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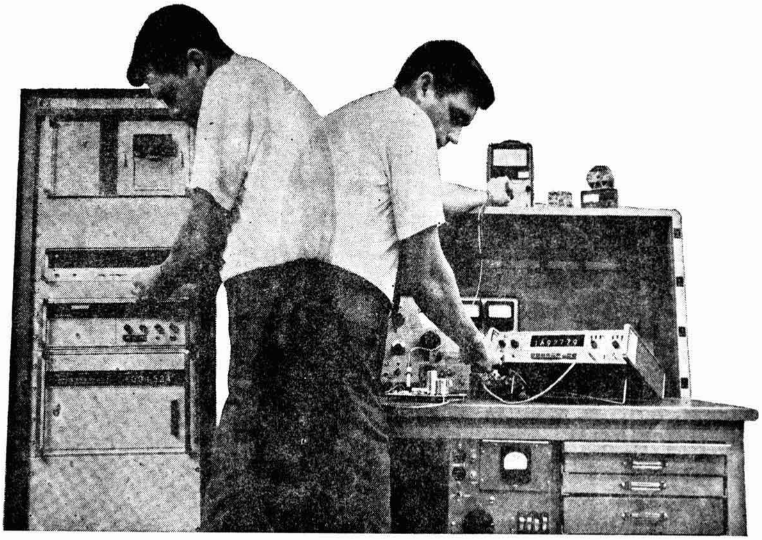

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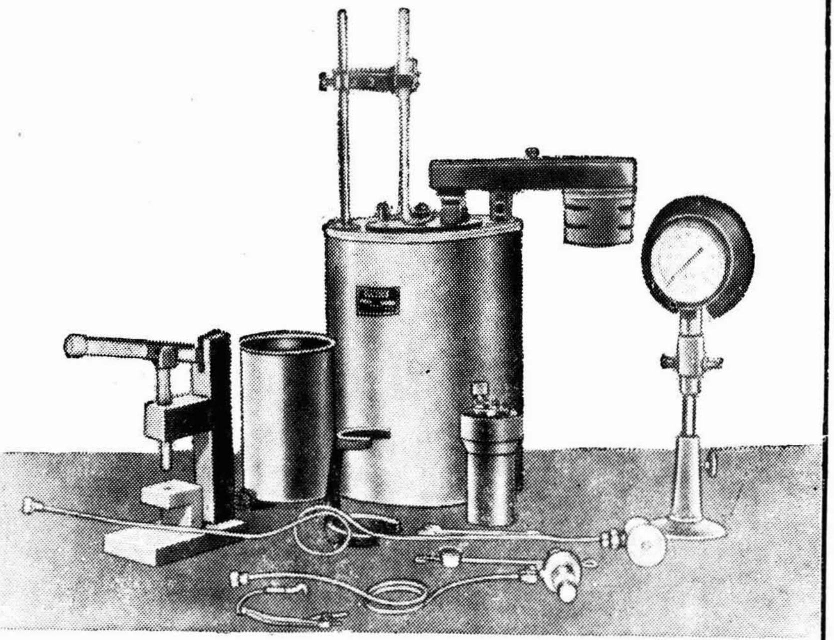

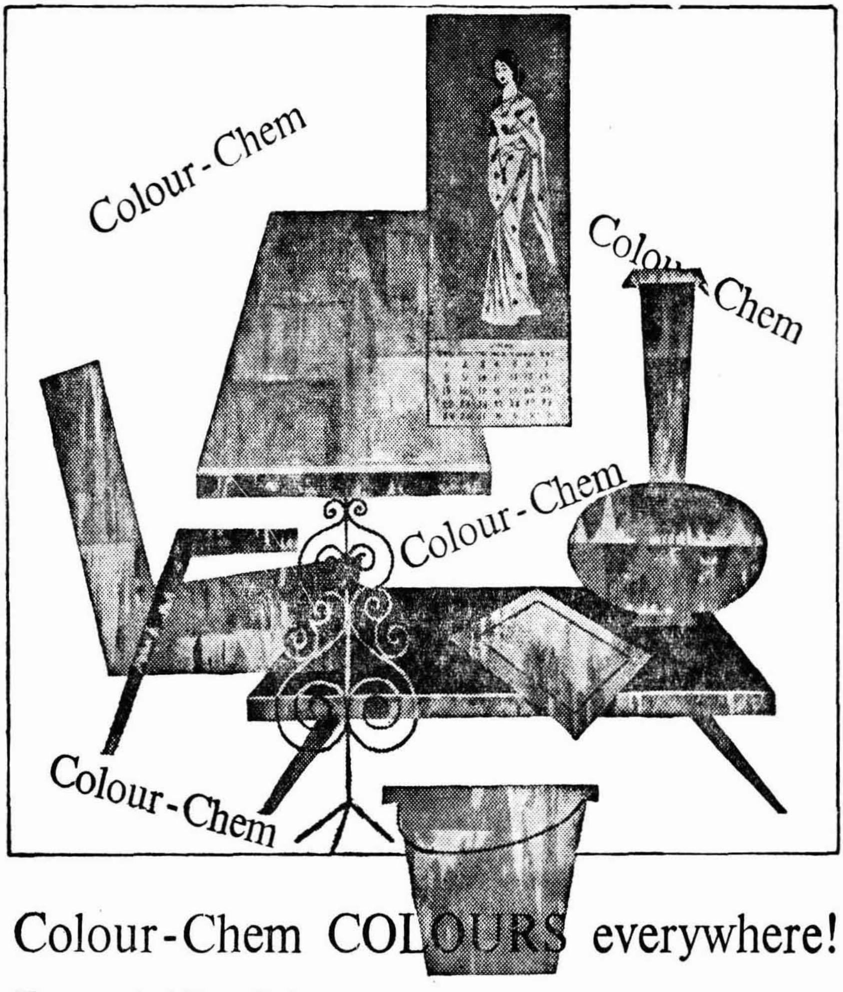
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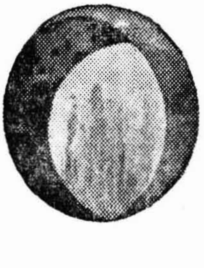

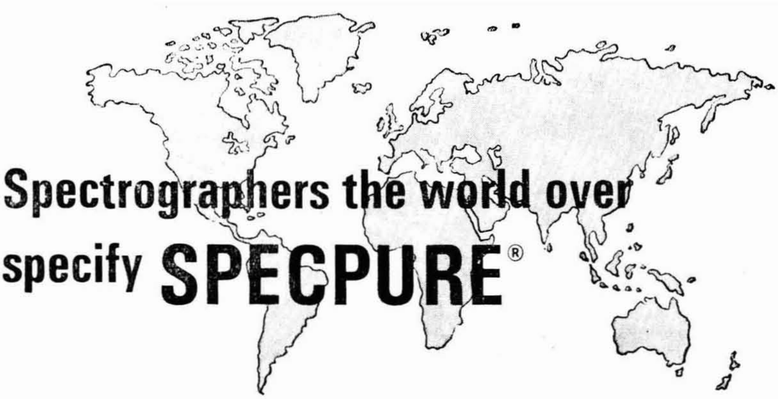

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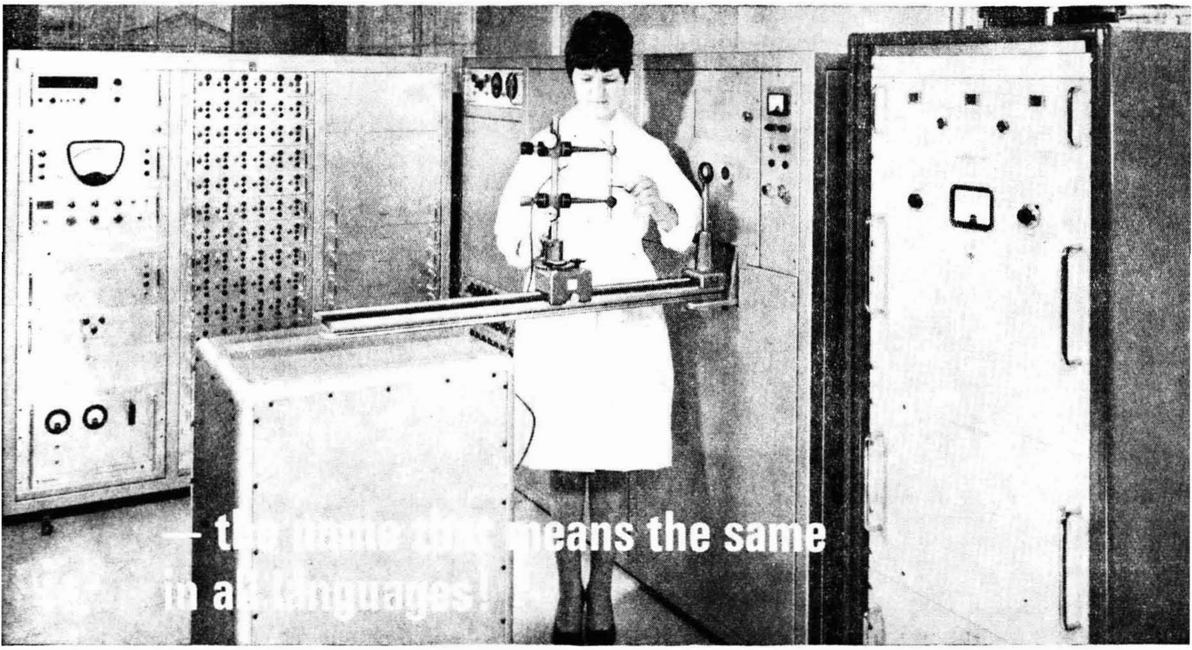

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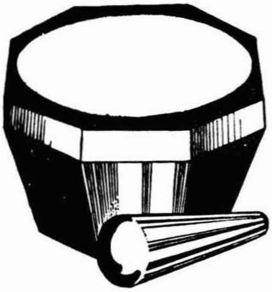

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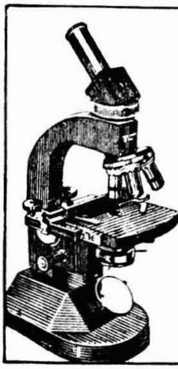

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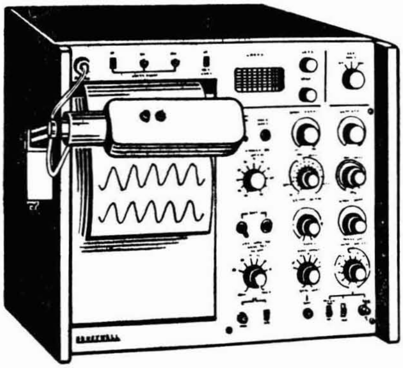

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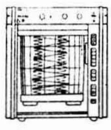

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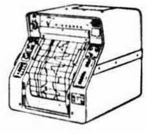

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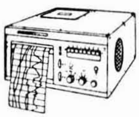

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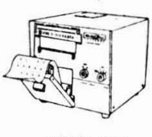

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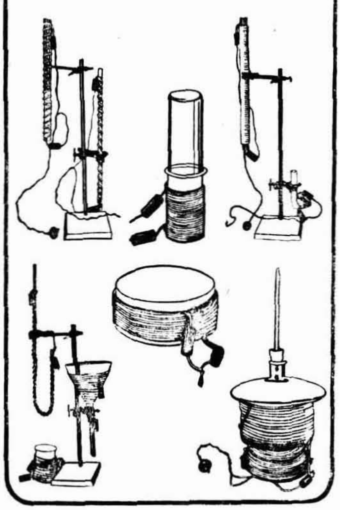

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R. N. Chopra, I. C. Chopra & B. S. Varma

In the year 1956, the Council of Scientific & Industrial Research, New Delhi published a Glossary of Indian Medicinal Plants with a view to presenting concise information regarding their properties, uses and important constituents. Over 2600 species, belonging to about 1350 plant genera, have been dealt with. The information is given under the botanical names of the plants, which are arranged in their alphabetical sequence; trade and vernacular names are also mentioned. The Glossary gives distribution of the plants, diseases for which the particular plant is used, and the active principles. Adequate literature references to the sources of information are also provided. The book ends with two comprehensive indexes: one pertaining to the vernacular and trade names, and the other to the chemical constituents.

In order to bring the Glossary up to date, this Supplement has been brought out. It follows the style of the Glossary and covers all relevant information published during the period 1955-64. The Supplement provides additional information on over 700 species already mentioned in the Glossary, and includes about 380 new species. Indexes covering additional vernacular and trade names and chemical constituents have been provided. The Supplement, like the original Glossary, will be useful not only to the practitioners of indigenous system of medicine, but also to all others who are interested in drugs of vegetable origin and common bazaar medicines.

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Current Topics

Chemistry: Need for Innovation

THE Indo-US conference on chemical education held at Srinagar and Bangalore during June-July 1969, under the joint sponsorship of the National Council for Science Education, the University Grants Commission and the US National Science Foundation, was an event of far-reaching significance to the future of science education and scientific research in India. The recommendations of the conference, if properly followed, have the potentialities of extricating chemistry teaching and research in India out of the morass of a tradition-bound outmoded style, and ushering in the much-needed radical change demanded by the fast rate at which new knowledge is being acquired. The conference, convened with the main purpose of assessing the status of chemistry and chemical education in India, and for developing guidelines for the next ten years, did an admirable job in identifying the lacunae in the chemical education system at various levels and delineating a wide range of areas for concrete action. With the participation of eminent chemists from USA, known not only for their research contributions, but also for their deep involvement in problems of chemical education, and their Indian counterparts with similar contributions and experience, the deliberations were marked by a business-like approach to the problems under consideration. The precision and thoroughness with which members from the participating teams from the two countries had prepared their preconference papers contributed in no small measure to the smooth functioning of the conference and its ability to provide clear-cut guidelines.

After the inaugural session at Srinagar, the participants broke up into three working groups to discuss: (1) Undergraduate teaching; (2) Post-graduate teaching and research; and (3) Laboratory instruction and educational resources. Later, the participants were regrouped to discuss three other topics, viz. (4) Placement of graduates and plans for future; (5) Relation of chemistry to other branches of science; and (6) Evaluation of chemical training. On reassembling at Bangalore, small working groups were formed to prepare plans for action on the following clear-cut and well-defined subjects: (1) College development project, a cooperative programme for the university and its affiliating colleges; (2) Centralization of instrumental facilities/requirements of colleges; (3) Library and literature resources; (4) Evaluation and examination procedures; (5) Organizational aspects; (6) Integrated laboratory programmes; (7) General chemistry course programme; (8) Production of teaching aids; (9) Collaborative programmes at the national and binational level; and (10) Workshops for development of chemistry faculty in other specific areas.

