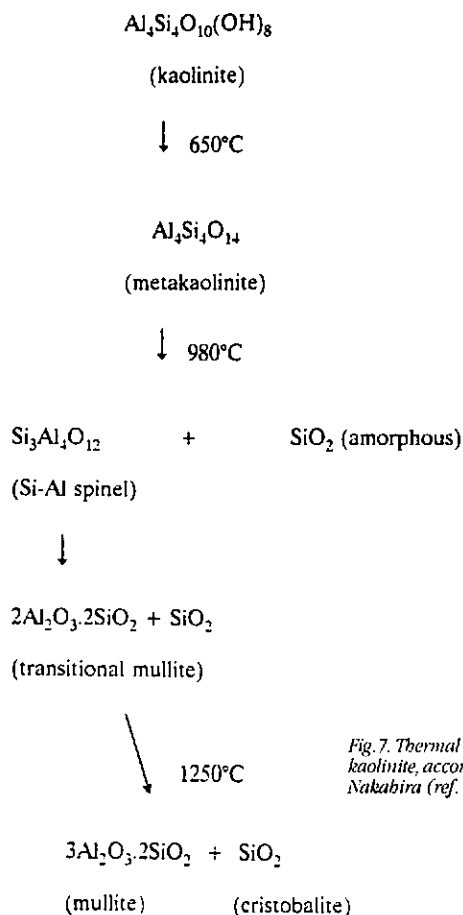


Fig. 7. Thermal reaction sequence of kaolinite, according to Brindley and Nakahira (ref. 8).

By that stage there were some doubts that this sequence was completely correct - no-one had managed to synthesise the silicon-aluminium spinel in the laboratory, there was x-ray fluorescence evidence that metakaolinite contains at least some 6-coordinate aluminium, (12), the interatomic distances of the metakaolinite structure were known to be wrong, (11), and lattice energy calculations suggested that a silicon-containing spinel would be less stable than γ -alumina (13). The time was right for a new look at the reaction using a new technique. That method turned out to be solid state NMR, a technique in which DSIR Chemistry Division was uniquely placed, having the only solid state NMR spectrometer in the country.

The key to successfully obtaining NMR spectra from solids is to spin the sample at 3000 revolutions per second, or faster if possible, at an angle of 54.73° to the magnetic field. This angle is known as the magic angle, and the whole method is known as high-resolution solid state MAS NMR. Magic angle spinning is not all that new in NMR - it was pioneered in the 1950s by Prof. Raymond Andrew at Nottingham University, (14), but it only took off in 1976 with the work of Stejskal and Shaefer from Monsanto, (15), who, by combining it with high-powered proton decoupling and cross-polarization, showed that it could reveal the fine structure in carbon-13 spectra of solid materials. This opened the door to its use for examining other nuclei such as 29-silicon and 27-aluminium. The latter is a quadrupolar nucleus, but with the advent of higher and higher magnetic fields, the aluminium results have improved dramatically. Nevertheless, the relatively modest 200 MHz machine at DSIR Chemistry Division was able to provide very worthwhile results. The first clay mineral investigation was of the intermediate stages in the kaolinite reaction.

Right from the start, it was apparent that the 29-silicon NMR spectra should be capable of giving information about the tetrahedral bond angles, and several groups had already published empirical relations between the 29-silicon NMR chemical shift and interatomic bond distances or the tetrahedral angle of pure silicas (16). We took the most promising of these relationships, shown in Fig. 8, and tested it for a number of aluminosilicate materials for which the crystal structures were accurately known and for which we measure the 29-Si chemical shift.

