Number 1

Fertilization by Exchange

A Research Letter Concerned with Ion - Exchange Fertilizers

January 1987

Why Ion-Exchange Fertilizers?

This research letter is being published to promote and coordinate research on ion-exchange fertilizers (IEF), and to encourage open and rapid communication of research results. Fertilization by ion exchange may prove to be a cheap, effective, long-lasting, and ecologically sound way to fertilize crops. Current worldwide interest in IEF has led to this publication. It will continue to be published as long as IEF systems continue to show promise, and as long as there is sufficient interest in the research community.

The normal practice of rating a fertilizer by its percentage of NPK does not apply to IEF.

The effectiveness of ion-exchange fertilizers is based on two concepts: (1) plants do not necessarily need large amounts of soluble nutrients at one time, but rather, they need a continuous supply of nutrients through time; and (2) the availability of nutrients for uptake by plants is not necessarily equal to the solubility of the nutrient. The first concept suggests that large concentrations of nutrients in the soil solution are unnecessary for good crop growth; concentrations can be small as long as they are buffered at a sufficient level. Thus the normal practice of rating a fertilizer by its percentage of NPK does not apply to IEF. The second concept suggests that other factors influence nutrient

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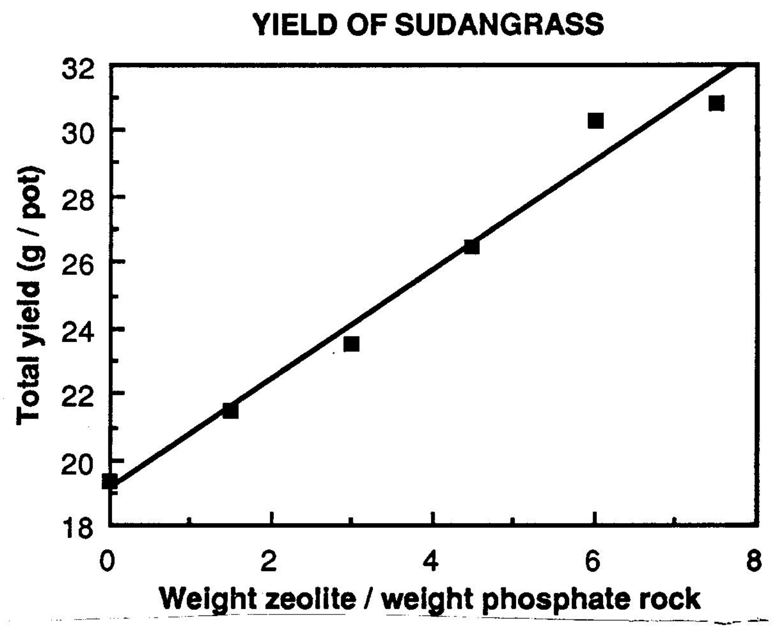

Yields for sudangrass correlate well with the weight ratio of NH_4-zeolite (clinoptilolite) to phosphate rock (North Carolina) for greenhouse experiments performed at Colorado State University by Barbarick, Lai, and Eberl. See article in Research Exchange.

Liebig's Suggestion

Liebig's suggestion, first published in 1840, that bones be treated with acids certainly contributed greatly to the establishment of superphosphate manufacture and to the acceptance of the product in agricultural circles....Liebig took no steps, however, to patent or otherwise exploit his idea...to which he apparently attached little importance. In fact, he remarked in 1851--and similarly as late as 1855--by which time superphosphate manufacture was firmly established in England: "The suggestion to dissolve bones in sulphuric acid...is from a scientific point of view of no greater importance than a useful recipe for boot polish."

K. D. Jacob, Chap. 2, Predecessors of Superphosphate, In <u>Superphosphate: Its History, Chemistry, and Manufacture;</u> U.S.D.A. & T.V.A., 1964.

Direct application of PR discussed in Malawi

Ion-exchange is just one of several techniques that can be used to enhance P-release from phosphate rock (PR). Several interesting technologies were discussed at a recent conference held at the University of Malawi in Zomba from the 23rd to the 27th of June, 1986. The conference was sponsored by the International Development Research Centre (IDRC, Ottawa), the Commonwealth Science Council, and the Malawi Government. One aim of the conference was to discuss methods by which PR could be used directly on fields, rather than by first subjecting it to acidulation. Acidulation may not be appropriate for many third world countries, because it is expensive, and because it requires that the country have a strong technological infrastructure to keep the fertilizer factories running.

