

Fig. 1. *a*, Large burst of June 9, 1968, 08.39 UT; *b*, the burst of January 15, 1968, 12.20 UT, right hand polarization; *c*, the burst of July 9, 1968, 18.07 UT, left hand polarization.

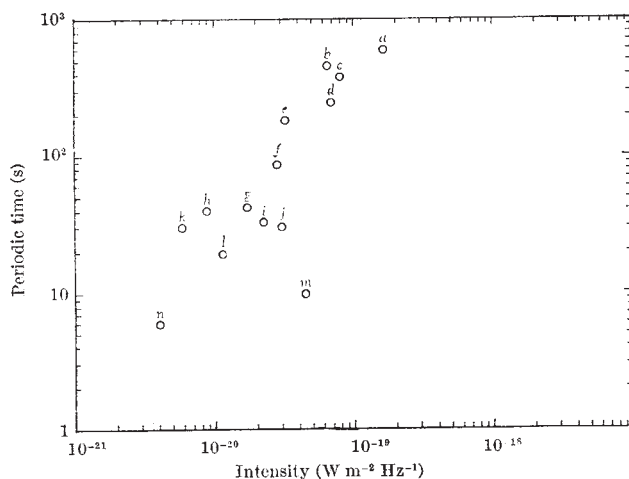


Fig. 2. Periodic time versus peak intensity of the burst.

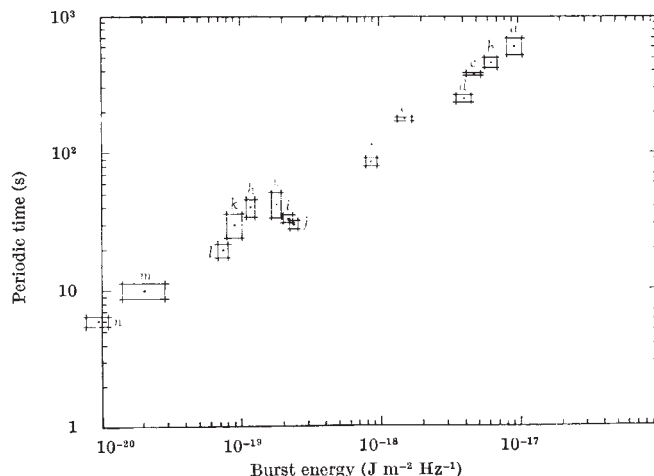


Fig. 3. Periodic time versus total burst energy.

significant that such an extreme form of burst should behave in this way.

The distribution of points approximates the curve

$$t = 2.6 \times 10^{15} E^{2/3}$$

where t is in s and E in $J m^{-2} Hz^{-1}$. Probable errors in estimating the period and energy of each burst are indicated in Fig. 3, and the bursts are identified in Table 1.

Table 1. BURST IDENTIFICATION

	Date	UT
<i>a</i>	July 8, 1968	17.08
<i>b</i>	September 11, 1957	02.40
<i>c</i>	June 9, 1968	08.39
<i>d</i>	July 6, 1968	09.42
<i>e</i>	September 29, 1968	09.30
<i>f</i>	July 9, 1968	18.07
<i>g</i>	January 30, 1968	04.59
<i>h</i>	March 24, 1968	07.45
<i>i</i>	May 8, 1968	14.15
<i>j</i>	June 11, 1968	09.35
<i>k</i>	January 1, 1968	03.38
<i>l</i>	February 14, 1968	15.34
<i>m</i>	July 6, 1968	07.16
<i>n</i>	April 12, 1968	12.52

This work was supported by the Ministry of Technology. One of us (A. H. C.) held a Science Research Council studentship.

A. H. CRIBBENS
P. A. MATTHEWS

Department of Electronic and
Electrical Engineering,
University College, London.

Received February 10, 1969.

"Anomalous" Water

COLUMNS of water and other polar liquids formed by the condensation of unsaturated vapours in narrow quartz or glass capillaries seem to have properties markedly different from those of the bulk liquids¹. It has long been suspected, especially from the work of Bangham, that a solid surface influences the structure of a liquid over large distances^{2,3}, but some of Derjaguin's experiments¹ indicate that this modified liquid can exist away from the solid surface as if it were a distinct stable molecular entity.

Derjaguin's anomalous water is distinguished by the following properties: (1) lower vapour pressure than the normal form; (2) higher viscosity (up to fifteen times normal); (3) greater density ($\rho = 1.2-1.3$); (4) different thermal expansion behaviour; (5) phase separation at low temperatures. These findings are sufficiently unusual and controversial to warrant an independent investigation.