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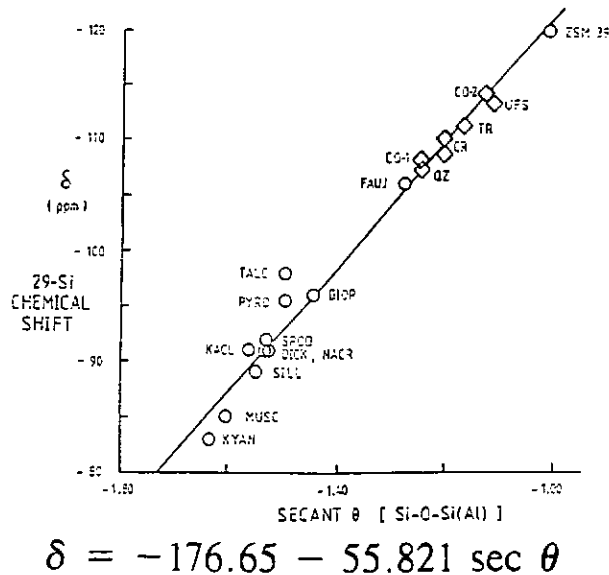


Fig. 8. Empirical secant relationship between the 29-Si chemical shift (δ) and the mean tetrahedral angle (θ) and its verification for silicas (open diamonds) and aluminosilicates (open circles).

The results are sufficiently encouraging to be used in the opposite sense, for deducing the mean tetrahedral silicate angle from the measured chemical shifts of unknown structures. The MAS NMR spectra of heated kaolinite (17) indicate a broadening of the 29-Si spectra and a change in the chemical shift upon the formation of metakaolinite (Fig. 9).

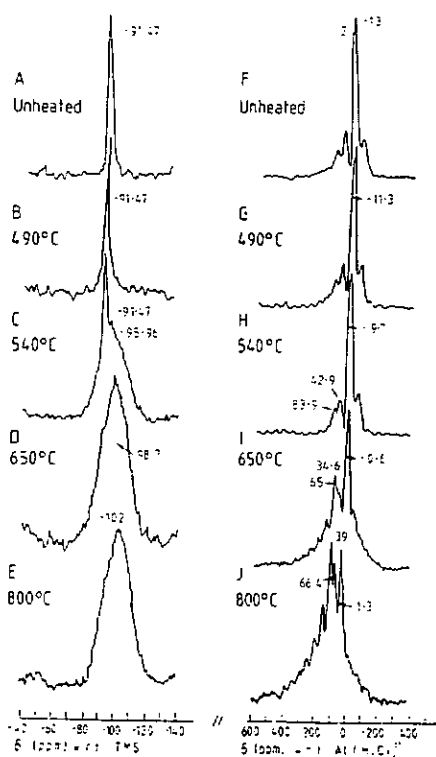


Fig. 9 A-E, 29-Si MAS NMR spectra; F-J, 27-Al MAS NMR spectra of kaolinite, heated to various temperature, from ref. 17.

Applying the Secant relationship to metakaolinite, the mean tetrahedral angle is calculated to be 138.5°. Unfortunately, similar information cannot be derived for the aluminium part of the structure from 27-aluminium NMR because of the quadrupolar nature of this nucleus. However, other useful information is obtained, because the aluminium NMR spectrum is able to distinguish very clearly and quantitatively between octahedral and tetrahedral aluminium sites. Interestingly, about 90% of the aluminium atoms in metakaolinite are not detected by NMR at all. These are the atoms in sites which are too distorted to be described as octahedral or tetrahedral. Any new structure of metakaolinite also has to take account of this degree of distortion, which nicely explains its lack of a proper x-ray pattern. Putting all of the available information together, a model was derived for metakaolinite which fits all the presently known experimental acts (Fig. 10).

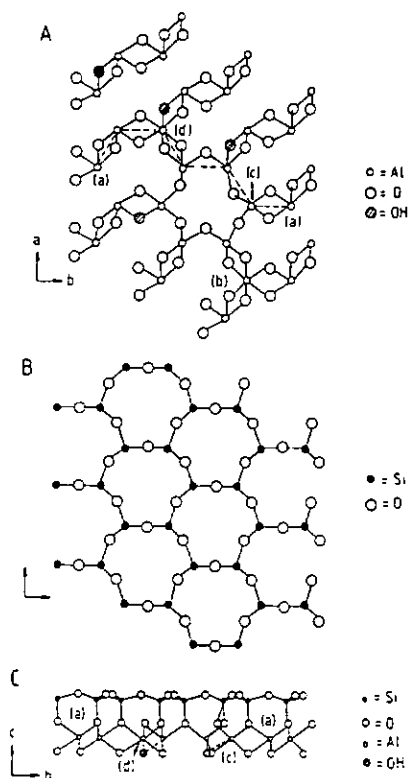


Fig. 10 Proposed structure of metakaolinite, from ref. 17.