P. H. Le Mare (University of Reading) summarized methods for the direct application of PR. Finely ground PR can be used directly with good results in some soils, provided the PR has a high enough solubility, which usually means that it has a substantial component of carbonate substitution in its structure, and provided the soil is acidic. Best results are obtained by broadcasting the PR throughout the fields, rather than by banding next to the crops. Evidently, PR becomes more reactive through interactions with soil: could this reactivity be related partly to the ion-exchange effect?

Other methods to boost PR reactivity that were discussed at the meeting include: (1) Intercrop with plants that are high-Ca feeders. These plants would serve the same function as the exchanger in the IEF by keeping Ca-activity low in the soil solution, thereby enhancing PR solubility. (2) Use partial acidulation of PR, a method that gave good results in experiments headed by Luis A. León at the International Fertilizer Development Center in Cali, Columbia. Partial acidulation is cheaper than full acidulation, and partially acidulated PR has both short and long-term P-release characteristics. (3) Inoculate the soil with PR-dissolving fungi and bacteria that occur naturally in the same soil. R. M. N. Kucey at the Agriculture Canada Research Branch in Lethbridge has had remarkable preliminary results with this cheap and effective method. Straw was sterilized using steam, and then was inoculated with the microorganisms, and incubated for several days. The straw then was banded in the fields with PR from Idaho. Yields obtained using the inoculated system were comparable to those obtained using soluble P-fertilizer, whereas PR alone had no effect on yield. Carry-over effects will be studied next growing season. (4) Mix the PR with pyrite and then add it to the soil. T. N. Jaggi from Pyrites, Phosphates & Chemicals Ltd., New Delhi, found that sulphuric acid formed by weathering of the pyrite attacks the PR, thereby rendering slow-release P available to crops. Thus acidulation is accomplished in the soil itself using locally available materials, rather than in a fertilizer plant. The method worked well with fruit trees, and less pesticide was required. The long-term effects of this method on soil pH were not reported. (5) Jaggi also reported on a mini-hydro plant that was being tested in northern India. Electricity produced in the plant from a small stream was used to form an electric arc which oxidized nitrogen from the atmosphere. The oxide then was dissolved in water to produce nitric acid. The acid was passed through a column containing PR, thereby producing enough P and N fertilizer to supply a small farm. (6) Increase the solubility of PR by heating it to 800 °C prior to application. This method works with some PR, but not with all PR. (6) Compost the PR with organic wastes. This promising technique for mobilizing P is being pursued by S. Mathur in Canada. (7) Use locally

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Opinions expressed in this research letter are solely those of the editor and the contributing authors. The content is not meant to represent the views of any group, public or private, but rather is meant to keep interested parties abreast of current research in this area.

This letter can continue if you will send your thoughts, opinions, comments, speculations, preliminary research results, reviews, photographs, news items, etc. to:

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News Exchange

From Krakow -- Dr. Jan Srodon, Institute of Geology, Krakow, has been awarded a 15 million zloty grant from the Polish government to support 5 years of work on IEF. Initially, twelve scientists will be involved in the research project, which will be a collaborative effort between the Institute of Geology, the Institute of Environmental Protection of the Academy of Mining and Metallurgy, and the Academy of Agriculture. They plan to begin field tests in Spring, 1987. These tests will be the first *field* tests ever conducted of the apatite -- ammonium-exchanger type of IEF. Locally available smectitic clay will be used as the exchanger. Forty 5 x 5 meter plots will be treated with 10 combinations of IEF and controls, with four replications of each combination.

From Guelph -- A paper on IEF entitled, "Solubility of apatite in clay and zeolite bearing systems: application to agriculture," by Ward Chesworth, Peter van Straaten, and Steven Sadura has been accepted for publication, and will appear in a future issue of *Applied Clay Science*.

From Colorado -- $6,500 has been given to K. A. Barbarick by the U.S. Geological Survey, Office of International Geology, to study the effect of exchangers on P-availability from igneous apatite. Greenhouse experiments are scheduled to begin soon at Colorado State University. T.M. Lai and D.D. Eberl also are involved in the study.