Following Derjaguin⁴, we have obtained columns of

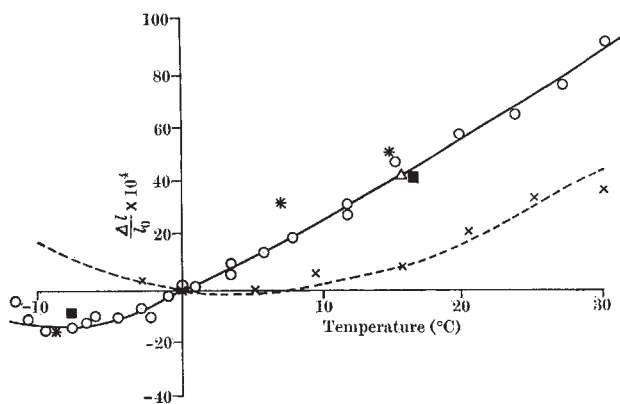


Fig. 1. Change in relative length with temperature for columns of: ---, normal water (literature); ×, normal water (this work); O, "anomalous" water (this work); * ■ Δ, "anomalous" water (ref. 4).

"anomalous" water in 'Pyrex' glass capillaries of radii 5–50 μm by exposing freshly drawn capillaries to 95 per cent saturated water vapour in a desiccator at room temperature. Liquid columns appeared in about 5 per cent of the capillaries after a few days. Measurements of the thermal expansion of these columns were in good agreement with those reported by Derjaguin (Fig. 1). When the columns were cooled below 0° C, we observed phase separations similar to those reported by Derjaguin (Fig. 2). The inner phase disappeared at –5° C. We were able to transfer columns of "anomalous" water from one end of a sealed capillary to the other by warming the end containing the column, but in some cases a non-volatile optically anisotropic residue was observed. A gel-like residue has also been observed by Derjaguin⁶ during evaporation experiments.

One batch of liquid columns was allowed to grow for a period of months. At intervals, the desiccator was opened and the capillaries examined. After inspection, the columns were put back into the desiccator, which was re-evacuated. After several cycles of this treatment some of the columns showed the two-phase appearance even at room temperature. In others, what appeared to be small crystals were visible.

On evacuating a vessel containing a column of "anomalous" water in an unsealed capillary, the rate of evaporation of the column progressively decreased while its refractive index increased. Eventually there remained a column about one-tenth of the length of the original which was quite stable at a pressure of about 10^{-3} mm Hg and had a refractive index close to that of 'Pyrex' glass (1.5). This column was judged to have a high viscosity, for the sudden opening of the vacuum system to the atmosphere caused little or no movement along the capillary.

We have attempted to investigate the structure of anomalous water using various physical techniques. An AEI MS 902 mass spectrometer was fitted with a glass inlet system in which were placed sealed capillaries containing "anomalous" water. The system was evacuated and kept at a pressure of 10^{-7} torr at room temperature for 12 h. The part of the system containing the capillaries was then cooled to liquid nitrogen temperature and the capillaries broken with a magnetic breaker. The rate of evaporation of the liquid columns was controlled by varying the temperature.

When the source was allowed to warm up to room temperature, the only peaks observed in the spectrum were for masses 17 and 18 as usually found for normal water. Subsequent examination of the broken capillaries revealed that several of the pieces still contained liquid columns, some of which had small amounts of an apparently solid material within them. This solid material was optically anisotropic. These pieces of broken capillary were then mounted on the direct insertion probe of the mass spectrometer and were placed into the machine

and the temperatures raised progressively up to 320° C. Again the only peaks in the spectrum were for 17 and 18 and on removal of the probe some liquid still remained in the capillaries.

The nuclear magnetic resonance (NMR) spectrum of "anomalous" water at 100 MHz was obtained from both a single capillary and from a bundle of about a hundred capillaries (containing, in all, about 10^{-3} ml. of liquid) by using a digital memory oscilloscope and external standards. The spectrum, obtained after one thousand scans, consisted of a single peak the chemical shift and saturation behaviour of which were, within experimental error, identical with those of normal water. These NMR results show that the electron environment of the protons, their participation in hydrogen bonding and their motion as part of a molecule are essentially the same in normal and "anomalous" water. Such behaviour has been observed for many types of gels where the "framework" molecules are present in concentrations less than about 5 per cent.

An infrared spectrum of "anomalous" water was obtained by injecting the contents of a capillary between barium fluoride windows. Because of the small amount of sample (about 10^{-5} ml.) we had to use a $\times 5$ scale expansion. The spectrum obtained was of poor quality, but the only peaks present were those characteristic of normal water.