There was unanimity of opinion that the existing system of chemical education produces graduates ill prepared to perform any useful role in the chemical professions, with little flexibility of attitude and lack of a coherent conceptual view of chemistry necessary to equip them to analyse and solve new problems met in real physical world. The present system has got stylized almost to the point of being ritualistic. One of the most important factors inhibiting the processes of change in the present university system was the predominantly paternalistic nature of the internal organization of universities, the academic staff making little input towards the university administration, Students are normally expected to listen and absorb knowledge than develop their own creative faculties by reacting to things that they hear, read, observe and measure. It was the consensus of opinion at the conference that university organization in India should undergo drastic change. An important aspect of the change in the instructional system would be the continuous involvement of teachers and students in dialogue to clarify the goals of such change.

The importance of the deliberations of the conference was adequately brought out by Prof. D. S. Kothari, Chairman, University Grants Commission, in his address. According to him, "We are not engaged in small changes here and there; we are not engaged in marginal changes, but in radical revolution in teaching and methods of teaching. Such a radical revolution can become possible through the cooperation of top researchers, university professors, and college and school teachers. If our science education is to be put in a proper place, it is necessary that the various interdisciplinary studies and the various programmes of science education are put under way. All the divisions within science and also within each discipline were arbitrary and made before the quantum revolution. Curriculum reform and examination reform go together. It is not a question of eliminating external examinations altogether and having only internal examinations. It is a question of having as it were a stream of internal assessment and external assessment. There must be a whole reorganization of experimental work in order not to make it a minor subsidiary to some lecture work."

Giving his impressions of the conference, Dr D. Hornig of the Eastman Kodak Co. and the University of Rochester said: While chemists have become specialized chemists, chemistry has become more unified and indeed all sciences have become more unified and the ideal structure extends across chemistry, physics and biology. While the structure of science has advanced at a great rate, our education system all over the world has become outmoded. Certain general ideas seem to run through all the discussions at the conference and we all recognize the need on both sides for drastic changes in our way of doing things. For example, in the sessions ranging from undergraduate education to graduate education, and from contacts with industries, it became clear that we are dealing with a great variety of students in the first place and even with a great variety of schools, faculties and styles. From the discussions emerged the absolute impossibility of prescribing in any country a uniform curriculum and a uniform syllabus. Therefore, one could not hope to prescribe a new system with a single set of changes. It is important to free the individual institutions from the notion of large-scale prescriptions so that the individual institutions, those which have quality, are free to undertake experiments — new curricular structures with flexible programmes — which can be discussed by the rest of the educational community.

In his final address to the delegates, Dr V. K. R. V. Rao, Union Minister for Education and Youth Services, dwelt upon the "inability to be discontended" in the academic circles and stressed the importance of a journal to keep the teachers and others concerned with education alive to new things that are happening.

The conference enunciated three basic principles in its design for innovation in chemical education, viz. (i) a system flexibility which affords freedom for educational experiments; (ii) a series of educational experiments which provide a continuous but probably changing pattern in chemical education (a) at individual institutions, (b) with groups of affiliated colleges, and (c) collaborative projects and interdisciplinary programmes; and (iii) a number of educational landmarks of a semi-permanent nature in the changing educational pattern, such as (a) regional instrumentation centres, (b) an Indian journal of chemical education, (c) workshops and institutes designed to overcome specific deficiencies in various areas, such as electronics and instrumentation, theoretical chemistry and various interdisciplinary subjects.

As priority recommendations, the conference called upon the University Grants Commission and the National Council for Science Education to initiate and support the following experiments in chemical education: (A) Teaching programmes — (1) Curriculum development; (2) Integrated laboratory courses; (3) College development programmes; (4) Teaching assistantships; (5) Post-doctoral fellowships; (6) Visiting faculty; (7) Interdisciplinary teaching positions; (8) Interdepartmental extracurricular courses; (9) National lectures in 'Frontiers of Science'; (B) Research support — (1) For junior staff in colleges and universities; (2) Research participation programmes for college teachers; (3) Research participation programmes for students; (4) Library development grants; (C) Educational facilities — (1) National instrumentation centres; (2) National library and resource centres; (3) An Indian journal of chemical education; (D) Institutes and short training courses — (1) General chemistry curriculum design; (2) Test construction and evaluation techniques; (3) Integrated laboratory programmes; (4) Design and construction of low-cost indigenous instruments for chemistry courses; (5) Electronics for chemists; (6) Specialized techniques (theoretical and practical aspects) — infrared spectroscopy, nuclear magnetic resonance, X-ray diffraction, electrochemical methods, gas chromatography, mass spectrometry, activation analysis, radiochemical techniques; (7) Advanced instrumental systems for research, particularly in areas that integrate several scientific disciplines, such as biology and chemistry, or geology and chemistry; and (E) Development of educational material — (1) Teaching aids; (2) Films and television programmes; (3) Reprinting of selected monographs.

A welcome feature of the deliberations was the recognition by the participants of the fact that many changes can be put into effect without waiting for the wheels of bureaucracy to turn or financial support to be committed.

The conference met at a time of great discontent and turmoil in the academic community of both students and the faculties, all the world over. There is almost complete dissatisfaction with the present-day chemical educational systems. The discussions at the conference exhibited a keen sense of urgency to build the future, and the conference ended with positive recommendations for self-renewal and practical plans for progress. What will be the scene in chemical education in India a decade or two decades from now? Will the conference have made an impact and served its purpose? The answer lies in how sustained the follow-up efforts of the participants will be in their individual settings, and how imaginative the coordination and leadership of the chemistry panels.

The conference has covered a wide field and the vastness of the programmes should not be allowed to defeat the main objectives. What is basic and what is urgent has to be clearly recognized and within the compass of the existing facilities, strict priorities have to be laid down to achieve the goals sought in a gradual way. To attempt to put all the recommendations into practice immediately would be too ambitious and the initial attempts must be modest and in consonance with the situations as are obtaining in the country in the field of chemistry teaching and research. It is not merely the panels but the large mass of teachers at various levels that must join whole-heartedly in the difficult tasks in hand, and steps must be taken to insure their active participation in the programmes laid down.

Studies of Horizontal Drifts & Travelling Wave Disturbances*

Horizontal Ionospheric Drifts

It has already been two decades since Mitra[1] made the first measurement of the ionospheric drift and a review of the preliminary results was given by Briggs and Spencer[2]. Later extensive measurements were made throughout the world during the IGY and afterwards, and the results were reviewed by Briggs[3]. In spite of these numerous studies the basic question about the origin of drifts remained still an unsolved problem. To understand this basic question, the dependence of ionospheric drifts on height, magnetic activity, time of day and season must be known at all latitudes and at different epochs of solar activity. Drift studies at Waltair (17°43'N, 7·4°N geomag. lat.) were started in 1954 and since then continued up to the IQSY covering a whole solar cycle. In what follows, the results reported from this station and the contribution to the understanding of the drift phenomenon will be briefly reviewed.

The following are some of the conclusions arrived at, regarding the drift and the harmonic vectors of the zonal (EW) and the meridional (NS) components at this station.

(1) The drift speed values in both the E- and F-regions are found to be higher during the winter season compared to summer[4-6].

(2) In general, the EW component points towards east during the night time and towards west during the day in both the regions at this station. The NS component points towards north during night and towards south during day. Fig. 1 shows the diurnal variation of EW and NS components for the E-region.

(3) The predominant periodic component is the 24 hr vector[5,7].

(4) The rotation of the 24 hourly drift vector is generally clockwise for the E- and F_2-regions in all seasons[5,7,8].

(5) The rotation of the 12 hourly vector is in general clockwise for the E- and F-regions in all seasons.

The Effect of Magnetic Activity

The drift speed in the E-region is found to increase with increase in K-index, whereas a decrease at this station is obtained for the F-region with increase of K-index[9-14]. From the slopes of the lines drawn for the velocity versus K-index, it is inferred that the effect of magnetic activity is more in both the E- and F-regions[9,13].

It is the EW component that is most affected in the case of the F-region compared to the NS component[13] by the magnetic activity. This agrees with the results of Briggs and Spencer[2]. The tendency for the EW to change from west to east in the F-region is similar to the one noticed by Hewish[15] from the study of radio-star scintillation.

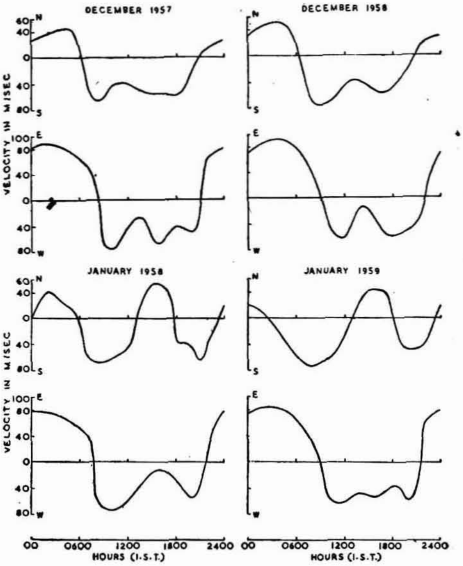

Fig. 1 — Average diurnal variations of NS and EW components for the December and January months

Rao and Rao[12] have obtained the values of $V_c/V = 0{\cdot}71$ and 0·6 for the E-region and 0·76 and 0·76 for the F-region during the quiet and disturbed conditions respectively.

The size of the irregularities a and the axial ratio r are found to increase from quiet to disturbed conditions[10,12].

Height Gradients

The height gradient of the drift speed is positive in the case of E-region[16,17] and the gradient is found to decrease from an average value of 0·74 m/sec/km to 0·59^{-1} with decrease of sunspot activity. Further, the gradients are small compared to 2·5 m sec^{-1} km^{-1} in the 12 hr component reported by Greenhow[18] and 3·6 m sec^{-1} km^{-1} in the drift speed reported by Elford and Robertson[19], both by meteor methods in the 80-100 km range.

As for the F-region, an average value of about 0·73 m sec^{-1} km^{-1} for the height gradient of drift speed has been obtained[20-22] in the height range 200-320 km.

It has been observed that the axial ratio r and the random velocity V_c are maximum in the range 250-300 km[21-23]. Since spread F also occurs at this height range at Waltair, it is felt that the irregularities responsible for the radio-star scintillation are located at this height range, lending support to Booker's[24] prediction that the scintillation phenomenon to be properly explained, the irregularities must be situated in the range 200-300 km.

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A positive gradient in the orientation Ψ° (N of E) of the major axis of the characteristic ellipse, viz. $d\Psi/dh = 1°28'\ \mathrm{km}^{-1}$, has been obtained by Rao and Ramana[21] and later confirmed by Rao and Rao[22], who obtained an anticlockwise rotation of the axis with height.

Latitude Variation

The latitude variation of the apparent drifts in the E- and F-regions has been studied by Rao and Rao[25,26]. The following are the main conclusions.

(1) In the E-region, the night time average drift speeds are greater than the day time drifts at all latitudes in both the hemispheres, the differences being higher at higher latitudes, but in the F-region the day time drift is higher at all latitudes, except near the equator where they are of the same order.

(2) In the E-region, the steady component is generally smaller than the diurnal and is of comparable magnitude with the semi-diurnal at equatorial regions, but at higher latitudes it is of the same order as the 24 hr and 12 hr vectors. The NS steady vector in the case of E is greater than the EW at lower latitudes and vice versa at high latitudes, but in the case of F at all latitudes the NS steady vector is less than the EW.

(3) The EW steady (or prevailing) component is towards east at low latitudes and towards west at high latitudes, the change taking place at 30°N geomagnetic latitude in the F-region.

(4) The diurnal drift vector has larger amplitude compared to the semi-diurnal at lower latitudes in the case of both E- and F-regions and they are of the same order at higher latitudes. The diurnal drift vector attains a maximum value at the equator, decreases up to 30° latitude and then begins to increase with further increase of latitude. These changes of sense and magnitude noticed above at 30° latitude lend partial confirmation to Martyn's[27] prediction.

(5) A general increase in the 12 hr drift vector is noticed in the case of F-region with latitude, but not in the case of E-region.

(6) The rotations of the 24 hourly and 12 hourly vectors are clockwise in the northern hemisphere and anticlockwise in the southern hemisphere. The latitude variation of the anisotropy properties in the E-region was studied by Rao and Rao[28] and for the F-region by Rao[29], using the data of autumn 1958 from many stations.

(7) The axial ratio r and the size of the irregularity a show a decrease with increase of latitude except for the polar regions, where there seems to be an abrupt change. The decrease is evident when a comparison is made of the results from various locations during the IGY (Table 1).

(8) There is a decrease in the true velocity V and in the westward orientation Ψ° (N of E) (Fig. 2) in both the regions with increase of latitude with the exception of polar regions, but with V_c/V, the matter is different and it shows a systematic increase with increase of latitude.

Long-term Variation

The importance of this aspect can best be illustrated by the observation made by Briggs[3] who reported the night time NS component to change in the F-region from north during the minimum sunspot epoch to south during the maximum epoch which, if it were confirmed as pointed out by Briggs, renders the agreement of drift with dynamo theory fortuitous. With a hope of getting quite a good information not only about the drift but also about the anisotropy parameters of the E- and F-region irregularities, a study of the long-term variation involving a complete correlation analysis of drift data at this station from the IGY to IQSY has been made and a few of the conclusions arrived at are listed below.

(1) There is a decrease in the true drift speed with decrease of sunspot activity in the E-region, but in the case of F-region, an overall increase is noticed with decrease of sunspot activity (Figs. 3 and 4) and this opposite behaviour is quite marked in the case of V_a and V_c (ref. 36). An explanation in this case for the F_2-region drift speed is given on the basis of winds considered by King and Kohl[37].

As far as the E-region is concerned, the decrease in drift is agreeing with the decrease in the apparent speed noticed by previous investigators at this station. In the case of F-region there is only an initial decrease in V_a up to the period 1960-62 that is agreeing with the previous results.