From South Dakota -- D.D. Eberl accompanied U.S.G.S. geologists Nick Raymond and George Densborough on a field trip to the Pine Ridge Indian Reservation in South Dakota. Samples of clinoptilolite were collected from the reservation for future study. The scientists also met with the Tribal Council, and with staff from Oglala Lakota College in Kyle. There is interest in IEF in Pine Ridge because the Reservation has surface or near-surface deposits that contain billions of tons of clinoptilolite.

From England -- The concentration of nitrates is increasing in many British watersheds, according to a report issued by the British Geological Survey, and reported on in *New Scientist* (11 September 1986, p.19). In eastern England, the nitrates in many water sources already top the limit set by the EEC of 50 mg/L. The chief suspect is nitrogen fertilizer. Similar problems are appearing elsewhere, such as in the agricultural regions of Colorado. Can the problem be alleviated by applying nitrogen fertilizer as ammonium ion in an exchanger? Is nitrogen uptake by plants more efficient from an exchange system?

From Chemical and Engineering News-- A full page article by Ward Worthy on IEF was featured in the 22 September 1986 issue. The article discussed a paper on IEF that was presented before the Division of Fertilizer and Soil Chemistry by Eberl, Lai, and Barbarick at the annual meeting of the American Chemical Society that was held in 1986 in Anaheim, California. ■

Insoluble Nutrients

In contrast to the confusion in our attempts to manage plant nutrition more efficiently than nature by our use of water soluble (salt) fertilizers in extra quantities, nature has long been using a simple practice of mobilizing the insoluble elements from the rock minerals into the adsorbed and insoluble condition on the clay and humus. By the same principle, nature moves them from there into the plant.... If we will comprehend and follow nature's practices and principles rather than our own confused thinking, there is still hope that we shall learn of, and have higher appreciation for, nature's successes in crop production for healthy plant survival. Perhaps we can see that nature practices scrupulous conservation, when, in fact, making *available* to plants--more generously than we realize--the essential fertility elements which we believe unavailable because we classify them as insoluble....

The Albrecht Papers, Vol 1, 1975, 118-119.

The power of clay

The clay is...the seat of the breakdown of the reserve silt minerals as this decomposition serves to restock the clay [with nutrients], which is especially noticeable while the soils are commonly said to be "resting."

The Albrecht Papers, Vol.1, 1975, p.58.