A projection of Al-O(OH) sheet on the 001 plane.

B project of Si-O sheet on the 001 plane.

C view along the a-axis.

Turning our attention now to the compound formed at 980°C, it was calculated from the spinel structure that if any silicon atoms were present, they would have an expected chemical shift of -79.9 ppm (18). No such silicon resonance was found in the spectrum of kaolinite heated at 980°C and which showed x-ray evidence of the cubic phase (17). The silicon chemical shift in this material was characteristic of pure silica. The 27-aluminium spectrum of γ -alumina showed both octahedral and tetrahedral aluminium, and was similar to the spectrum of kaolinite heated at 980°C; the latter however contained a higher proportion of tetrahedral aluminium. This suggests that the cubic compound at 980°C contains less than 3% Si, and is probably γ -alumina rather than silicon-aluminium spinel, but there is also present non-crystalline silica and a form of mullite. As the reaction continues, the γ -alumina and silica react, forming more mullite, and the excess silica crystallises as cristobalite (Fig. 11).

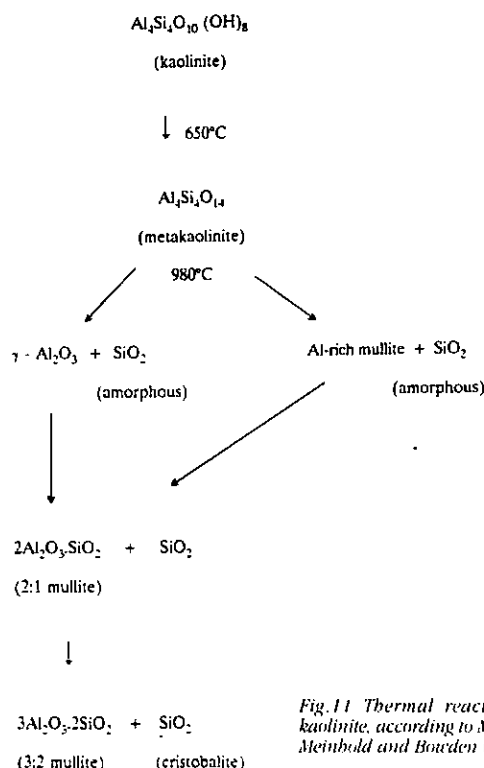
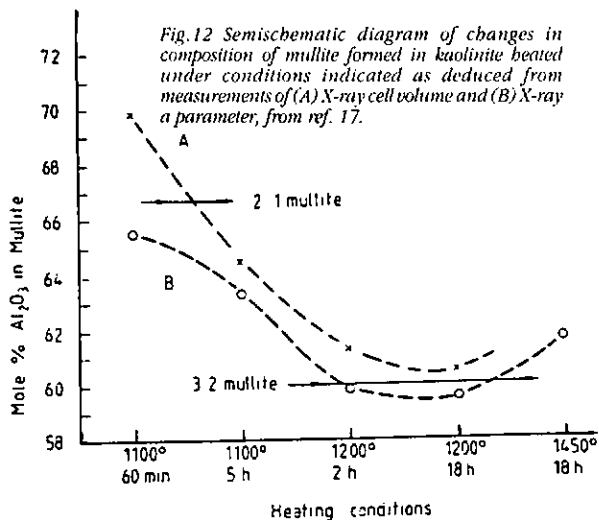
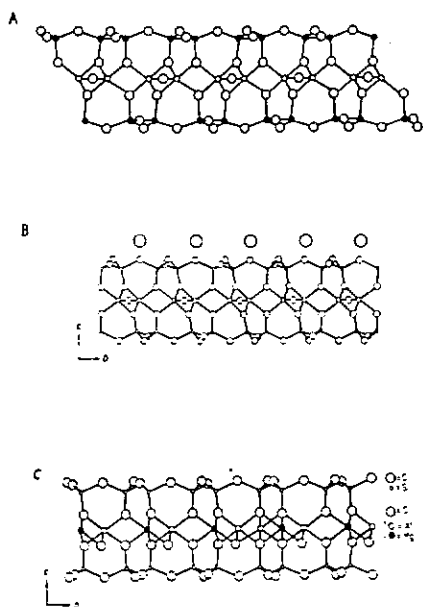