TABLE 1 — COMPARATIVE VALUES OF r FOR DIFFERENT STATIONS

E-region		Axial ratio	F-region		Axial ratio
Station	Latitude		Station	Latitude	
Ibadan (Skinner *et al.*[30])	7°N	5·0	Ibadan (Skinner *et al.*[30])	7 N	10·0
Waltair (Rao and Rao[28])	17°N	2·1	Banaras (Singh[33])	25·3°N	3·4
Yamagawa (Tsukamato and Ogata[31])	31·1°N	1·6	Moscow (Mirkotan[34])	55·0°N	2·3
Cambridge (Fooks and Jones[32])	52°N	1·5	KJeller (Becken and Machlum[35])	60°N	1·9

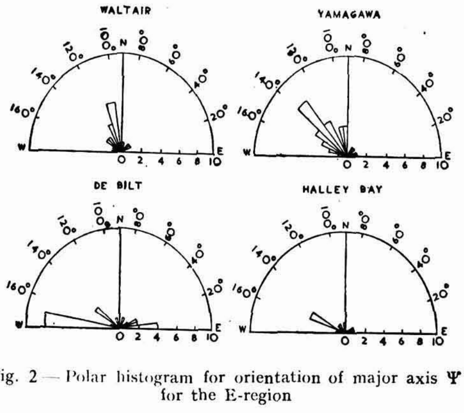

Fig. 2 — Polar histogram for orientation of major axis Ψ for the E-region

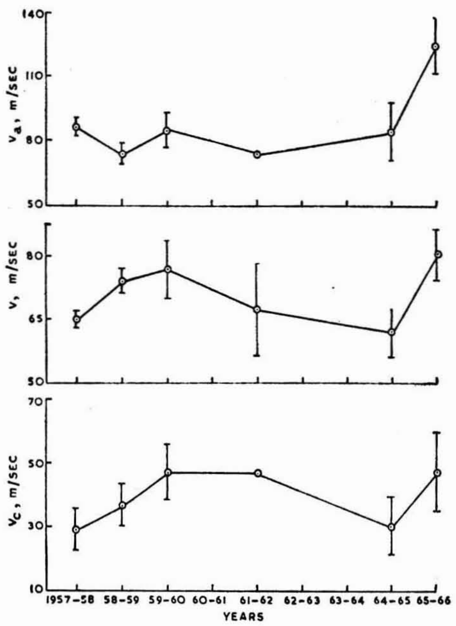

Fig. 3 — Sunspot variation of *Va*, *V* and *Vc* for the E-region

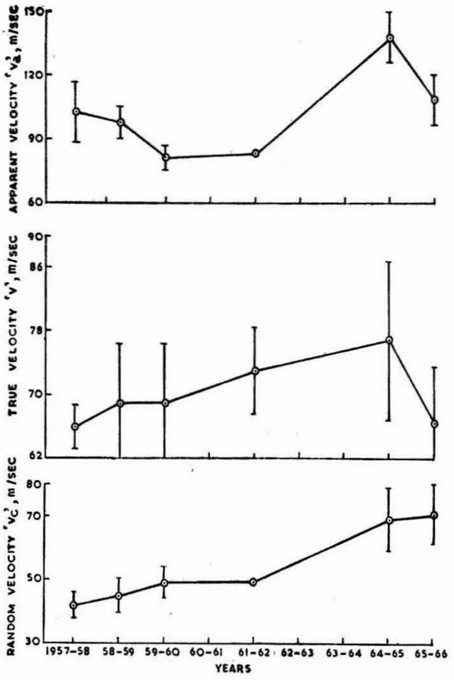

Fig. 4 — Sunspot variation of *Va*, *V* and *Vc* for the F-region

(2) The axial ratio decreases in both the regions but the size *a* shows a decrease in E and an overall increase in F (Figs. 5 and 6).

(3) The angle $|\phi - \phi_a|$, which is a measure of the anisotropy, shows a systematic decrease with decrease of sunspot activity in E but less so in F, as can be seen from Figs. 7 and 8.

(4) The westward orientation $\Psi°$ (N of E) of the major axis increases (Figs. 7 and 8) with decrease of sunspot activity and P_Ψ, the percentage occurrence of the axis close to NS within ±20° is maximum during the maximum sunspot epoch.

(5) There seems to be a mutual relationship between the various parameters in both the E- and F-regions. A significant direct relationship between V and V_c and an inverse relationship between $(r-1)$ and V_c in the case of E-region confirm well the findings of Keneshea *et al.*[38]. Similar functional relationships are also found in the case of F-region.

Lunar Variations

The volume of data available at Waltair for the period 1956-62 has been analysed for the lunar components separately[39,40] for the periods 1956-59 and 1959-62.

Significant values for the lunar semi-diurnal component have been obtained and the values for different seasons show maximum values in winter.

Effect of Meteor Activity

From the investigations of Lovell[41-43], Nicolet[44], Kotadia[45] and Wright[46] a sort of influence of the meteor activity on the E-region ionization is taken

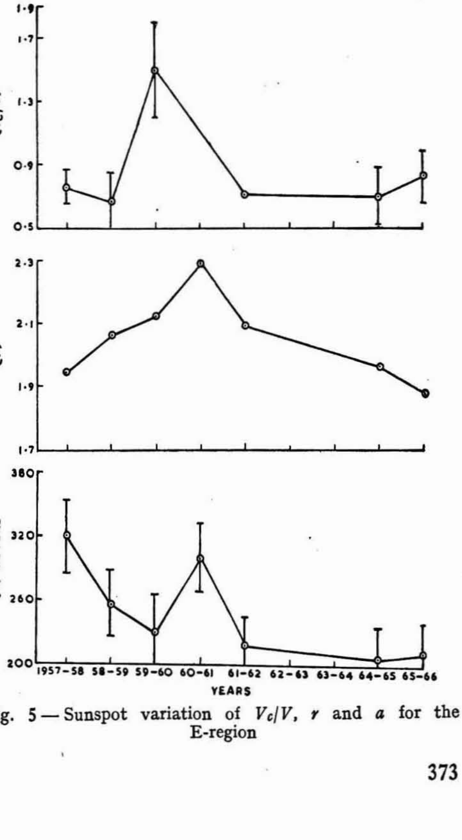

Fig. 5 — Sunspot variation of *Vc*/*V*, *r* and *a* for the E-region

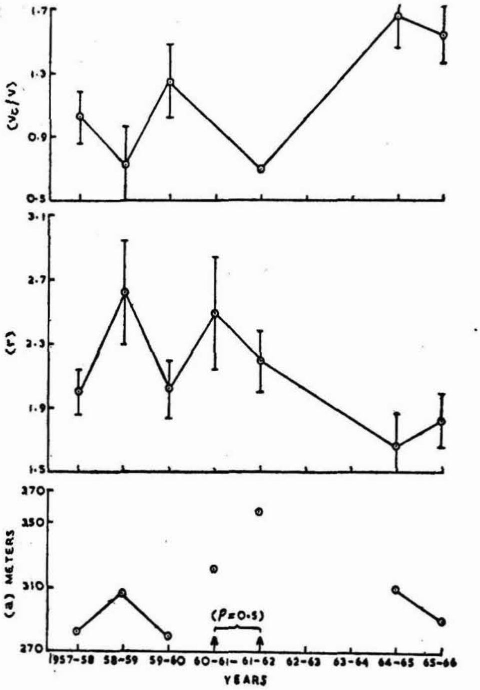

Fig. 6 — Variation of V_c/V, r and a with sunspot activity for the F-region

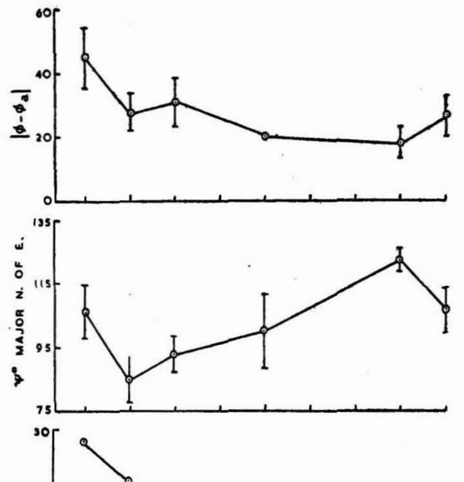

Fig. 7 — Sunspot variation of $|\phi-\phi_a|$, Ψ and $P\Psi$ for the E-region

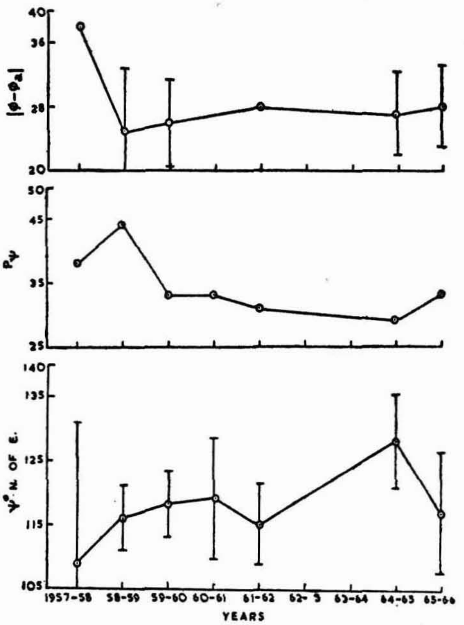

Fig. 8 — Variation of $|\phi-\phi_a|$, $P\Psi$ and Ψ with sunspot activity for the F-region

for granted. It has been of interest to study the fading characteristics of the radio waves reflected from E during the days of meteor activity and results obtained[47] in this regard at Waltair are given below.

(1) The annual variation of the fading frequency of the E-region reflections shown in Fig. 9 is similar to the annual variation of the sporadic meteors that enter the earth's atmosphere.

(2) During Geminid shower 1963 and Leonid shower 1964 (Fig. 10) it was found that both the visual meteor rate and the E-region fading frequency attained maximum values at about the same time.

(3) There is a general increase in the drift parameters V_a, V and V_c with the meteor shower activity. Plausible explanations are given for this[48].

(4) There is a general decrease in the axial ratio r and the size of the irregularity a. The decrease in r and a is supposed to have been caused by the smoothening effect of the rather random influx of ionization due to shower meteors on the existing anisotropy of the E-region irregularities under normal conditions.

(5) The orientation of the major axis of the characteristic ellipse has behaved in a systematic manner, in that it has rotated towards north from its usual NW disposition and except in the case of the quadrantids, it has crossed the NS line towards east during the interval of peak activity. A simple explanation can be given in terms of the relative abundance of the ion trails (or their projections on the level of interest) produced along the NE-SW direction, while the earth traverses

the meteor orbit during the shower period, and this seems to be quite a good possibility also.

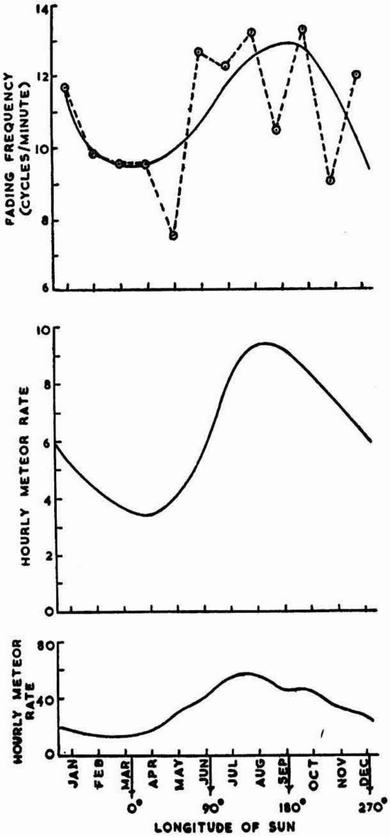

Fig. 9 — Annual variation of fading frequency and sporadic meteor rates

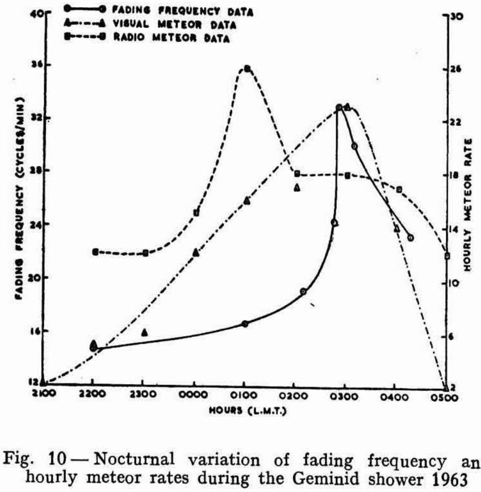

Fig. 10 — Nocturnal variation of fading frequency and hourly meteor rates during the Geminid shower 1963

Structure and Drift of E_s Layer

The extent of phase path variations of E_s echoes on 5·6 MHz was a few wavelengths of the operating frequency over long intervals of time of about an hour. Under these conditions, it can be inferred that the bottom surface of the E_s from which the signal can be supposed to have been returned is very smooth and sharply bounded.

In some of our records the extent of phase path changes during the entire life period of E_s echo was only a few wavelengths, which indicates that the formation of E_s was a highly localized phenomenon, and that it occurs at a particular preferred height. We cannot, however, take this to indicate that the E_s occurrence height is the same for all occurrences.

Sometimes it was found that the E_s echo was diffused with different echoes fading differently. The phase path variations across the width of the echo under such conditions were not the same and were not correlated. The different components constituting the echo could be produced by reflection of the signal at discrete points separated either horizontally or vertically or both.

As such it may be inferred that the structure of sporadic-E layer is not the same always.

A general decrease of phase path of the *O* and *X* components in the F_2-region echo on 5·6 MHz was observed during the formation of E_s. The total decrease of phase path of the *X* component was more than that of the *O* component. The difference between the phase path decreases of the *O* and *X* components can be expressed in terms of the Faraday rotation angle, which in turn can be related to the change in the total electron content per unit column of the propagation path due to the formation of E_s. It was inferred that the formation of E_s at Waltair does involve an accumulation of ionization by a horizontal transportation.

From a study of horizontal drifts of E and E_s echoes using spaced phase path records it was found that the magnitudes of E and E_s drift speed were of the same order. However, the EW component of E_s drift was eastward, whereas for the E-region it was westward during daylight hours.

Whitehead[49] proposed a theory for the formation of E_s from vertical gradients in horizontal wind. This was considered in terms of gravity waves by Hines[50]. The neutral wind motion directed towards east at a level will set the positive ions into motion towards east by collisional interaction. But because of the earth's magnetic field the positive ions tend to move upward. As overlying oppositely directed wind results in an opposite motion of the positive ions, and thus, ionization is accumulated in between the two levels. The resulting electric field tends to get the electrons follow the positive ions. In the present ground based experiment the bottom part of E_s layer reflects the signal and hence it can be taken that the drift velocity and direction obtained correspond to the bottom of the E_s layer. The eastward direction of the EW component of E_s drifts observed in the present investigation agrees with the theoretical requirement for the formation of E_s.