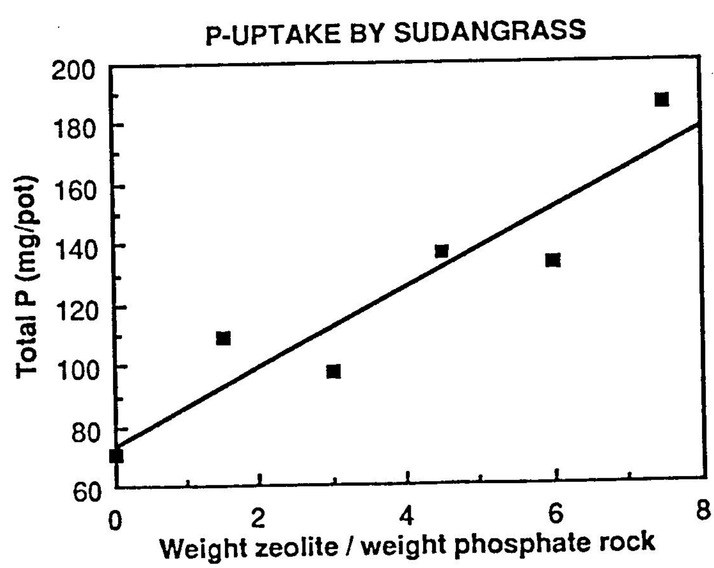
Research Exchange

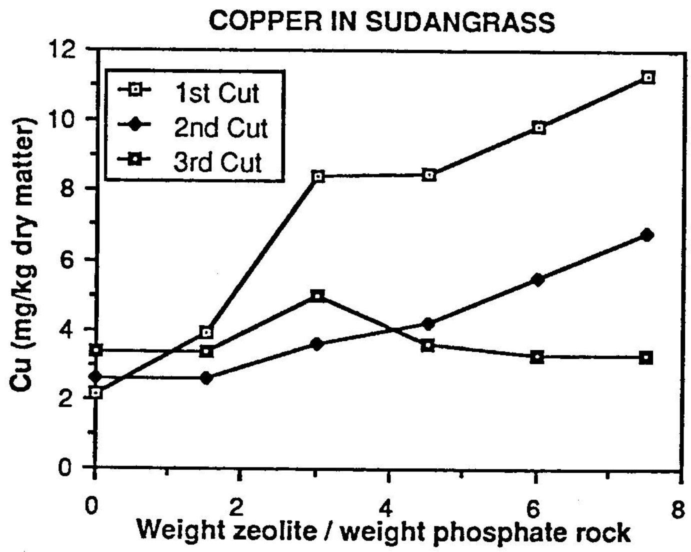
Field tests of an ammonium exchanger Mary Ann Maclean, Paul Voroney, Peter van Straaten and Ward Chesworth, University of Guelph, report that field tests were conducted on corn using an ammonium exchanger (clinoptilolite) as a N-source. Although the data still is being analyzed, preliminary results indicate that for a sandy soil, yields from the exchange system were much higher than those found for a conventional, soluble N-fertilizer. For a clay-rich soil, however, the yields for the two systems were approximately equal. Has the exchanger prevented N-loss in the sandy soil? Is N-uptake by plants more efficient from an exchange system? These questions may be answered by further data analysis, because the experiments were performed with labeled nitrogen.

Is clay better than zeolite? Jan Srodon, Polish Academy of Sciences, feels that P is released faster and more efficiently from PR by using clay rather than zeolite as the exchanger. He compared the amounts of P released from PR using zeolite and several clays as exchangers. The zeolite was ammonium - exchanged clinoptilolite, and the clays were ammonium - exchanged smectite and mixed-layer illite/smectites from local weathering crusts and shales. Although the clays had only l/3 the exchange capacity of the zeolite, approximately the same amount of P was released from both systems for an equal weight of exchanger after 48 hours of shaking in water. When the systems were subjected to wetting and drying, the clays released up to three times as much P as in the shaking experiments; the zeolite system was unaffected by wetting and drying. In greenhouse experiments, yields were larger for the sum of two cuttings for clay systems than for zeolite systems. Both exchange systems gave up to 60% larger yields than did superphosphate systems.

IEF increases yield, P-uptake and trace element uptake The first series of greenhouse tests have been completed by K. A. Barbarick (with T. M. Lai and D.D. Eberl) at Colorado State University using IEF composed of ammonium-clinoptilolite and PR (from North Carolina). A direct correlation was found between yield and the zeolite/PR ratio of the systems for a Colorado agricultural soil (see graph on page one). A direct correlation also was found between this ratio and P-uptake and uptake of some trace elements, as is shown in the accompanying graphs. In a K-defficient mountain soil, the zeolite tended to sequester K, thereby decreasing yields with increasing amounts of zeolite, although P-uptake by the plants continued to increase with the zeolite/PR ratio. Soil pH tended to decrease with time, probably due to nitrification of ammonium released from the exchanger.

Remarkable results for corn Ward Chesworth, Peter van Straaten, Peter Smith and Steven Sadura, University of Guelph, report a 6-fold increase in yield for corn grown in zeolite-apatite mixtures, compared with corn grown in apatite alone. The experiments were conducted in a greenhouse using quartz sand as the soil substrate. Laboratory experiments showed that the probable cause for the increase in yield was an increase in P-availability related to the presence of an exchanger. Using 1:1 ratios of exchanger to apatite (1 g each), 100 ml of water, and shaking times of 24 hours, they found that P-release with exchangers present was many fold greater than that found for apatite alone: zeolite A gave





172 times as much P in solution as did apatite alone; clinoptilolite gave 42 times; vermiculite 69 times; palygorskite 6 times.

Reclamation of "fixed" P T.M. Lai, U.S.G.S Denver, following Mattson's original idea, found that P can be made available in some soils simply by adding a monovalent (e.g. ammonium or potassium) ion exchanger. No phosphate rock is needed. This technique may be used to reclaim P that has been "fixed" as calcium phosphates in soils by the previous application of soluble phosphate fertilizers.