Fig. 11 Thermal reaction sequence of kaolinite, according to MacKenzie, Brown, Meinhold and Bowden (ref. 17).

An interesting point about mullite is that its alumina-to silica ratio can vary between 2:1 and 3:2. By measuring the cell parameters, which change with composition, the mullite which is first formed is found to be very rich in alumina, as would be expected from the proposed reaction sequence (Fig.12). As heating continues, the silica content of the mullite increases until the ideal 3:2 composition is reached (Fig.12).



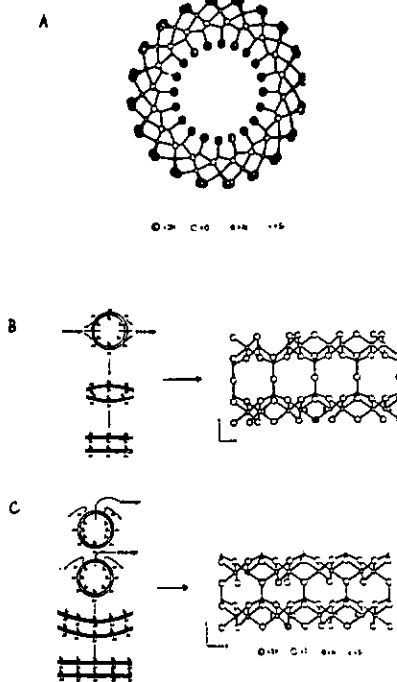
Although the elucidation of the kaolinite reaction sequence was a very real achievement for the application of solid state NMR, it was the end of the story. A number of other aluminosilicate clay minerals were tackled in the same way, concentrating especially on the structures of their dehydroxylated products, since these were even less well understood than metakaolinite. The 2:1 layer silicates were especially interesting, since it would be predicted that their dehydroxylated structures contain 5-coordinate aluminium. Some of the dehydroxylated structures deduced from 29-silicon NMR data did indeed contain 5-coordinate aluminium, for example, pyrophyllite dehydroxylate (19), muscovite dehydroxylate (20) and montmorillonite dehydroxylate (21) (Fig.13). However a major disappointment has been the inability to detect 5-coordinate aluminium in the 27-aluminium spectra obtained from our 200 Mhz equipment. This is one of the things which will be looked for, if and when New Zealand gets a high-field spectrometer, as we hope to do some day, perhaps not too far into the future.



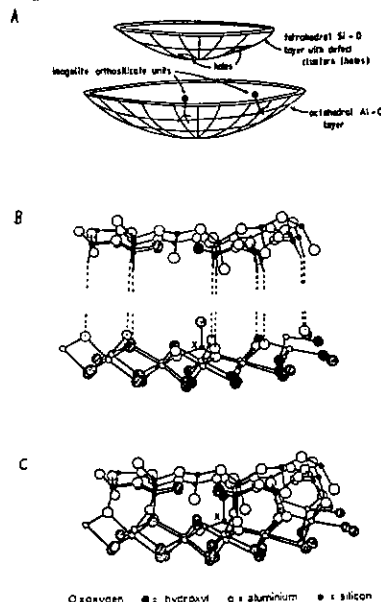
Another series of minerals which seem to be tailor-made for solid state NMR studies are the allophanes and the related tubular mineral imogolite, which are x-ray amorphous hydrated aluminosilicates of variable composition. We have studied the silicon and aluminium NMR spectra of a series of these minerals, and have been able to suggest what might loosely be term 'crystal structures' for these disordered compounds, and the compounds

which form when they are thermally dehydrated (22,23).