It may be noted that the essential process considered in the wind shear theory for the accumulation of E_s ionization is a vertical transport caused by a horizontal movement of the ionization along the earth's magnetic field lines. Thus the E_s formation implies a horizontal movement of ionization besides the vertical transport. This explains the observed increase in the total ionization in the propagation paths of O and X components in the F_2-region echo during the formation of E_s.

Travelling Wave Perturbations in F_2-Region

Large-scale irregularities which are known as travelling ionospheric disturbances (TID) were studied by Heisler[51] using anomalies in ionosonde records, by Twenten[52] using HF backscatter soundings, by Bramley[53] using direction of arrival measurements, by Davies[54] using doppler shift in HF transmissions, and by Thome[55] using Thomson scatter technique. Satellite transmissions were also used extensively for such studies. All these investigations were confined to higher latitudes in northern and southern hemispheres and none of these workers studied all the various characteristics of travelling waves and interdependence between their various characteristics, which is very important, according to Hines[56], for understanding their origin.

At Waltair we have built a phase path ionospheric sounder which enabled us to record continuously phase path variations of radio waves reflected from the ionosphere. The experimental technique is a modified version of Findlay[57] technique and enabled us to study phase path variations on any frequency. Further, records could be taken on both O and X components of F_2-region echo at one or more aerials on the ground. Fig. 11 shows some typical phase path variations. The quasi-periodic variations in O and X components can be attributed to the travelling wave disturbances being propagated in the F_2-region. Using such records it has been possible to scale the period and vertical amplitude of hundreds of travelling wave perturbations.

Fig. 12 shows the histograms of the percentage of occurrence of travelling wave disturbances of different periods observed on O and X components. The period of the disturbances was in the range 3-39 min. Smaller periods were of more frequent occurrence than larger periods. Out of 210 disturbances detected over a period of 4 months only 161 permitted scaling of periods on both O and X components, whereas for the remaining it was possible to measure the period on one of the components only.

In order to see if there is any height dependence of the period of the disturbance, the periods of perturbations observed on the X component were plotted against the corresponding values of the same disturbance on the O component and the resulting plot is shown in Fig. 13. It can be seen from this figure that the periods of the disturbance observed on O and X components are nearly equal. Similar plot shown in Fig. 14 of amplitudes observed on the X component against the amplitudes on

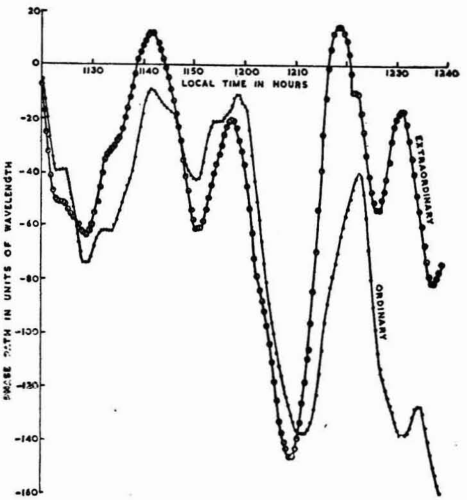

Fig. 11 — Typical phase path variations of ordinary and extraordinary components in the F_2-region echo

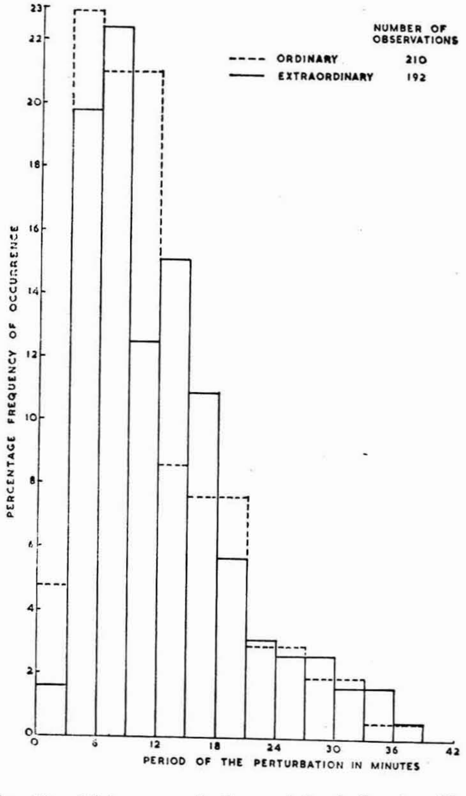

Fig. 12 — Histograms of the period of the travelling wave perturbations on the ordinary and extraordinary components

the *O* component gave no clear evidence of any consistently larger or smaller value on any one of the two components, although there is a slight tendency for the vertical amplitude being slightly larger on the *O* component. The vertical amplitude is seen to vary from 3 to 40 free space wavelengths. From Figs. 12-14 it can be seen that waves with relatively small period and vertical amplitude are of frequent occurrence.

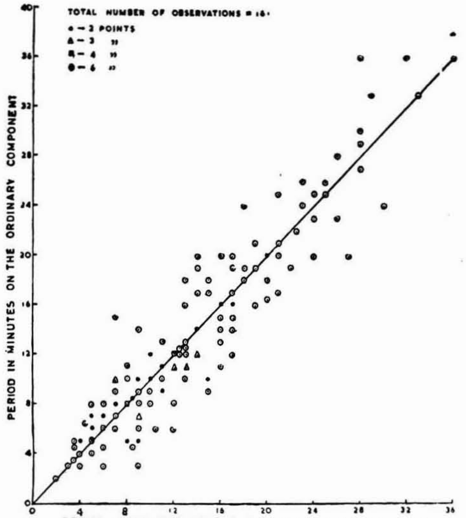

Fig. 13 — Plot between the periods of travelling wave perturbations observed on the ordinary and extraordinary components

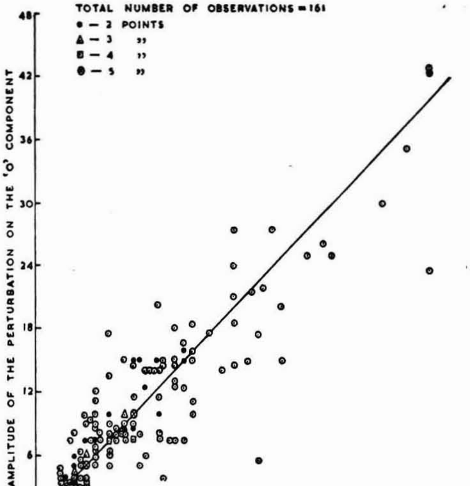

Fig. 14 — Plot between the vertical amplitudes of the travelling wave perturbations observed on the ordinary and extraordinary components

To see if there is any proportionality between the period and vertical amplitude, mass plots of the period of the disturbances versus its vertical amplitude were plotted separately from the waves observed on the *O* and *X* components. Figs. 15 and 16 show the plots obtained for the *O* and *X* components. These figures show that although there is some scatter in the points, there is a clear tendency for the waves of larger periods to have larger vertical amplitudes. To show this more definitely, the coefficients of the correlation between the period and vertical amplitude of the waves have been calculated using standard formulae and these are presented below:

	Correlation coefficient	Standard error
O component	0·682	0·043
X component	0·694	0·041
All the observations	0·517	0·042

The correlation between the period and vertical amplitude of the waves observed on the *O* and *X* components, and on both the components together, were significant at less than 0·01 level. The continuous lines shown in Figs. 15 and 16 are the regression lines. For obtaining the average constant of proportionality between the period and vertical amplitude, an average straight line passing through the origin has been fitted through the points, and they are shown as broken lines in both Figs. 15 and 16. The slope of the average straight line for the *O* component was 0·83 and that for the *X* component was 0·87. For all the points, the slope of the average straight line was 0·85. The difference between *O* and *X* average straight line slopes is of the same order as the standard error.

Thus, the average wave in the F_2-region can be represented by

$$A = 46{\cdot}49K \sin \frac{2\pi t}{K}$$

where *A* is the vertical amplitude of the disturbance in metres; *K*, the period of the disturbance in the range 3-39 min; and *t*, the time variable in min.

The Direction of Movement of F_2-Region Perturbations

During the passage of a travelling wave disturbance over an observation station, there will be gradual changes in the elevation and azimuth angle of arrival of a radio wave from the transmitter on the ground received at the same point after reflection from the disturbance. Also, the phase path undergoes gradual increases and decreases. By ray theory considerations[58] it can be shown that the azimuth angle of arrival of the received signal at the time of a reversal in phase path due to the travelling wave disturbance is normal to the direction of movement. The ambiguity of 180° in the direction of movement of the disturbance can be very easily resolved from a knowledge of the sense of the NS component of the disturbance movement,

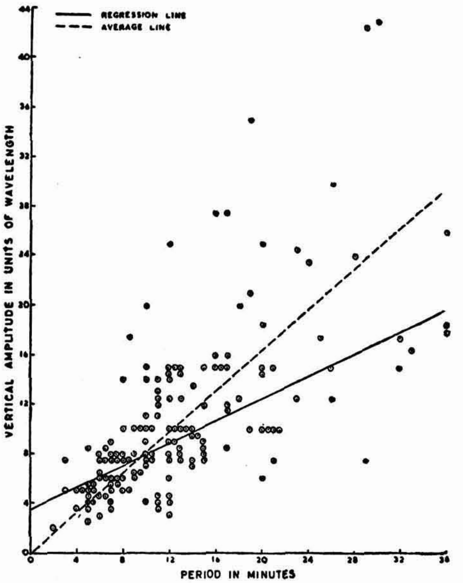

Fig. 15 — Plot between the vertical amplitude and period of the travelling wave disturbances observed on the ordinary component

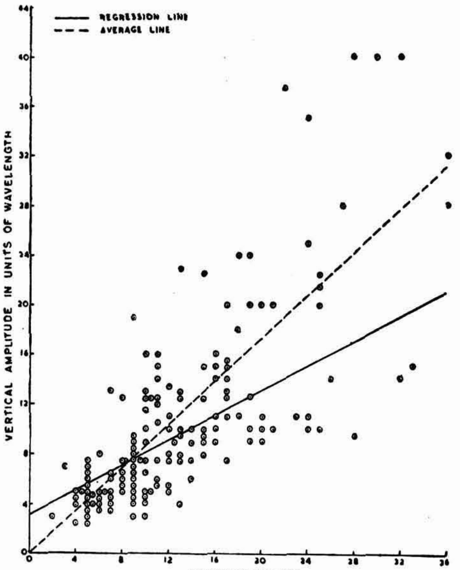

Fig. 16 — Plot between the vertical amplitude and period of the travelling wave perturbations observed on the extraordinary component

which can be had from the sense of the time delay between the reversals in phase path on the O and X components. For the northern hemispheric stations, a phase path reversal occurring earlier on the O component compared to that on the X component indicates that the NS component of the velocity is towards south.

From our experimental spaced phase path records, it was found that the values of directions of movement of the disturbances were mostly within 230° to 250° east of north, and were found to be independent of the time of the day (Fig. 17).

The Speed of the Travelling Wave Disturbances

The reversals in phase path due to the travelling wave disturbances occur at different times on the O and X components. The magnitude of the time delay depends on the horizontal and vertical separation between reflection points of the O and X components, the speed and direction of movement of the disturbance and on the forward tilt of the disturbance front in the vertical plane. For a parabolic F_2-layer of critical frequency of 10·5 MHz, and semi-thickness 140 km, the horizontal and vertical separations between the O and X reflection points at Waltair can be calculated and shown to be 8·22 and 4·5 km respectively. It can be shown that the actual horizontal distance to be traversed by the disturbance in the meridional plane is $D_H \pm D_V \tan\theta$, where D_V and D_H are the vertical and horizontal separations between the O and X reflection points and θ is the forward tilt of the disturbance front. The +ve and −ve signs are to be taken when the sense of the NS component of velocity is towards south and north respectively for the northern hemispheric stations. If τ is the time delay between the reversals in phase path on the O and X components, then the expression for the speed of the disturbances V can be written as

$$V = \frac{[D_H \pm D_V \tan\theta] \cos\phi}{\tau}$$

where ϕ is the direction of movement of the disturbance.

From a general survey of all the experimental records, it was found that τ is not directly related to the group path separation between the O and X components. Histograms showing the frequency of occurrence of different ranges of time delay τ are shown in Fig. 18. The histograms show that the values of the time delay were in the range −2 min to 5 min 20 sec. The value of τ was measured as +ve and the phase path reversal occurs earlier on the O component and later on the X component. Nearly 90% of the values of τ were positive and 75% of these observations gave values in the range 20 sec to 2 min.

The values of the time delay were distributed over a very wide range. A plot of time delay versus local time showed no direct dependence of the magnitude of the time delay on the local time.

Assuming that the value of $D_V \tan\theta$ is negligible compared to D_H and taking the values of $D_H =$ 8·22 km and of $\phi = 235°$ east of north, the speed of the disturbances was calculated and found to be in the range 14-2·5 km/min. From the frequently occurring values of the time delay of 50 sec, the frequently occurring speed of the disturbance comes out to be 6 km/min.