Wetting and drying releases K from insoluble K-minerals K-minerals such as microcline, muscovite, phlogopite, glauconite and illite have long been thought to be too insoluble to be used as effective K-fertilizers. Currently, the chief K-fertilizer is KCl, a substance that requires the introduction of chloride into soil. A recent publication shows that wetting and drying insoluble K-minerals in the presence of the exchanger smectite causes K to move into the exchanger, where it is available for plant uptake. Both wetting and drying and the smectite exchanger are essential to the process: simply shaking these minerals in water with smectite does not release much K, and neither does using zeolite as the exchanger in a wetting and drying system. Because wetting and drying is a process that occurs in all soils, it should be possible to fertilize for K with locally available K-minerals, provided smectite also is available locally. Smectite is a very common mineral that occurs worldwide in soils, shales, weathering crusts, bentonites, and hydrothermal deposits. The publication that describes this phenomenon is: D.D. Eberl, J. Srodon and H. R. Northrop (1986) Potassium Fixation in smectite by wetting and drying: In, *Geochemical Processes at Mineral Surfaces,* J.A. Davis and K.F. Hayes, eds., American Chemical Society Symposium Series 323, Washington, D.C., 296-326. Reprints are available from the authors.

New journal on alternative agriculture A quarterly journal entitled *American Journal of Alternative Agriculture* is available from the Institute for Alternative Agriculture, 9200 Edmonston Road, Suite 117, Greenbelt, MD 20770, U.S.A.. Phone 301-441-8777. Articles in the Spring, 1986 issue include topics such as: bacterial solubilization of mineral phosphates; reduced input agricultural systems; and the potential for regenerative agriculture in the developing world. ■

Why Ion-Exchange?

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availability in addition to the solubility product of the compound that contains the nutrient. One such factor is the presence of exchangers that can aid in the release of nutrients to plants. For cation nutrients, for example, the exchanger serves as a kind of half-way house between the insoluble mineral and the completely mobile cation in solution. As the nutrient is removed from the exchanger by the plant, more is released to the exchanger from the mineral, according to the law of mass action, as described by the exchanger's selectivity coefficient and by the mineral's solubility product.

The chemical principle behind one type of IEF is simply to use an ammonium- or a potassium-exchanger, such as zeolite, peat, or swelling clay, to lower Ca-activity in the soil solution, thereby boosting the dissolution of phosphate rock (PR), and thereby releasing soluble N, P, and exchangeable K and Ca for uptake by plants. An approximate reaction for an ammonium-exchanger (NH_4X) is:

$$PR + NH_4\text{-}X = Ca\text{-}X + NH_4^+ + H_2PO_4^-.$$

Theoretically, the molar ratio of N to P released by this reaction in a slightly acidic solution should be 10 to 3, but the stoichiometry remains to be investigated in detail. The reaction can occur at neutral pH. This system

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is described in more detail in an article by Lai and Eberl in *Zeolites*, 1986, Vol. 6, 129-132.

Phosphorous in conventional fertilizer is rendered soluble and available to plants by treating PR (composed mostly of the mineral apatite) with acid. This basic idea has remained unchanged since the development of the superphosphate fertilizer industry in England during the early to middle part of the 19th century. Despite the tremendous advance in agriculture related to the use of soluble fertilizer, soluble fertilizer is not the elegant solution to the fertilization problem. For example, the acidulation of phosphate rock produces enormous quantities of waste gypsum and clay. These by-products fill large disposal ponds in areas that are mined for phosphate rock, such as those in Polk and Hillsborough Counties, Florida. This land is difficult to reclaim. Manufacturing plants for processing phosphate ore by acid-treatment cost hundreds of millions of dollars. The purpose behind this effort is to render the P in phosphate rock soluble. When this soluble fertilizer is put on the soil, however, some or most of the P becomes insoluble once again. This fixation of soluble P by soils is especially a problem in some tropical soils.

The exchanger serves as a kind of half-way house between the insoluble mineral and the completely mobile cation in solution.

Apatite in the ion-exchange fertilizer described above, however, dissolves slowly in the soil itself; thus there should be little pollution connected with its manufacture, and there is no wasted effort in making it soluble. Nutrients are released as they are required by growing plants, due to the buffering effect of the chemical reaction. N is protected from loss by the exchanger. The fertilizer can be regenerated while in the soil by resaturating the exchanger with NH_4^+ or by adding additional exchanger, and the rate of P + N release can be controlled by varying the exchanger/PR ratio. In principle, trace nutrients can be released in a similar fashion (e.g. add Zn to the system by using the mineral sphalerite).