Imogolite is comparatively crystalline (Fig.14A), but its dehydration raises some interesting questions about the way the tubes split and unroll. Two possibilities can be proposed (Fig. 14B & C), which lead to quite different layer structures for the dehydrated compound. When the 29-silicon chemical shifts calculated for these layer structures are compared with the experimental shift of -93 ppm, option A, with a calculated chemical shift of -95.6 ppm (Fig 14B) is much more likely than option B, which has a calculated shift of -80.1 ppm (Fig.14C).



The atomic arrangement in allophane is a more difficult matter altogether, because account must be taken of two quite different silicon sites which are detected by NMR. One site has the characteristics of the silicon atoms in imogolite, while the other is more like that of a layer lattice silicate structure. To make matters worse, the morphology of the particles is spherical, rather than tubular as in imogolite, which means that a crystallographic model must be curved in two dimensions. It also has to be capable of losing its structural water and giving a sensible dehydrated structure which also has the right chemical shift. The structure meeting all these criteria consists of a kaolinite-type layer, curved into a sphere, with silicon vacancies in the tetrahedral sheet into which the imogolite orthosilicate units can fit (Fig.15). This structure and its dehydrated form both have calculated 29-Si chemical shifts agreeing with the observed shifts, and all the bond lengths and atomic linkages are sensible.



And so, what might the future hold?

I strongly believe that solid state NMR has a very great future in the chemistry of materials, not just in low-technology ceramics, but in high-technology ceramics, cements and catalysts. For example, a huge range of high-technology engineering ceramics called sialons can be made by reducing aluminosilicate minerals with carbon in a nitrogen atmosphere (24). Some silicon and aluminium NMR work has been done on these materials overseas, but the technique has not yet been used to follow the reaction sequence, which is very complex. This is something which we would be well-placed to do especially if New Zealand was able to acquire a high-field spectrometer as a national facility. Given the costs involved, this would have to be a joint purchase between several organisations and universities, but the benefits would be enormous. A high-field machine would not only provide the ability to do much better work on existing quadrupolar nuclei such as 27-aluminium, but it would also open up to prospect of studying many other elements. One of these of great interest is magnesium (25), because this would make it possible to study the whole range of magnesium silicates analogous to the aluminosilicates which have already been studied so fully. Many of these magnesium minerals are also commercially important, for example talc, steatite and serpentine.

Other elements which could become accessible with higher-field instruments are titanium and zirconium. Titanium is a component of many advanced ceramics including titanium nitride and carbide for wear-resistant cutting materials, and various titanates for electronic and magnetic applications. Zirconium also occupies an important place in advanced engineering ceramics. I am sure too, that many other applications for high-field solid state NMR suggest themselves when such a facility becomes available in New Zealand.

I would like to think that although we are proud of our past successes, we will not be content to let it rest there, but we will build on our special strengths, and once more, in the not-too-distant future, lead the way in this field.

ACKNOWLEDGEMENTS

I am grateful for the assistance of many colleagues in the work which has been honoured by the 1990 ICI award. Particular mention should be made of the varied insights and skills of Ian Brown, Richard Meinhold, Mark Bowden and Clay Cardile, without whom the work described here would not have been possible.

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LETTER FROM AUSTRALIA

Since I wrote to you about the chemists in Australia's first private university, their fortunes have taken a turn for the worse. In a recent commentary, a former Bond University chemist has written about the closure of the Graduate School of Science which 'occurred here at 11 a.m. on Tuesday November the 6th'.

Without explaining the precision evident in the statement, he went on to demolish a number of myths which surround the closure. It wasn't because students didn't come to Bond, nor that the opposition of professors in state universities killed it, nor yet that Bond salaries were inflated beyond economic levels.