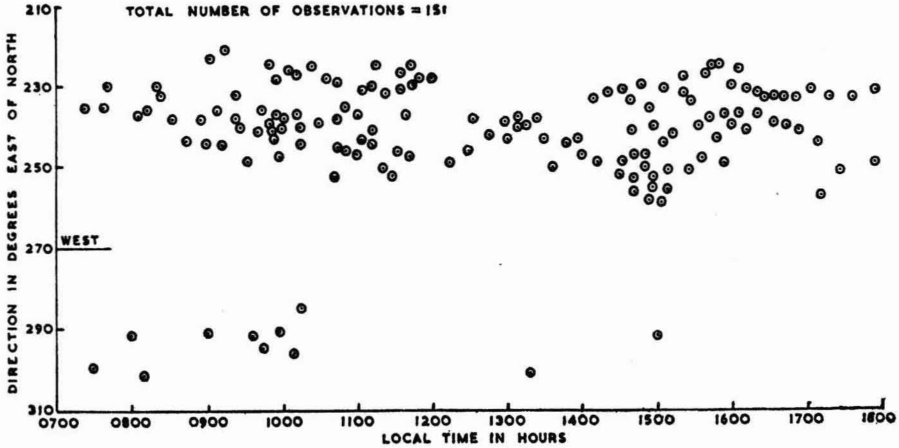

Fig. 17 — Plot between the direction of movement of the travelling wave disturbances and local time

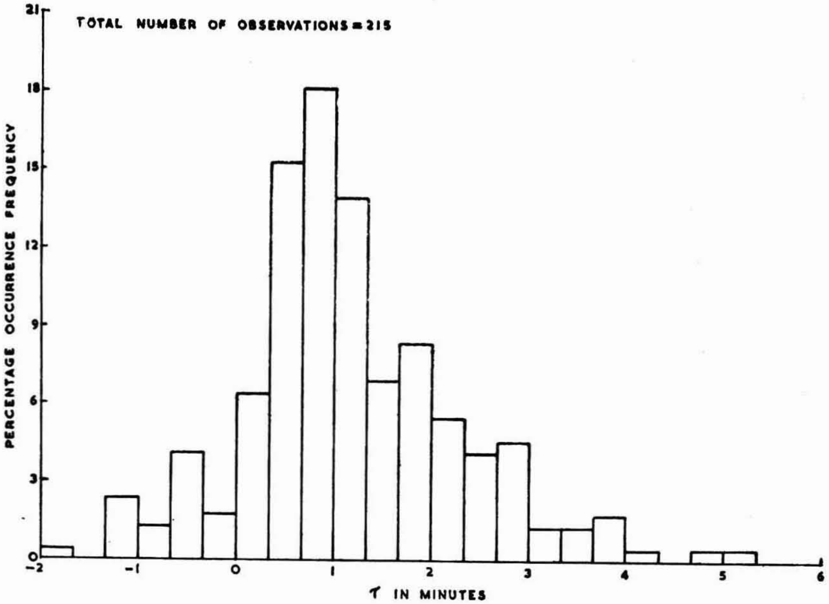

Fig. 18 — Histogram of τ, the time delay between the phase path reversals on the ordinary and extraordinary components

It must be noted that the values of the speed of the disturbances obtained above should correspond to the phase speed of the disturbances. If the ionosphere acts as a dispersive medium for the propagation of the travelling wave disturbances, then the phase velocity of the disturbances will be very much different from the group velocity of propagation.

It was found that the wide variability of time delay τ leads to speeds of disturbances in the range 2-14 km/min, which correspond to disturbances of different periods. A plot of the period T of the travelling ionospheric disturbance versus τ, the time delay, presented in Fig. 19 shows almost a linear relation between them. This points to a phase speed which decreases with increase of period and a group speed which is very much different from phase speed of the disturbance. Assuming the well-known relation between the phase path P and group path P'

$$P' = P + f\frac{dP}{df}$$

and the relation that τ varies linearly as T, it can be shown that the group speed is twice the phase speed.

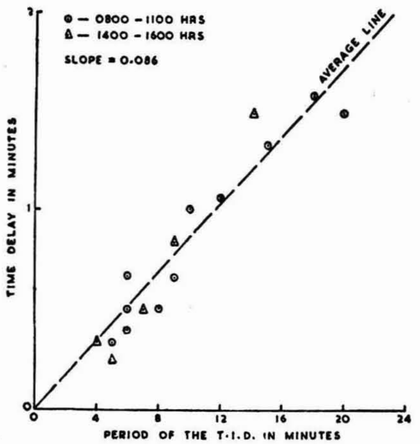

Fig. 19 — Plot between τ, the time delay between the phase path reversals on the ordinary and extraordinary components, and the period of the travelling ionospheric disturbance (TID)

By a simple calculation it can be shown that the minimum radius of curvature of a disturbance assumed sinusoidal is given by

$$r_{\min} = \frac{\lambda^2}{4\pi^2 A}$$

where λ is the wavelength of disturbance and A is the amplitude.

It can be shown that if the value of $r_{\min}$ is less than H, the height of the wave above ground, then there would be more than one point on the disturbance surface from which signals can be received simultaneously on the ground. This simultaneous reception of more than one reflected signal would be observed as the complexities in P'-t records. Since no complexities were observed for all the disturbances studied, it can be inferred that the height of the disturbance H above the ground is less than $r_{\min}$, or

$$H < \frac{\lambda^2}{4\pi^2 A}$$

If V is the phase speed of the disturbance and T the period, then $\lambda = VT$. Substituting $\lambda = VT$ and rearranging, we get

$$V > 2\pi \sqrt{\frac{AH}{T}}$$

We have found in our investigations that the value of $A/T = 46{\cdot}49$ m/min. Substituting this value for A/T and a reasonable value for $H = 200$ km in the above equation, we get

$$V > 2\pi \sqrt{\frac{9{\cdot}3}{T}} \text{ km/min}$$

For the range of values of 3-39 min for T observed in the present study, the corresponding range of values of V will be 9·8-2·5 km/min. It may be noted that the speed of the most frequently observed time delay is slightly greater than the value of 5·7 km/min, obtained experimentally for the most frequently observed period of disturbance and as such no complex reflections were observed in the records.

The above results lead to the important conclusion that the phase speed of a travelling disturbance through the ionosphere varies significantly with the period and as such the ionosphere acts as a highly dispersive medium for these disturbances.

Discussion

Earlier investigators obtained different values for the speed of travelling disturbances, and this depended on the techniques which were suitable for waves of different periods. For example, speeds of waves having periods of about 15 min, observed by Munro[59], Munro and Heisler[60] and Munro[61] gave speeds in the range 7-10 km/min. Waves of relatively smaller period observed by Rao and Yeh[62] using satellite signals were found to travel with speeds of 42 km/min. Heisler and Whitehead[63,64] measured the phase speed and group speed of some individual disturbances and showed that the phase speed of the disturbances was 4-6 km/min, whereas the group speed was about 10 km/min. This indicated that the ionosphere is a highly dispersive medium in so far as the propagation of travelling wave disturbances is concerned, which emphasizes that the speed of the disturbances varies with period.

There seems to be a latitude dependence on the direction of movement of the disturbances. Further, there was a predominant diurnal and seasonal dependence of the direction of movement of the disturbance at some of the stations[65-67]. The one important result that can be obtained from a survey of all the earlier results on the direction of movement of the travelling wave disturbance is that the NS component velocity is towards the equator in both the hemispheres. The southern sense of the NS component of the velocity of the disturbance observed in our investigations agrees with this general finding.

The identification of the travelling wave disturbances in terms of the theoretically possible waves at the ionospheric levels has not been possible so far. Many investigators tried to check their results of some isolated characteristics against the theoretically expected values for different types of waves. For example, Titheridge[68] interpreted the range of values of 15-60 min, for the period of the perturbations with a cutoff period of 15 min to be in fair agreement with the expected behaviour of gravity waves at the F_2-region, and Rao and Yeh[62] interpreted that the value of the speed observed by them was the velocity of sound in the neutral atmosphere at the ionospheric levels.

All the theoretical work done so far concerning the characteristics of travelling waves deals with the propagation of different types of waves in the neutral atmosphere at the ionospheric levels. Assuming that the waves in the neutral air produce identical distortions in the electron densities through collisional coupling, many investigators attempted to interpret the characteristics of the distortions in the electron densities obtained from radio methods. For example, Heisler and Whitehead[63,64] observed that the ionosphere acts as a highly dispersive medium for the propagation of travelling wave disturbances, and they contended that the travelling wave disturbances may not be gravity waves. It is not known whether we are justified in assuming that the disturbances we observe in the electron distributions have identical characteristics of the waves in the neutral atmosphere and much less that their propagation characteristics for the electron motion are constrained by the earth's magnetic field.

At this juncture, the results of Georges[69] obtained from HF doppler shift experiments merit special mention. He explained that the large-scale disturbances with period in the range 15 min to 2 hr could be due to imperfectly ducted gravity waves, whereas the medium-scale disturbances with period of about 3 min could be produced by the atmospheric filtering of acoustic waves travelling into the ionosphere from below. From these results it is evident that different characteristic waves could be propagated in the ionosphere and these different waves could have different propagation characteristics.

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Some Aspects of Reinforcement Corrosion & Its Prevention: Work Carried out at the Central Electrochemical Research Institute, Karaikudi

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AS a result of an extensive survey conducted by the Bihar Government during 1950 on 250 houses which were 20-40 years old, it was found that reinforced brick (RB) constructions had either considerably deteriorated or failed. In 1960-61, therefore, the National Buildings Organization (NBO), New Delhi, entrusted the Central Electrochemical Research Institute, Karaikudi, with the task of investigation into the causes of corrosion of RB work and reinforced cement concrete (RCC) constructions.

Survey of Deteriorated RB and RCC Structures

A project team of the Institute went round the country and inspected a number of deteriorated RB and RCC structures. The RB structures located at Agra, Delhi, Lucknow, Patna and Bombay were inspected. The observations made by the team are summarized below[1]:

(i) Though a distance of 2 in. is specified between adjacent bricks or hollow tiles, the actual distance left between was generally less and often as small as $\frac{3}{4}$ in. In quite a few cases, it was noticed that rods were almost touching the bricks and there was no cover of cement mortar over them.

(ii) Cracks had appeared in most buildings after 20-25 years. There are some instances where the plaster had been replaced just 12 years after construction and one or two instances of failure in 7-8 years.

(iii) The incidence of damage due to corrosion was found less where the top of the roof was adequately protected from direct exposure and where there was adequate slope given in the terrace to ensure that the rain water did not stagnate.

(iv) In the houses inspected, the areas worst affected were in the kitchen and servants' quarters.

(v) The corrosion of reinforcement was generally detected by cracks in the ceiling just below the reinforcement. In cases where reinforcement was severely attacked, a considerable volume of oxidized material or dark colour in the form of thick flakes was usually visible. While removing the flakes it was noticed that $\frac{1}{2}$ or $\frac{3}{8}$ in. diam. bar was reduced to about $\frac{1}{4}$ in. over a major portion of its length and to $\frac{1}{8}$ in. at other portions.

The team also inspected RCC structures located at Bombay, Devakottai (Madras State), Mandapam (Madras State), Trivandrum, Nagpur, Nasik, Akola and Samayanallur (Madras State). The observations made by the team are summarized below:

(i) The corrosion of reinforcement was generally detected by swelling and spalling of the ceiling plaster.

(ii) The corrosion of reinforcement was noticed to be more severe in roofs of latrines, bathrooms and urinals.

(iii) The residential buildings located in highly industrialized areas showed heavy rusting of reinforcement in all parts of structures.

(iv) Terminal ends of roof slabs directly exposed suffered earlier attack.

(v) In the case of multi-storeyed RCC structures, columns, beams and staircases were the worst affected portions. The columns facing the sea were more readily affected than those which were protected from the direct sea breeze.

(vi) Corrosion of reinforcement in buildings within a period of 10-15 years after construction appeared to be due to inadequate cover thickness.

(vii) Where the roofing was given a good slope, the deterioration was slow even in lime concrete constructions of 40 years age (inspected at Nasik).

Analysis of concrete samples — Samples of concrete and bricks from the deteriorated structures were collected at the time of inspection and analysed in the laboratory to determine the chlorides and sulphates contained in them. Several samples had high salt contents.

EXPERIMENTAL DETAILS

Materials

Building materials — The specifications of the different materials used are as follows:

Cement: Portland cement conforming to IS Specification No. 269-1951.
Lime: Locally available lime.
Bricks: Locally available bricks for all the work and also for making brick jelly.
Granite jelly: Locally available aggregates.
Sand: Local sand conforming to class 'B' of IS Specification No. 383-1952.
Mild steel: Abraded on 120 emery wheel and degreased with trichloroethylene.

Chemicals — AR grade chemicals were used for estimation and LR grade for other studies.

Analytical Procedures

Analysis of cement — Portland cement was analysed according to IS Specification No. 269-1951.

Analysis of natural waters — All the constituents were estimated according to the standard method[2]. Chloride was estimated by silver nitrate titration using potassium chromate as indicator and sulphate estimated as SO_3 by the barium sulphate precipitation method. Total hardness and calcium hardness were estimated by the EDTA method using Eriochrome black-T and Murexide respectively as indicators. The alkalinity was estimated by titration with standard hydrochloric acid using methyl orange as indicator. The total solids were estimated by evaporating a known volume of distilled water kept in a weighed dish on a steam bath and drying the same at 110°C in an oven and finding the increase in weight of the dish. The pH was measured using a pH meter. The pH_s (the saturation pH value) of water was found from the chart of Powel *et al.*[3] by taking the sum of the values of p_{ca} (negative logarithm of calcium concentration expressed as g moles of $CaCO_3$ per litre), p_{alk} (negative logarithm of alkalinity to methyl orange expressed as g equiv. of $CaCO_3$ per litre) and $C(pk_2 - pk_s)$ at 90°F. The saturation index was found from the difference between pH and pH_s.

Preparation of Aqueous Extracts and Their Analysis

Cement extracts — Mixtures of cement and distilled water in various ratios were shaken in a microid flask shaker for different periods and then filtered. The alkalinity of the extracts was estimated by titration with standard hydrochloric acid. Chloride and sulphate of calcium and magnesium in aqueous extracts were analysed according to the standard methods for water analysis[2]. The quantity of water was kept constant in one series of experiments and the quantity of cement was varied. In another series, the quantity of water was varied and the quantity of cement was kept constant. Extracts of cement were also prepared for various cement samples received from various factories in India and the percentages of chloride and sulphate estimated as above.

Extracts of cement concrete and cement mortar — Concrete (1 : 2 : 4) and mortar (1 : 2) specimens were prepared using river sand, sea sand and standard sand. Specimens were dried and powdered so as to pass through a 200 mesh sieve. Aqueous extracts were prepared by adding a known quantity of distilled water to a known quantity of powder and shaking in a microid flask shaker. The extract was then filtered and the alkalinity, calcium, magnesium, chloride and sulphate were estimated as per the procedure given for cement extracts.

Fresh building materials — Fresh building materials like brick, river sand and granite jelly received from various places in India were powdered so as to pass through a 200 mesh sieve. Aqueous extracts of these were prepared and chloride and sulphate in the extract estimated as per the procedure given for cement extracts.

Hollow Space Experiments

Cylindrical specimens were prepared such that a hollow space of 2 in. diam. was produced in the centre of the specimen (Fig. 1). In one set of experiments, the hollow space was closed by a concrete stopper and the rate at which solution permeated through the concrete wall into the hollow space from outside was studied. In another set of experiments, the hollow space was filled with distilled water and the specimen placed in the test solution so as to study the rates of diffusion of chloride and sulphate. Changes in the pH of the distilled water were also studied.

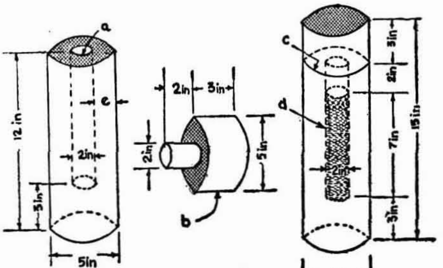


Fig. 1 — Details of the specimen for hollow space experiments [a, lower portion containing hollow space; b, closure; c, beeswax-resin joint; d, solution collected in the hollow space; and e, concrete cover]

Electrochemical Measurements

Potential-time studies — Potentials of bare steel specimens and specimens laid in cement mortar and concrete in various solutions were measured against saturated calomel electrode (SCE) by Poggendorff null method and the changes with time followed.