Soluble P fertilizer requires high-grade PR for its manufacture, a resource that is limited, whereas IEF can use low-grade ores. In fact, many natural deposits currently considered to be low-grade already contain an exchanger (smectite-rich clay) and phosphate rock; it would be necessary only to exchange the clay with a monovalent cation.

This ion-exchange fertilizer should be gentle-acting, and thereby not harm soil ecology, should not suppress nitrogen fixing bacteria, should not lead to imbalances in nutrient uptake, and should decrease N-pollution. It should improve the soil through time by increasing the soil's cation exchange capacity (thereby improving the soil's ability to hold nutrients), and by increasing the soil's water-holding capacity. Some exchangers, such as the smectite montmorillonite and the zeolite clinoptilolite, are very stable chemically in many types of soil.

Data suggest that the ion-exchange fertilizer may be particularly effective in high P-fixation, tropical soils.

The ingredients used to manufacture this IEF, an exchanger such as zeolite, peat, or smectite, and phosphate rock, are available world-wide in near-surface deposits. Two methods for saturating the exchanger with ammonium ions are: (1) using the exchanger to remove ammonia from industrial and sewage effluents (a process being used today); and (2) exposing H-saturated exchanger to NH_3 gas. In addition, the group at the University of Guelph (Ontario) has experimented with using manure and cow urine to saturate zeolite. This process suggests the possibility of using zeolite to reduce pollution and to trap nitrogen in animal feed lots. When the zeolite starts to smell, it is ready to be mixed with phosphate rock. The group at Guelph is experimenting with IEF because they are trying to develop low-cost, locally available fertilizers for the third world (for Tanzania, in particular). Data suggest that the ion-exchange fertilizer may be particularly effective in high P-fixation, tropical soils, because, unlike soluble P-fertilizer, P is released slowly, and therefore is not completely fixed early in the growing season.

The ion-exchange fertilizer described by the above equation will not work well in soils that contain significant amounts of calcium minerals such as calcite, anhydrite and gypsum, because these compounds, rather than apatite, will be dissolved by the exchanger. Most soils, however, do not contain these compounds. Calcium can be present in the soils as an exchange ion without poisoning the system. Another limitation is that most IEF will be heavier and bulkier than ordinary fertilizer. This limitation suggests that IEF should be manufactured locally in order to avoid high transportation costs. The economics of IEF are as yet unknown.

IEF should be manufactured locally in order to avoid high transportation costs.

The current crisis in farming, which includes problems such as high input costs, soil degradation, and the pollution of ground and surface water by agrochemicals, suggests that new agricultural methods are required. Can IEF help alleviate some of these problems? ■

Bread from rocks: the science of agrogeology

Two issues of *Agrogeology* have been published. This research letter describes work being conducted in this field by scientists at the University of Guelph and elsewhere.

The science of agrogeology combines the disciplines of agronomy and geology. As practiced at Guelph, the first stage in an agrogeologic study is to locate potential agronomic resources in a region that is being farmed. This phase requires the skills of a modern field geologist. For example, Dr. Peter van Straaten uses aerial magnetic surveys to locate carbonatite intrusives in southern Tanzania. Igneous phosphate rock (mostly apatite) frequently is associated with these carbonate bodies. Once a carbonatite has been located, it is prospected for zones (e.g. fault zones) that have been weathered sufficiently to dissolve the carbonates and to concentrate the apatite.

Once such an agronomic resource has been delineated, it must be tested in greenhouse and field trials using local soils. This step is being carried out in southern Tanzania, for example, by J. M. R. Semoka and P. N. S. Mnkeni at Sokoine University in Morogoro, and by J. Kamasho at Uyole Agricultural Center in Mbeya. They have found that a local igneous apatite is effective in acidic soils, but is not effective in the more neutral soils which comprise most of the agricultural soils in this region. Dr. Mnkeni plans to test whether the use of igneous apatite can be extended to the neutral soils by using exchangers to enhance solubility. The group from Guelph has discovered deposits of exchangers in southern Tanzania that include the zeolites chabazite and phillipsite.

The third stage in an agrogeologic project would be to mount an extension program to encourage farmers to use these local resources once they have been proven to be safe, effective, and economically viable.