There is a grain of truth in the last contention, however, because ultimately the university's council decided not to keep on funding the school while they waited for it to bring in more money. The spokesman was also disingenuous in omitting a key element from his story, that of the resignation of Bond's Vice-Chancellor, former chemist Don Watts, which took effect in mid-1990.

With their champion gone, the expensive scientists were in jeopardy and the business downturn which made life uncomfortable for their sponsors was eventually translated into an abrupt outplacement. Other parts of the new university have survived, notably business, computing and law schools, and the enrollment is over 1000 as the university enters its third year of teaching.

All that on an annual budget of just under \$40 million (wish I had that ratio of dollars to bodies in my faculty), \$5 million of which represents earnings from the university hotel and \$18 million of which comes from student fees.

Many of the 35 science staff to go down the gurgler were chemists. At the time of writing, the University of Queensland is negotiating to take over the medical chemistry group. However, the names of some of its members have been turning up on short lists for jobs in other parts of the country, so Queensland will have

to move fast if it hopes to salvage one of Australia's leading research groups.

As in private, so it is in the public domain. Australia's government announced last year a scheme to fund Cooperative Research Centres to the tune of millions of dollars over the next three years. The jostling for a place on the big list has been going on for months, but the initial successes were announced recently and there is not a single chemistry proposal among them.

The aim of the CRC funding is to bring together university and government (CSIRO) researchers with industries who can benefit from applications of local research. The government see the venture as part of its thrust to make ours the Clever Country, but chemists are asking if it is really clever to exclude the central science from a place in the financial sun.

'Clever Country' was introduced last year by the Prime Minister, Bob Hawke, as taking Australia away from the feeling that it was the Lucky Country. I wonder if the PM knew that 'Lucky Country' was a deliberate irony coined by Australian author Donald Home as long ago as 1964? Many of us see a similar irony in 'Clever Country'. Maybe Mr Hawke needs to be reminded that although he may claim, as Humpty Dumpty did, that 'a word ... means just what I choose it to mean - neither more nor less' he can't make us believe it.

But that's enough gloom. The good news of the summer was the ease with which it became possible to make a booking on an international airline. And not just for a seat - you could have a whole row if you asked politely!

Within the country there are plenty of seats, too, now that air travel has been deregulated. I suppose it's only a matter of time ... but while it lasts it is good to have the companies fawning over us. The change has also helped fill up popular magazines with articles about which airline has the best food, gives most legroom (a point of special interest to me), and takes off closest to the scheduled time.

Kind regards
Ian D. Rae

AUCKLAND BRANCH NEWSLETTER - APRIL 1991

Environmental subcommittee

NZIC is currently in the process of reviving the above subcommittee under the auspices of the Auckland Branch. As we work in a field which is much affected by environmental legislation and with current sensitivity to environmental issues it is appropriate that the Institute has a voice in this area. Norm Thom has agreed to act as convenor for the committee and Auckland branch is currently looking at how we can assist with getting the committee up and running.

The declared objectives are to:

- liaise with the Ministry of the Environment.
- prepare statements giving a chemists point of view on environmental issues.
- comment on environmental impact reports.
- comment on proposed legislation concerning the environment.
- comment on the safe use and transport of chemicals in the laboratory and the community.

As one of the first steps we are seeking to extend the library of resource material we have on hand, particularly with regard to chemicals handling and disposal. If you

feel you have material which would be useful in this respect, or if you have other contributions to make in this area, please get in contact with me (c/o Chemistry Department, University of Auckland) or Norm Thom (c/o Environmental Science, University of Auckland).

Jim Metson
Branch Chairperson

MANAWATU BRANCH NEWS

Branch Meetings:

The Branch has had three meetings so far this year. On February 20, Dr Alfred Gartner spoke to the meeting on aspects of downstream biochemical processing of proteins from recombinant DNA organisms. Dr Gartner is employed by Genencor, a large California-based biotechnology company specialising in enzyme production. The talk covered the origins of Genencor a joint venture between Coming Glass and Genentech Inc. to the present ownership including Staley Continental and Eastman Kodak. Genencor currently has 90,000 sq ft of facilities and employs 60 scientists. The company focuses on the development of enzymes genetically modified to suit specific industrial conditions and applications. Most expression of engineered enzymes is achieved in fungi. Much hilarity was added to the evening by

an errant slide projector which insisted on ejecting the speaker's slides with great vigour, and accompanied by a loud bang.