Polarization measurements — Two types of polarization measurements were made: (a) A constant current of 290 $\mu A/cm^2$ was applied to the mild steel specimen which was made as the anode using an auxiliary steel cathode and the potential was measured against SCE with time. (b) The steady potentials of the test specimen at various current densities (both anodic and cathodic) were measured.

Cement Slurry Coating to Steel

Brushing method — Portland cement sieved to pass 240 mesh was mixed with half of its weight of distilled water containing inhibitive mixture. The first coat was applied to mild steel panels using a fibre brush. After 24 hr, the surface was wetted with distilled water and a second coat was applied, allowed to dry for 24 hr and the surface was periodically (3 times a day) brushed with the sealing solution. This was carried out for 7 days.

Spraying method — The same procedure was followed as in the brushing method except that (i) the weight of water added was 65% of the weight of cement and (ii) the coats were applied by means of a spray gun held at a distance of 12 in. from the surface.

Collection and Analysis of Samples of Different Building Materials

Portland cement — Samples were obtained from 20 different sources in various parts of the country and analysed. The total soluble chloride content varies from nil to a maximum of 0·05% and the soluble sulphate content varies from a minimum of 0·042% to a maximum of 0·18%. The average value works out to 0·0072% for chloride and 0·084% for sulphate. Further experiments have shown that most of the chlorides and sulphates are absorbed as insoluble complexes in cement concrete during its setting. On the average the chloride contents decrease to one-fifth and the sulphate contents decrease to one-sixtieth of the original value. Visual observations of corrosion of steel embedded in 1:2:4 concrete prepared from different cements showed that corrosion is not observed in 7 cement samples out of a total of 20 cement samples examined. It is, therefore, considered worth while to prescribe a corrosion test in the specifications for cement.

Sand — Seven samples from different places were obtained and analyesd. Except two samples which were obtained from the coastal areas, all the other samples contained no soluble chloride. The soluble sulphate content varies from a minimum of 0·003% to a maximum of 0·013%. The average value works out to 0·009%, which is a fraction of that extracted from cement.

Stone aggregate — Seven samples of stone aggregate from various sources were collected and analysed. The soluble chloride was nil for all the samples, whereas soluble sulphate content varied from a minimum value of 0·005% to a maximum value of 0·014%. The average value works out to 0·009%, which again is a fraction of that extracted from cement.

Bricks — Four samples of bricks from different places were obtained and analysed. The soluble chloride content was nil in all the samples, whereas the soluble sulphate content varied from a minimum value of 0·005% to a maximum value of 0·01%. The average value comes to 0·006%.

Lime — Only one lime sample was obtained locally and analysed. It contained 0·12% soluble chloride, which is quite high. It is, therefore, necessary to make sure that the lime used for making lime concrete to be used in RB or RCC constructions is free from chloride.

Water — Thirty-two samples of water from various places were collected and analysed[4]. The chloride content varied from a minimum of 7 ppm to a maximum of 9494 ppm. The sulphate content varied from 3·4 to 1142 ppm. The average value works out to 517 ppm (0·0517%) for chloride and 111 ppm (0·0111%) for sulphate.

ALKALINITY AND COMPOSITION OF AQUEOUS EXTRACT OF CEMENT MORTAR AND CONCRETE

The relevant results of studies on this aspect, discussed at length elsewhere[5], are briefly mentioned here.

Alkalinity of Cement Extracts

The alkalinity of cement extracts after shaking cement with water for various time intervals and cement-water (C-W) ratios were determined. It was found that maximum alkalinity is reached for all C-W ratios in less than 24 hr. The maximum alkalinity obtained for C-W ratio of 1:0·7 was 0·15*N*, for C-W ratio 1:1 it was 0·11*N* and it gradually reduced to 0·04*N* for C-W ratio of 1:100. It was also observed that for high C-W ratios of 1:1, 1:1·5 and 1:2, the alkalinity is mainly contributed by the free alkali (Na_2O+K_2O), which is of considerable practical interest, since the presence of free alkali is more helpful than that of lime in keeping iron passive in the presence of corrosive constituents than free lime. (The alkalinity in extract consisting mainly of free lime is likely to be lost by carbonation and precipitation of calcium carbonate.)

Alkalinity of Extracts of Mortar and Concrete

The alkalinities of extracts from cement-sand mortar (1:2) and cement concrete (1:2:4) were observed and the results are given in Table 1. The alkalinity ranges between 0·05*N* and 0·06*N*. The composition of extracts suggests that nearly one-third of the normality would have come from the free lime produced during hydration and the rest from the alkali brought into solution. In the course of time, with alternate wetting and drying, it is likely that free lime may get carbonated and the alkalinity in the concrete which is brought about by free alkali may only remain. Therefore, an alkalinity of 0·04*N* has been assumed in 1:2:4 cement concrete, which is normally used in RC construction.

Diffusion of Water and Other Corrodents Through Concrete (by Hollow Space Technique)

The rate of permeation of water through 1:2:4 cement concrete was observed for three cover thicknesses, viz. 0·5, 1 and 1·5 in., which are normally adopted in RCC work. It was seen that the rate of permeation increased during the first few days, then diminished to give a fairly steady value after 45 days. The final steady rate was 34 cc/sq dm/year, which is more than adequate for complete destruction of the usual type of reinforcement rod in the course of a few years if the alkaline conditions were not maintained around the reinforcement rods.

The rate of permeation of water through 1:4:8 cement concrete (CC), 1½:1½:5 and 1:1:3 lime-surkhi-brick jelly concretes (LC) and 1:2:2 lime-surkhi-sand mortar (LM) were also studied and

TABLE 1 — ALKALINITIES OF AQUEOUS EXTRACTS FROM CEMENT MORTAR (1:2) AND CONCRETE (1:2:4)

	CaO	Alkalis as Na_2O	Alkalinity
CEMENT-SAND MORTAR (1:2)			
Using river sand	37·7	60·5	0·05*N*
Using sea sand	14·9	69·4	0·06*N*
Using standard sand (Ennore)	31·1	66·5	0·05*N*
CONCRETE (1:2:4) MIX			
Using river sand	49·6	51·0	0·06*N*
Using sea sand	32·7	33·4	0·06*N*
Using standard sand (Ennore)	37·8	58·6	0·06*N*

the results are given in Table 2. It is seen that the permeation rate for 1:4:8 concrete is 33700 times that obtained for 1:2:4 concrete and that for lime concrete is 168-4000 times that of 1:2:4 cement concrete. It is also observed that the permeation rate for 1:2 cement mortar is 44% of that obtained in 1:2:4 cement concrete and that of neat cement mortar is negligible.

The results of studies on diffusion of chloride and sulphate through various types of concrete are given in Table 3. It is significant that the rates of diffusion of chlorides as well as sulphates for ½ and 1½ in. cover thicknesses in the case of both 1:2:4 and 1:4:8 CC differ enormously. Also, the diffusion rates for sulphates and chlorides are much higher for 1:4:8 CC compared to the 1:2:4 CC. Further, it may be seen that the rate of diffusion of chlorides and sulphates through lime concrete is enormous compared to that through 1:2:4 CC, though the same is comparatively less than that for 1:4:8 CC.

These results point to the necessity of using 1:2:4 or richer CC for RCC work and also indicate the necessity of rendering the reinforced concrete with cement plaster of proportion 1:2 or 1:3 and preferably finishing the same with a neat coat of cement.

ELECTROCHEMICAL BEHAVIOUR OF STEEL IN ALKALINE ENVIRONMENT CONTAINING CHLORIDE AND SULPHATE

We now consider the different methods of study of the electrochemical behaviour of steel in alkaline environment in the light of the present knowledge regarding the significance of potential and polarization measurements in corrosion studies.

TABLE 2 — WATER PERMEATION RATES IN CEMENT CONCRETE (1:4:8) AND LIME CONCRETE

[CC (1:4:8) was cured for 7 days in water. LC and LM were cured for 7 days in air and then for 7 days in water.]

Cover thickness in.	Permeation rate, cc/sq dm/day			
	1:4:8 CC	1½:1½:5 LC	1:1:3 LC	1:2:2 LM
1·5	3200	83	16	162
1·0	3200	80	49	372

CC = cement-sandstone jelly concrete.
LC = lime-surkhi-brick jelly concrete.
LM = lime-surkhi-sand mortar.

Potential-Time Studies

Potential-time curves for bare mild steel rod in 0·1*N* NaOH, 0·01*N* NaOH and 0·01*N* NaOH containing various concentrations of NaCl and similar measurements with saturated $Ca(OH)_2$ solution and $Ca(OH)_2$ containing various concentrations of NaCl are shown in Fig. 2 in comparison with measurements made in 3% NaCl solutions. It is seen from Fig. 2 that the initial potential of steel in 3% NaCl is the most negative and this moves further in the negative direction. On the other hand, in 0·1*N* NaOH, the potential is more positive by 200 mV and moves in the positive direction so that, at the end of 14 days, there is nearly 650 mV difference between the specimens in 0·1*N* NaOH and the specimens in 3% NaCl solution, which is the difference in potential between steel in passive condition and steel in active condition. In an environment of NaCl solution, steel is highly active and corrodes. In an environment of 0·1*N* NaOH, it is completely passive and behaves like a noble metal and would not corrode. It was pointed out earlier that an alkalinity of 0·1*N* NaOH and higher is obtained only at high C-W ratios and only in the case of pure cement. It was shown[5] from the hollow space study that under conditions of considerable dilution, the alkalinity at the reinforcement may fall to 0·01*N*. The potential-time curve for 0·01*N* NaOH (Fig. 2) is strikingly different from that obtained in 0·1*N* NaOH in the sense that high positive potential is not maintained indefinitely, but there is a sudden change in the potential in the negative direction after 2 days. This change in the potential in the negative direction is attributed to the contamination of the medium by chloride in the salt-bridge employed for potential measurements. However, this brings out the extreme sensitiveness of the medium at this alkalinity to chloride contamination.

The potential of a corroding metal in aqueous medium was interpreted elsewhere[6] in terms of the polarization characteristics of the anodic and the cathodic reactions. It was pointed out that polarization is influenced by the nature of the electrode reaction as well as the current density. If the current density increases, because of reduction in anodic area or cathodic area, the corresponding

TABLE 3 — DIFFUSION RATES OF CHLORIDES AND SULPHATES IN DIFFERENT CONCRETE MIXES

(Curing conditions and periods were the same as in Table 2)

Cover thickness in.	Diffusion rate, ppm/day									
	1:2:4 CC		1:4:8 CC		1½:1½:5 LC		1:1:3 LC		1:2:2 LM	
	Cl	SO_3	Cl	SO_3	Cl	SO_3	Cl	SO_3	Cl	SO_3
1·5	1-2	—	2400	1840	30	300	12	9	610	793
1·0	5	—	6180	3300	274	146	133	142	820	1354
0·5	20	<1	6280	5280	—	—	—	—	1770	1727

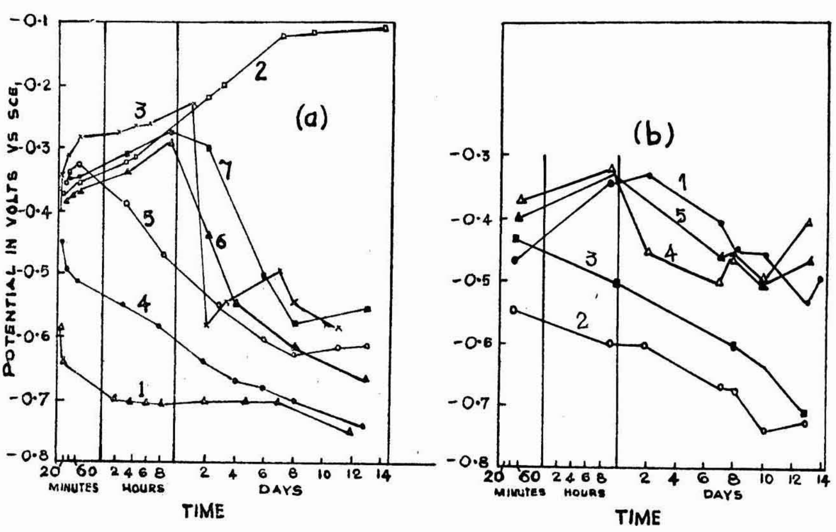


Fig. 2 — Curves showing the results of potential-time studies for bare steel (in NaOH and $Ca(OH)_2$ [(a) bare steel in NaOH: (1) 3% NaCl; (2) 0·1*N* NaOH; (3) 0·01*N* NaOH; (4) 0·01*N* NaOH+0·3% NaCl; (5) 0·01*N* NaOH+0·03% NaCl; (6) 0·01*N* NaOH+0·003% NaCl; and (7) 0·01*N* NaOH+0·0003% NaCl; and (b) bare steel in $Ca(OH)_2$: (1) saturated $Ca(OH)_2$; (2) $Ca(OH)_2$+0·3% NaCl; (3) $Ca(OH)_2$+0·03% NaCl; (4) $Ca(OH)_2$+0·003% NaCl; and (5) $Ca(OH)_2$+0·0001% NaCl]

polarization would also be more. Increased anodic polarization or decreased cathodic polarization would shift the corrosion potential to more noble values and increased cathodic polarization or decreased anodic polarization would shift it to less 'noble' values. In the present case, the shift in the positive direction can be understood in terms of a decrease in anodic area brought about by progressive coverage of the surface with an oxide film and consequential increase in anodic polarization. Similarly, the shift in a negative direction may be understood in terms of progressive enlargement of the anodic area by the action of chloride ions on the oxide film originally present on the surface. Visual observations showed that specimens dipped in 0·1*N* NaOH remained bright for a period of 12 days, for which observations were made, while in the case of specimens dipped in 0·01*N* NaOH and 0·01*N* NaOH+0·03% NaCl, rusting was observed after 2 days and this coincided with a fall in the potential. Rusting was observed within hours in 3% NaCl and 0·01*N* NaOH+0·3% NaCl. It is likely that the initial potential shift in the positive direction in the borderline concentration may be due to the coverage of the surface by the oxide film before chloride ions are able to lodge themselves on the oxide-covered surface and bring about destruction of the oxide film.