We have been able to confirm several of Derjaguin's findings but have not succeeded in identifying the entities responsible for the anomalous behaviour. Such identification is made difficult by the minute amounts of material which are at present available and in these circumstances the possibility of contamination cannot be entirely eliminated.

We conclude that the "anomalous" water we have obtained in 'Pyrex' glass is composed chiefly of normal water and that some of its properties are consistent with those of a gel. It is possible that a gel could be formed by the leaching of silicates from the glass. Indeed, a 25 per cent solution of common water glass has a high viscosity and refractive index, but it is difficult to reconcile this explanation with the observation that bulk water placed in similar capillaries retained its normal properties indefinitely. Further, Derjaguin has worked with pure quartz capillaries where such leaching is most unlikely.

The existence of "anomalous" water as a stable and distinct molecular entity will only be established when it becomes available in amounts sufficient for an unequivocal characterization.

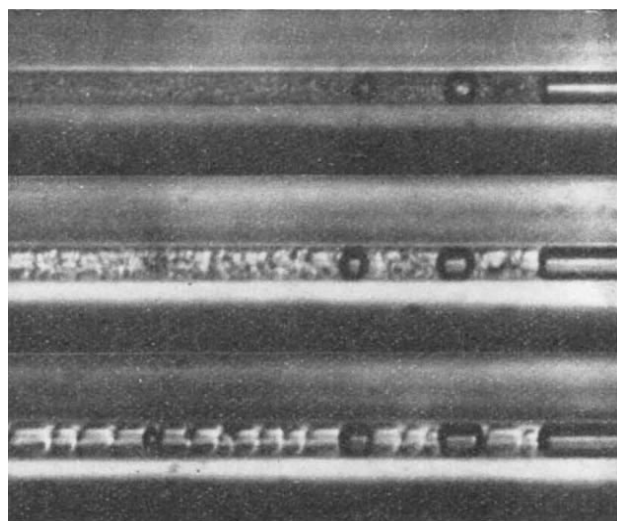


Fig. 2. Photomicrographs of "anomalous" water columns in a 'Pyrex' capillary ($r=10 \mu\text{m}$) at –27° C (top), –14° C (centre) and –5° C (bottom).

We thank Mr J. Clifford, Mr W. K. Thompson and Dr W. T. Pike for their help and Dr A. D. Bangham, Dr J. Hockey and Dr C. J. Danby for useful discussions.

E. WILLIS
G. K. RENNIE
C. SMART
B. A. PETHICA

Unilever Research Laboratory,
Port Sunlight,
Cheshire.

Received November 27, 1968; revised January 22, 1969.

¹ Derjaguin, B. V., Churaev, N. V., Fedyaikin, N. N., Talaev, M. V., and Ershova, I. G., *Izv. Akad. Nauk SSSR*, (Russ.), 10, 2178 (1967); *Bull. USSR Chem. Sci. (Eng.)*, 2095 (1967).

² Henniker, J. C., *Rev. Mod. Phys.*, 21, 322 (1949).

³ Bangham, A. D., and Bangham, D. R., *Nature*, 219, 1151 (1968).

⁴ Anisimova, V. I., Derjaguin, B. V., Ershova, I. G., Lychnikov, D. S., Rabinovich, Ya. I., Simonova, U. K. L., and Churaev, N. V., *Russ. J. Phys. Chem.*, 41, 1282 (1967).

⁵ Fedyaikin, N. N., Derjaguin, B. V., Norikova, A. V., and Talaev, M. V., *DAN SSSR*, 165, 862 (1965).

Exchangeable Acidity in Unburnt Colliery Spoil

THE more usual methods of soil extraction and chemical analysis are not entirely applicable to assessment of the potential of unburnt colliery spoil as a medium for plant growth. This is particularly true for spoil heaps in the West Riding of Yorkshire with surface spoil pH values well below 4.5. Such spoil often contains FeS₂ which oxidizes to produce Fe²⁺, SO₄²⁻ and H⁺. It may also contain the carbonate mineral ankerite which is potentially capable of neutralizing the acidity. These reactions produce large quantities of soluble salts, chiefly sulphates.

Three sites in the West Riding of Yorkshire have been investigated to obtain information on the exchangeable cation status in the surface spoil. These sites were Bullcroft (SE535098), Hound Hill (SE337046) and Maltby Main (SK545925), and the surface age of the spoil was 10 yr, 50 yr and 8 yr respectively. Twelve random samples of surface spoil (0–10 cm) were taken, each yielding about 5 kg of spoil, and each sample was air-dried before sieving through a 1 cm diameter riddle. The determinations were carried out on separate 10 g sub-samples of the ≤ 1 cm fraction.