The March meeting was a panel discussion about the new Crown Research Institute proposals. Panelists were Dr Magriet Theron (MoRST), Dr G Page (Director NZDRI, a member of the CRI working party), Dr I Watson (Assistant Vice Chancellor, Research, Massey University, also a member of FRST), and Mr D Munro (Bay Milk Products, and industry representative, also a consultant to FRST). The meeting was an open one, and about 90 local scientists attended. Questions at the meeting were mainly concerned with the proposed criteria for establishment of the institutes, how they were to be administered and by whom (Scientists or accountants). A cautionary tale was given by a visitor from Australia who recounted the problems encountered commercialising research by the Food Research Institute in Melbourne - now in Queensland (!) Most of those attending seemed to retain an air of optimism at the close of the meeting and came away with the impression that the formation of the CRI's would help R & D in New Zealand/ (A newspaper report on this meeting is appended).

In April we held our student meeting. This was a dinner meeting, attended by about 60 people, about half of them students. The local student prizes for the 1990 academic year were presented (for 300 level chemistry and biochemistry). Recipients were Cherie-Ann Stayner for biochemistry, and Michael Halstead for chemistry. The

meeting was addressed by Dr Frank Martley of NZDRI on 'Cheesemaking : Art or Science?'. The lecture was accompanied by practical examples for organoleptic assessment.

Other Branch News:

Recently returned:

Dr Gavin Hedwig (Massey University) has recently returned from four months leave spent in the fjords of Norway. While in the Department of Chemistry at the University of Bergen, he investigated the compressibilities of aqueous solutions of small peptides.

On the move:

Dave Greenwood of DSIR Plant Protection moved to Auckland at the beginning of the year. Peter Vlieg retired in March from DSIR crop research, ending a long career in bloat research and the nutritive value of NZ fish. Don Otter of DSIR Industrial Development has taken a job at NZDRI working with Rex Humphrey.

Congratulations:

Congratulations to John Shaw on his appointment as Group manager for Post harvest and Food Science in DSIR Fruit and Trees, and to Paul Reynolds of the same division for a 1990 commemoration medal in recognition of his work in plant molecular biology. Congratulations also to Rex Humphrey on his appointment as head of a new section at NZDRI.

Conference notices cont.

XIITH INTERNATIONAL CONFERENCE ON PHOSPHORUS CHEMISTRY

TOULOUSE, FRANCE, July 6-10, 1992

The XIth International Conference on Phosphorus Chemistry will be held in Toulouse (France) from July 6 to July 10, 1992.

The Conference will be concerned with all aspects of phosphorus chemistry:

- Phosphorus in organic synthesis. Structure and reactivity of organic phosphorus compounds.
- Chemistry of phosphorus compounds with unusual coordination and bonding.
- Biochemical aspects of phosphorus chemistry.
- Inorganic phosphorus, new materials.
- Phosphorus and transition metals.
- Physical methods and theoretical chemistry applied to phosphorus.

Besides the usual topics discussed in the previous conferences, emphasis will be on bio-chemistry, calcium- phosphates, condensed phosphates, polyphosphazenes and industrial applications of phosphorus.

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Watson Victor Ltd are suppliers of Lancer Washing Units in New Zealand.

THERMAL VALUES DETERMINED SIMPLY AND RELIABLY

In the determination of my thermal values, the behaviour of the materials under investigation can render the analysis more difficult and hence necessitate the use of standard methods. The new METTLER FP81HT and FP83HT Measuring Cells from Watson Victor Ltd, are efficient working aids to facilitate thermal analyses in day-to-day operations. The measuring range has now been extended to 375°C and allows additional application possibilities.