Plowmate of the month:
Agrogeologist Ward "Babu" Chesworth and friend. Dr. Chesworth is inspecting maize grown by using locally available fertilizers in southern Tanzania.

Thus the focus of geologic prospecting in east Africa and elsewhere may be changing from precious materials such as diamonds, gold, and copper, to more prosaic agronomic resources such as phosphate rock, limestone, zeolite, and as yet undiscovered agro-materials. The possibility exists that "ordinary" rocks can be pulverized and applied to the fields as fertilizer in areas where weathering rates are high, such as in the wet tropics. The agrogeologist can not be content simply with finding a resource, but he also must have the material tested, and then introduced into the local economy before his job is finished.

Copies of *Agrogeology* can be obtained by writing: Dr. Ward Chesworth, Department of Land Resource Science, University of Guelph, Guelph, Ontario, Canada N1G 2W1. ■

Malawi,

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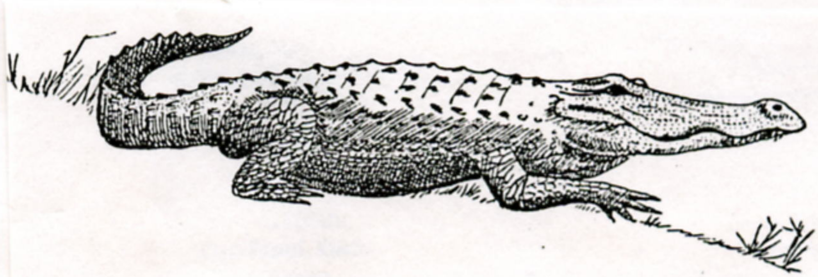
available ion-exchangers (e.g. zeolites, clays, peat) to enhance PR solubility. The experimental results of T. M. Lai and D. D. Eberl (U. S. Geological Survey, Denver) were discussed by D. D. Eberl. (8) Use P-sources other than PR. Promising results using, for example, scoria (basaltic volcanic glass) as a fertilizer were discussed by J.M.R. Semoka (Sokoine University of Agriculture, Tanzania), and by W. Chesworth and P. van Straaten (University of Guelph, Canada).

The development of local fertilizer resources seems to be essential to the development of third world economies. Presently, many of these countries experience a vicious economic cycle related to the need to import fertilizer to grow crops to produce enough foreign exchange to import more fertilizer. Many countries can afford less fertilizer each year. This problem is particularly acute for some African nations, where the need for fertilizer has grown as population pressure makes traditional methods of slash and burn agriculture less practical. It is hoped that some of the interesting methods discussed at the Malawi meeting will lead to the discovery and use of local resources for fertilization. ■



The Prison of Oeth and Annoeth

...about the middle of the first century,...Caradog (Caractacus, king of the Silures, inhabiting South Wales) was warring against the Romans, and slaughtering them most terribly. After those wars, in which so many of the Caesarians had been killed, their bones, which had been left by the wolves, ravens, and dogs, like a white sheet of snow in many places, covered the face of the earth. Manawyddan, the son of Llyr, caused these bones to be collected together into one huge pile from one of the battlefields, with other bones found throughout his dominions, so that the heap became of marvellous magnitude. It then came to his mind to form a prison of these bones, in which to confine such enemies and foreigners as might be taken in war; and he set himself to work and constructed a large edifice with exceedingly strong walls of the bones, cemented together with lime. It was of circular form, and of wonderful magnitude, the larger bones being placed on the outer face of the walls, and within the enclosure were many smaller prisons, or cells, formed of the lesser bones. This was called the "Prison of Oeth and Annoeth," which was demolished several times by the Caesarians, and rebuilt by the Cymry stronger than before. "And in the course of a long time...the bones became decayed, so that there was no strength in them, and they were reduced to dust: then they carried the remains and put it on the surface of the plowed land; and from that time they had astonishing crops of wheat and barley, and of every other grain *for many years.*

Quoted from Browne by K. D. Jacob, Chap. 2, Predecessors of Superphosphate, In *__Superphosphate: Its History, Chemistry, and Manufacture;__* U.S.D.A. & T.V.A., 1964.

Work and Rumors of Work

The following scientists either already are conducting experiments with IEF, or have expressed an interest in beginning such experiments.

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