Exchangeable acidity was estimated by the BaCl₂-triethanolamine method¹ and total cation exchange capacity by NH₄⁺ saturation². The method described by Jackson³, in which the spoil is treated with 0.1 N HCl, was used as a measure of acid extractable cations. Where ankerite is present in the spoil, this procedure gives a measure of its potential neutralizing capacity. The pH was measured using a glass electrode in a 2:1 0.1 M CaCl₂-spoil suspension.

Table 1. MEAN VALUES AND SIGNIFICANT DIFFERENCE ($P=0.05$) FOR CERTAIN SPOIL FACTORS FOR THREE SITES

Site	Total C.E.C.	Exch. acidity	Acid extr. cation	pH
Bullcroft	13.22	19.75	-0.33	2.76
Hound Hill	10.88	0.03	46.42	3.43
Maltby Main	10.64	6.70	99.00	3.75
Isd ($P=0.05$)	0.94	2.09	35.81	1.25

Table 1 shows mean values for the four sets of determinations for each site, together with the significant difference between means ($P=0.05$).

Fig. 1 shows the regression of the ratio of the exchangeable acidity to total cation exchange capacity on acid extractable cations and shows a consistent relationship between the degree of saturation of the ion exchange sites

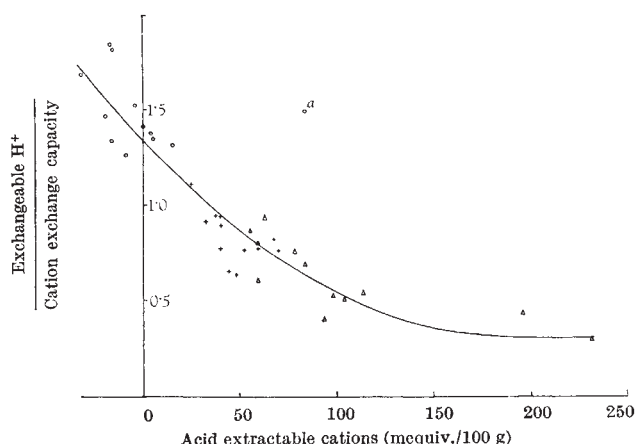


Fig. 1. The relationship between the exchangeable acidity : total cation exchange capacity ratio and acid extractable cations for unburnt spoil samples from three sites. O, Bullcroft; +, Hound Hill; Δ, Maltby Main. Point a has been omitted in calculating the regression: $y = 1.341 - 0.0109x + 0.0000288x^2$.

with acidic ions, and the potential neutralizing capacity of the spoil. It also indicates that some spoil (Bullcroft) has no net neutralizing capacity. Field experience indicates that this site is particularly inhospitable to plant establishment and growth. The values recorded for the exchangeable acidity of spoil may include acidic ions not adsorbed on exchange sites, hence the values of greater than unity for the saturation ratio. It has been established (unpublished work of M. E. P.) that the detrital fraction of the spoil contains significant quantities of amorphous aluminium hydroxides which may become a source of additional acidic cations in pyritic spoil.

Confirmation of a simple relationship such as this may help to identify problem sites which are unlikely to respond to conventional amelioration treatments for reclamation.

We thank the West Riding County Council and the Nuffield Foundation for supporting this work.

M. J. CHADWICK
S. M. CORNWELL*
M. E. PALMER

Department of Biology,
University of York,
Heslington, York.

Received February 25, 1969.

* Present address: Department of Landscape Architecture, University of Sheffield, Sheffield 10.

¹ Chapman, H. D., and Pratt, P. F., in *Methods for Analysis of Soils, Plants and Waters* (Calif. Univ., 1961).

² Black, C. A., Evans, D. D., White, J. L., Ensminger, L. E., and Clark, F. E., in *Methods of Soil Analysis* (Amer. Soc. of Agronomy, Madison, 1965).

³ Jackson, M. L., in *Soil Chemical Analysis* (Constable, London, 1958).

Quenching of the Fluorescence of the Cerous Ion in Aqueous Solution by some Organic Ligands

THE fluorescence of the cerous ion in aqueous solution has been the subject of a number of studies¹⁻³. The emission maximum occurs at about 355 nm, this being excited by absorption at about 265 and 305 nm. The fluorescence is little affected by temperature in the range 10°–40° C, or by strong acids. Nitric acid, however, oxidizes the cerium to the non-fluorescent ceric state. The fluorescence is also affected by the presence of the ceric ion¹ and of some other cations².