In the potential-time curves obtained in saturated $Ca(OH)_2$ solution, it is seen that the potential does not move to such positive values as those obtained in 0·1*N* NaOH. The potential moves in the positive direction during the first 2 days and then there is a shift in the negative direction. The fall is apparently brought about by the carbonation of the lime solution. Similar behaviour is observed up to a concentration of 0·003% NaCl. At higher concentrations of NaCl, the potential steadily moves in the negative direction, thereby showing that the corrosion of steel commenced almost immediately at such salt concentrations. The behaviour in saturated $Ca(OH)_2$ solution is similar to that in 0·01*N* NaOH. It was shown elsewhere[7] that a passive film of ferric oxide is formed in 0·1*N* NaOH solution around —0·55 V versus SCE. This potential will become more positive by 60 mV in the case of 0·01*N* NaOH, i.e. —0·49 V. It may, therefore, be expected that the passive film formed in 0·01*N* NaOH at potentials more positive than —0·49 V versus SCE would cease to be stable at potentials more negative than this value. The potential-time curves in saturated $Ca(OH)_2$ solutions containing NaCl indicate that at 0·03% NaCl concentration, the potential becomes sufficiently negative for the passive film to become unstable.

Steel embedded in cement-sand mortar — Potential-time curves for steel embedded in various cement-sand mixtures prepared in distilled water and tested in 3% NaCl solution are given in Fig. 3. It is seen from Fig. 3 that the potential falls with time in all cases. The fall is very gradual for a cement: sand: water ratio of 1 : 5 : 0·6. At a ratio of 1 : 10 : 1·2, there is an abrupt fall in the beginning from about —0·2 V to —0·45 V, after which it decreases gradually. At 1: 20: 1·2 and 1: 40: 2·4, the initial potential itself is —0·430 V and this comes down to —0·6 V, which is the potential for a bare steel specimen corroding freely in NaCl solution. It may be noted that the initial potential in the case of richest mortar is even more positive than the initial potential observed for bare steel in 0·1*N* NaOH and saturated $Ca(OH)_2$ solution. With the embedded steel specimen, the growth of a protective oxide film is facilitated at the time of the preparation of the specimen itself, but in the case of bare steel specimen immersed in 0·1*N* NaOH or $Ca(OH)_2$, this can take place only during the test. This would explain the more noble initial potential with embedded steel specimen. The absence of a rise in potential of the embedded steel specimen indicates that the action of chloride ions is more significant than the further growth of the oxide film. That the action of chloride ions is very rapid in the more porous mortars is brought out by the fact that the potentials first observed are much more negative than —0·2 V observed in the richest mortar.

Steel embedded in 1: 2: 4 *concrete* — The movement of potential in the negative direction is also observed in 1: 2: 4 concrete both in 0·1% and 1% NaCl solutions (Fig. 4), again suggesting that the action of chloride ion is more significant in the case of embedded steel specimen as compared with the further growth of oxide film.

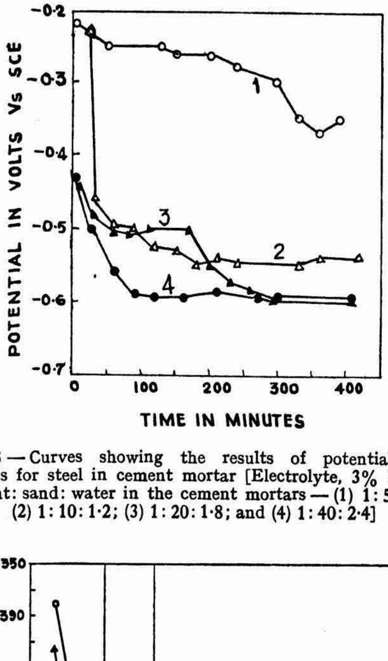


Fig. 3 — Curves showing the results of potential-time studies for steel in cement mortar [Electrolyte, 3% NaCl; cement: sand: water in the cement mortars — (1) 1: 5: 0·6; (2) 1: 10: 1·2; (3) 1: 20: 1·8; and (4) 1: 40: 2·4]

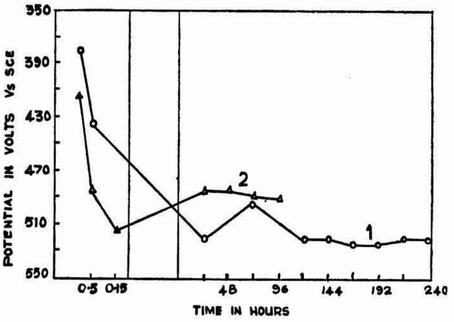


Fig. 4 — Curves showing the results of potential-time studies for steel embedded in 1: 2: 4 concrete with 1 in. cover [Concrete cured for 7 days in distilled water before immersion in NaCl solution; (1) 0·1% NaCl and (2) 1·0% NaCl]

Polarization Studies

It was mentioned earlier that the reduction in the anodic or cathodic area on a corroding metal surface is made known by the change in the slope of the polarization curve. It was also pointed out that the direction of shift of potential does not give unambiguous information, since both increase in anodic area and decrease in cathodic area can bring about shift in the negative direction and vice versa in regard to shift in the positive direction. A steep increase in the cathodic polarization would suggest a decrease in the area available for the cathodic reaction and vice versa. Hence, more definite information about the behaviour of a corroding metal in aqueous solution is given by considering both potential-time behaviour and polarization behaviour as indicated by the *E-I* curves.

E-I curves for bare steel in NaOH and $Ca(OH)_2$ solutions containing NaCl and cement extract containing NaCl are given in Fig. 5. It is seen from Fig. 5 that in 3% NaCl solution, cement extract containing 3% NaCl and saturated $Ca(OH)_2$ solution containing 3% NaCl, the initial potential is around —0·6 V and there is hardly any anodic or cathodic polarization. The cathodic polarization is little affected in 0·1*N* NaOH, $Ca(OH)_2$ and cement extract solutions containing 0·1% NaCl. In these solutions, anodic polarization has become much steeper and the increase in the slope of the anodic polarization curve is in the order 0·1*N* NaOH > saturated $Ca(OH)_2$ > cement extract. This gives strong support for the interpretation put forward earlier that if other factors can be considered to be constant, a more positive initial potential is indicative of the true anodic area being smaller.

E-I curves for steel embedded in cement-mortar of varying ratios of cement and sand and immersed

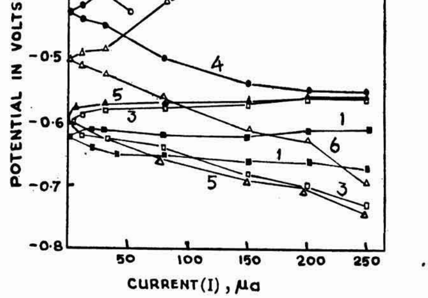


Fig. 5 — *E-I* curves for bare steel [(1) 3% NaCl; (2) 0·1*N* NaOH+0·1% NaCl; (3) $Ca(OH)_2$+3% NaCl; (4) $Ca(OH)_2$ +0·1% NaCl; (5) cement extract+3% NaCl; and (6) cement extract+0·1% NaCl]

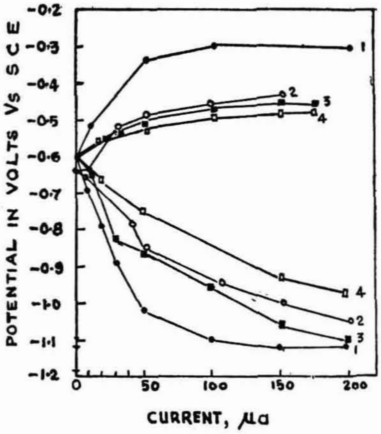


Fig. 6 — *E-I* curves for steel embedded in cement-mortar of varying ratios of cement and sand and immersed in 3% NaCl for 15 days [Cement: sand: water ratio — (1) 1 : 1 : 0·6; (2) 1 : 2 : 0·6; (3) 1 : 3 : 0·6; and (4) 1 : 4 : 0·6]

in 3% NaCl for 15 days are given in Fig. 6. It is seen that only in the case of the richest mortar, i.e. 1 : 1 ratio, a steep curve is obtained both in the anodic and cathodic polarization. In the case of leaner mixes like 1 : 2, 1 : 3 and 1 : 4, it is observed that cathodic polarization gradually decreases with increase in porosity, confirming the earlier view on rate of diffusion of oxygen.

The anodic polarization curves for leaner mixes are close to each other, thereby suggesting that except the richest mortar, namely 1 : 1, in all the other cases chloride diffuses at sufficiently fast rate, so as to modify the anodic polarization behaviour.

E-I curves for steel embedded in 1 : 2 : 4 concrete and immersed in solutions containing various concentrations of chloride and sulphate are respectively given in Figs. 7 and 8. It is seen that in both cases, the cathodic polarization curves in the different salt concentrations are close to each other. Considerable difference is observed in the case of the anodic polarization curves in the different solutions. It is seen that the anodic polarization curve is very steep up to 0·01% sodium chloride and up to 0·5% sodium sulphate. The cathodic polarization curve obtained with the embedded specimen is very much steeper than what was observed with bare steel in 3% NaCl solution. This would suggest that the increase in the cathodic polarization curve for embedded steel is perhaps brought about by concentration polarization, the supply of oxygen to the surface for the cathodic reaction being limited by the rate at which it can diffuse through concrete. Since the composition of the concrete is constant, the concentration-polarization curve can be expected to be the same for all solutions and this is what is observed. So the cathodic polarization curve for concrete can give useful information on the rate of diffusion of oxygen to the metal surface. In the anodic polarization curve, the steep rise in the case of 0·01% NaCl and distilled water indicates that in both cases, the electrolyte at the metal surface is the same. A similar behaviour is observed in sodium sulphate solution up to 0·5%, which is in conformity with the very much slower rate of diffusion of sulphate through concrete mentioned earlier. At a concentration of 0·1% NaCl and 0·75% Na_2SO_4, sufficient chloride or sulphate diffuses to the surface to modify the anodic polarization behaviour.

It was shown elsewhere[8] that useful information on the passivation of steel in NaOH-NaCl system can be obtained by a study of the anodic polarization at a constant current of 290 μA/cm². If the potential rises to the potential of oxygen evolution and stays at this value, it may be concluded that the system is likely to remain passive. If, however, the potential falls or it does not rise to the potential of oxygen evolution, this is indicative of breakdown of the protective oxide film by chloride present in the medium. The results obtained by this method (procedure given in the section entitled 'Experimental Details') for 0·04*N* NaOH-NaCl, 0·04*N* $Ca(OH)_2$-NaCl and 0·04*N* cement extract-NaCl systems are compared in Fig. 9. It is seen from Fig. 9 that in the case of NaOH solution, the potential falls at 0·05% NaCl, in $Ca(OH)_2$ solution it falls at 0·025% NaCl and in cement extract it falls at 0·03% NaCl. This confirms the earlier observation from polarization measurements that NaOH solution is more effective than cement extract in causing passivation. The behaviour of cement extract is very similar to that of a saturated $Ca(OH)_2$ solution. This method can, therefore, be usefully employed to find out the corrosive or inhibitive nature of cement extracts and to determine the tolerable limits of corrosive salts in alkaline solutions

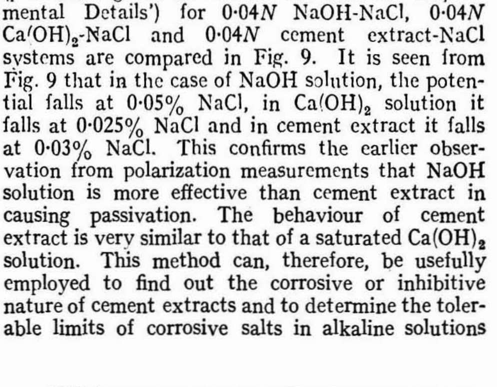


Fig. 7 — *E-I* curves for steel embedded in 1 : 2 : 4 concrete and immersed in solutions containing different concentrations of chloride [Chloride concentration: (1) distilled water; (2) 100 ppm NaCl; (3) 1000 ppm NaCl; and (4) 10000 ppm NaCl]

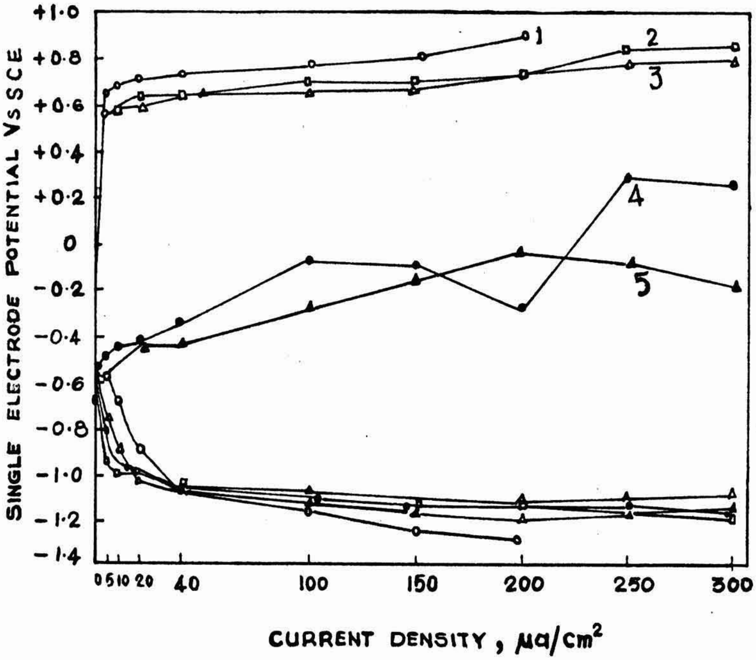


Fig. 8 — *E-I* curves for steel embedded in 1:2:4 concrete and immersed in solutions containing different concentrations of sulphate [Sulphate concentration: (1) distilled water; (2) 20 ppm Na_2SO_4; (3) 5000 ppm Na_2SO_4; (4) 7500 ppm Na_2SO_4; and (5) 10000 ppm Na_2SO_4]

corresponding to cement extracts. It is observed that all extracts from fresh cement are corrosive, while those from set cement are inhibitive. As pointed out earlier, the inhibitive quality of extracts from set cements arises from the fact that during the setting of cement, the free chloride and sulphate concentrations are reduced to one-fifth and one-sixtieth respectively of the original value. It may, therefore, be concluded that corrosion of these cement samples may not be prevented during setting. However, after the concrete is set, subsequent wetting of the concrete may not induce corrosion for obvious reasons.