With the FP81HT Measuring Cell melting, boiling and cloud points as well as melting ranges are determined. Melting points can be determined either accordingly to a pharmacopeia (measuring cell temperature) or thermodynamically with correction of the heating rate. Melting point determinations can be performed in the three measurement stations of the FP81HT simultaneously thus assuring a high sample throughput.

With the FP83HT Measuring Cell dropping and softening points of fats, resins and pastry products can be determined automatically. This METTLER measuring cell is recommended in the following standards: ASTM D 3461-85 (Softening Point of Asphalt and Pitches), ASTM D 3104-82 (Pitches), DIN 51920 (Binders and Impregnating Agents).

The analyses are controlled and evaluated by the FP80HT Central Processor. This offers digital and analog recording facilities as well as bidirectional data interchange with a computer or an LIMS thanks to the standard interfact fitting.

PARTICLE DETERMINATION PERFORMED SIMPLY AND RAPIDLY

The determination of carbon black particles of engines or fuels, of particles in wastewater, lubricants, oils, etc. or the particle analysis of photocopier toners is usually performed with appropriate filters. Since such determinations involve extremely small quantities, the balances such

as the METTLER AT20 from Watson Victor Ltd which are used, must have a correspondingly high resolution.

METTLER has developed a special kit for the AT balances for the weighing of filters (up to max. 105 mm diameter). This covers most applications in particle determination. The constant load disk included in the set also allows weighings with the AT201, AT261 and AT200 higher-capacity balances. For weighings of electrostatically charged filters, two special plates are enclosed that shield against electrostatic influences. The entire kit can be mounted simply and quickly. A few manual operations are all that are needed to reconvert the AT balance to conventional weighing operation. For more information contact Watson Victor Ltd.

SEVEN NEW ORION METERS

The new range of Orion pH, temperature, mV and concentration meters is now available from Watson Victor Ltd. there are seven new meters to choose from, each cleverly designed, with a particular set of user requirements in mind. All models feature a ready indicator light, tactile audible keypads, user prompting and locked in display reading of results until you're ready for the next reading.

An affordable, portable pH/temperature meter, the 230A is ideal of performing routine field pH measurements. It is housed in a splash and chemical resistant case and includes a built-in electrode storage sleeve.

A step up, the Model 250A is also designed for field operation and features accurate two-step auto calibration and automatic temperature compensation. For added convenience all previously entered calibration information can be immediately recalled.

The Model 290A is the ultimate portable meter for pH and ISE measurements. It performs up to five point pH and concentration calibration with a choice of significant digits for speed or accuracy.

And for pH analysis in the laboratory, there are four sleek new benchtop meters from Orion. The 420A is a microprocessor - controlled meter that gives you the basics for fast, accurate pH measurement. Calibration is faster and more accurate with two-step autocalibration using built in buffer recognition.

The Model 520A offers all these features with the option of a combination pH electrode.

For concentration and pH measurement with the option of data collection as well as selectable resolution and alarm limits the 720A is the model to choose.

The Orion Model 920A is the top-of-the-line meter which offers all the features you need for advanced analysis: automatic recognition of ion or cation ISE's, temperature-corrected concentration measurement, direct reading in any concentration units and data review at any time.

With the option of the Orion 900A printer for a permanent record of your results (except with 230A) the new Orion meter range from Watson Victor, winner of a 1990 Industrial Design Excellence Award must surely be the choice for your workplace.

VERSATILITY AND ECONOMY

The outstanding features and advantages of Sorvall centrifuges add up to unparalleled versatility and enhanced user convenience - giving you the edge you need for your research.

Whether you're performing simple or complex separations you will find that the RC28S is in a class of its own. Able to perform separations that include all superspeed applications plus those that extend into the low end of the ultracentrifuge range, the RC28S bridges the gap between super and ultra offering new levels of versatility.

The RC28S is an 'intelligent' instrument: with the capacity to store 20 programs in the memory, a slow start and slow-stop facility, user friendly controls and a full range of SUPRA and Superspeed rotors, you can program and operate the RC28S efficiently and effectively to your precise requirements.

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