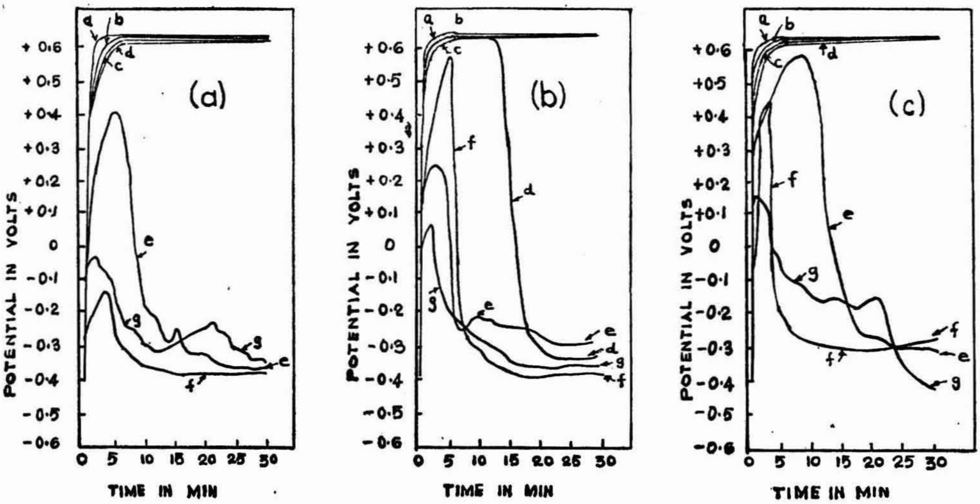
The Passive-Active Cell

Considering several types of cells which may be responsible for corrosion of reinforcement in concrete it was pointed out earlier[9] that the most powerful cell is likely to be the one set up between the portion of steel embedded in permeable concrete having high chloride content and low *p*H and the portion of steel embedded in less permeable concrete having low chloride content and high *p*H. It was pointed out earlier in this paper that a potential difference of nearly 650 mV is observed between 'passive' steel and 'active' steel. It was further seen that steel is made active in the presence of sufficient amount of chloride and sulphate. It may be expected that in well-laid concrete, the alkalinity obtained in the concrete will be of the same order throughout the concrete. However, as a result of fine cracks produced during exposure to sun and rain, water-containing salts may reach the steel through the cracks. Hence, a passive-active cell is likely to be set up, with the steel below the cracks acting as the anode or active member of the couple and the steel, out of reach of the cracks and protected against corrosion by the maintenance of passivity, acting as the cathode. While dry concrete may have resistance running to several hundred kilo-ohm-cm, wet concrete may have a fairly low resistance (less than hundred ohm-cm). Thus, the electrical resistance of the concrete will not come in the way of operation of the passive-active cell when the concrete is wet.

TOLERABLE LIMITS FOR CHLORIDE AND SULPHATE IN ALKALINE ENVIRONMENT

Degree of Corrosive Influence of Soluble Salts

The effect of *p*H of aerated water on corrosion of iron at room temperature is shown in Fig. 10. Within the *p*H range 4-10, the corrosion rate is constant and its value depends on how rapidly oxygen diffuses to the metal surface. The corrosion rate increases steeply in the acid region ($pH < 4$) and decreases to a negligible value between *p*H 10 and 13. Steel is said to be passive in this region. It was mentioned earlier that concrete is permeable



	(a)	(b)	(c)
	In 0·04N NaOH	In 0·04N Ca(OH)$_2$	In 0·04N cement extract
(a)	0·005% NaCl	0·004 and 0·005% NaCl	0·005, 0·007 and 0·008% NaCl
(b)	0·01% NaCl	0·01% NaCl	0·009% NaCl
(c)	0·02% NaCl	0·02% NaCl	0·01% NaCl
(d)	0·03% NaCl	0·025% NaCl	0·025% NaCl
(e)	0·05% NaCl	0·03% NaCl	0·03% NaCl
(f)	0·07% NaCl	0·05% NaCl	0·05% NaCl
(g)	0·1% NaCl	0·07% NaCl	0·07% NaCl

Fig. 9 — Curves showing the results of anodic polarization studies at constant current

to water and aqueous extracts of concrete are alkaline and fall in the *p*H range 10-13. It would, therefore, be expected that steel is likely to remain passive, when it is embedded in concrete. However, this condition is likely to hold good only when the aqueous environment is free from salts which can induce corrosion. The question that arises is how the inhibitive environment provided by the alkalinity of 0·06-0·01N is modified by the presence of soluble salts like chloride and sulphate. It was mentioned earlier that a very sensitive method of finding this out is by means of the anodic polarization technique. The concentrations at which chloride and sulphate are corrosive when present individually and when present together are given in Table 4.

Soluble Chloride and Sulphate Present in Building Materials

The minimum, average and maximum amounts of soluble chloride and sulphate present in the fresh building materials and natural waters used for building construction have been worked out on the basis of results discussed earlier. The values are given in Table 5. The total amounts of soluble chloride and sulphate (in ppm) in raw mix of 1 : 2 : 4 concrete have been calculated from the data given in Table 5 and are presented as ppm in Table 6. As mentioned earlier the available chloride and sulphate in concrete after hydration will be only one-fifth of the total chloride and one-sixtieth of the total sulphate present in the fresh materials and can be easily calculated from the values given in Table 6.

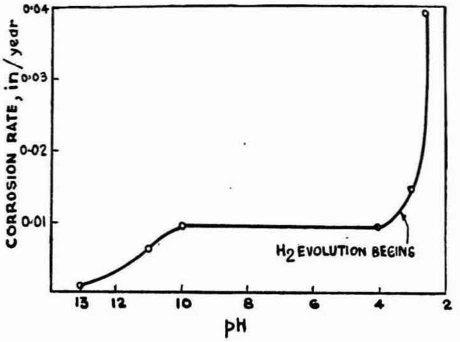


Fig. 10 — Effect of *p*H of aerated water on corrosion of iron at room temperature

Corrosion Behaviour of Steel in 1 : 2 : 4 Concrete

It may be seen from Table 7 that when the minimum amounts of chloride and sulphate are present

TABLE 4 — TOLERABLE LIMITS FOR CHLORIDE AND SULPHATE TO BE INHIBITIVE OR CORROSIVE

Normality of NaOH *N*	Amount of Cl or SO_3, ppm	
	Inhibitive	Corrosive
0·01	5 Cl	6 Cl
0·01	20 SO_3	22·5 SO_3
0·02	60 Cl	65 Cl
0·02	170 SO_3	175 SO_3
0·04	130 Cl	150 Cl
0·04	2750 SO_3	2900 SO_3
0·06	225 Cl	250 Cl
0·06	3250 SO_3	3300 SO_3
0·08	375 Cl	400 Cl
0·08	7200 SO_3	7300 SO_3
0·10	575 Cl	600 Cl
0·10	13250 SO_3	13500 SO_3
0·02(+100)*	50 Cl	55 Cl
0·04(+500)*	100 Cl	105 Cl
0·06(+1000)*	175 Cl	200 Cl
0·06(+1250)*	24 Cl	27 Cl
0·06(+2500)*	12 Cl	15 Cl
0·06(+3000)*	—	5 Cl

*The figures in parentheses represent SO_3 in ppm present in the aqueous environment.

TABLE 5 — CONSTITUENTS PRESENT IN THE BUILDING MATERIALS AND NATURAL WATER

Cl or SO_3 content wt %	Water	Portland cement	Sand	Jelly
	CHLORIDE CONTENT			
Min. value	0·0007	0·0004	0	0
Av. value	0·0517	0·0072	0	0
Max. value	0·9494	0·05	0·12	0
	SULPHATE CONTENT			
Min. value	0·0003	0·042	0·003	0·005
Av. value	0·0111	0·0841	0·009	0·009
Max. value	0·1142	0·18	0·013	0·014

TABLE 6 — CALCULATED CHLORIDE AND SULPHATE IN 1:2:4 CONCRETE*

	Chloride ppm	Sulphate ppm
Minimum value	1	82·5
Average value	50	178
Maximum value	1180	408

*Water/cement/sand jelly ratio: 0·7:1:2·6:4·4 by wt.

TABLE 7 — ELECTROCHEMICAL BEHAVIOUR OF STEEL EMBEDDED IN CONCRETE UNDER ORDINARY CONDITIONS

	Salt content in capillary water* (free of concrete), ppm		Normality reqd to keep the environment inhibitive	Remarks
	Cl	SO_3		
Min. val.	2	14	0·01-0·02	Inhibitive conditions maintained
Av. val.	100	30	0·04	Inhibitive conditions likely to be maintained
Max. val.	2360	70	—	Highly corrosive conditions obtained

*Salt content in capillary water has been calculated assuming the porosity of 1:2:4 CC to be 10%.

in 1:2:4 concrete (porosity, 10%), inhibitive condition will be maintained, since an alkalinity of 0·01-0·02*N* is only required to obtain inhibitive conditions, and this is readily obtained in good concrete. In the case of average amounts, even though the steel can tolerate the corrosive salts at a normality of 0·04*N*, if the alkalinity is brought down by carbonation, etc., then the conditions are more likely to be corrosive. It was shown earlier that the highest alkalinity that can be obtained in 1:2:4 concrete using portland cement is 0·06*N*. The environment around steel will be highly corrosive from the beginning itself, when the maximum amounts are present.

Entry of Corrosive Salts from External Atmosphere

It was earlier mentioned that in a marine atmosphere or an industrial atmosphere, corrosive salts (along with the rain water) can get into the pores of the concrete and are thereby likely to increase the salt concentration at the reinforcement. The effect of increase in the salt concentration on the environment around steel reinforcement is shown in Table 8. The rates of diffusion of chloride and sulphate through good concrete obtained for a cover thickness of 1 in. (as given in col. 2) are made use of in obtaining the data presented in Table 8. It is of interest to note that even good concrete (originally inhibitive with the available alkalinity and salt content) is likely to become corrosive in less than two years under extreme marine conditions if the concrete becomes wet for 15 days in the year only. It is to be remembered in this connection that the thickness of concrete cover over the reinforcement is much greater than 1 in. in the upward direction in roofing and the quantity of sea salts entering inside the buildings in marine atmosphere is perhaps much less than outside. Under milder atmospheric conditions, the concrete is likely to become corrosive within 17 years or 27 years, depending upon the salt content of the condensed moisture. On the other hand, even under the extreme industrial atmosphere, it takes not less than 40 years even if the concrete becomes wet for 90 days in a year. When the average amount of salts is present in concrete, the number of years required to obtain a corrosive environment is further decreased as shown in Table 8. The life of concrete construction is principally determined by the free chloride content in the concrete, since under all conditions, the free sulphate content remains small in comparison with the chloride content and the tolerable limit for sulphate is very much higher than that for chloride.

TABLE 8 — ELECTROCHEMICAL BEHAVIOUR OF STEEL EMBEDDED IN 1:2:4 CONCRETE UNDER ACCELERATED CONDITION

Salt conc. in rain water	Diffusion rate ppm/sq cm/day	Rainy days per year	Added salt content per year	Total salt content in a year, ppm		No. of years reqd for environment to be corrosive
				Cl	SO_3	
CONCRETE CONTAINING MINIMUM AMOUNT OF FREE SALTS						
1% NaCl as Cl (marine atmosphere)	8·64	15	130	132	14	Less than 2 years
0·1% NaCl	0·864	15	13	15	14	About 17 years
0·01% NaCl	0·09	90	8	10	14	About 27 years
1% Na_2SO_4 (industrial atmosphere)	0·86	90	77	2	90	About 40 years
CONCRETE CONTAINING AVERAGE AMOUNT OF FREE SALTS						
1% NaCl as Cl (marine atmosphere)	8·64	15	130	230	30	Less than 1 year
0·1% NaCl	0·864	15	13	113	30	About 10 years
0·01% NaCl	0·09	30	3	103	30	About 45 years
1% Na_2SO_4 (industrial atmosphere)	0·86	60	52	2	82	About 60 years

TABLE 9 — ELECTROCHEMICAL BEHAVIOUR OF STEEL EMBEDDED IN DIFFERENT CONCRETE MIXES

Ratio of the mix	Salt content in capillary water (free of concrete), ppm		Normality reqd to keep the environment inhibitive	Remarks
	Cl	SO_3		
CEMENT/SAND/GRANITE				
1:1½:3	54	16	0·02	Inhibitive conditions likely to be maintained
1:1:2	66	20	0·03-0·04	do
1:2:4	100	30	0·04	do
LIME/SURKHI/BRICK JELLY				
1½:1½:5	300	10	0·08	Corrosive conditions obtained
1:1:3	320	10	0·08	do

Comparison of Corrosion Behaviour in Various Cement Concrete and Lime Concrete Mixes

The data presented in Table 9 give an idea of the free chloride and sulphate salts that are likely to influence reinforcement corrosion when salts are present in the building materials at average value level. It is seen from Table 9 that under average conditions, inhibitive conditions are likely to be obtained in cement concrete. In the case of lime concrete, the free chloride content is likely to be higher than that can be tolerated by the alkalinity that would develop in lime concrete, which would never exceed 0·06*N*. However, it is also to be pointed out here that the chloride values mentioned in Table 9 have been obtained from the chloride present in lime and water. The other building materials, namely brick jelly and sand, are considered to be free from chloride. If lime free of chloride is used in the lime concrete, the soluble chloride in the concrete would be much less and inhibitive conditions may perhaps be obtained.

PREVENTIVE MEASURES

Inhibitor for Corrosion Prevention in Reinforced Concrete and Brickwork Constructions

It was shown earlier that reinforcement corrosion takes place when corrosive salts, such as chlorides and sulphates, increase and sufficient alkalinity is not obtained within the concrete to maintain steel passive. An inhibitive mixture has, therefore, been developed which ensures that alkalinity of concrete is maintained at a sufficiently high level consistent with the physical characteristics required of good quality concrete and the inhibitor concentration within the concrete is adequate to keep steel passive in the presence of maximum amounts of chloride and sulphate that may be introduced along with the building materials and water.

In order to develop the inhibitor, experiments were first carried out with 0·06*N* NaOH solution, which is believed to be the highest alkalinity that can be obtained in 1:2:4 concrete. This solution was made corrosive by the addition of adequate amounts of sulphate and chloride and the effect of adding inhibitive substances like glue and ammonium stearate was considered. From anodic polarization measurements it was observed that all these substances were unable to make the solution inhibitive. It was also observed that when sodium carbonate or trisodium phosphate was added to a corrosive cement extract, the cement extract became inhibitive. Experiments were, therefore, conducted by mixing the substance with cement and preparing extract with water or by dissolving the substance in water and preparing extract with cement and estimating the alkalinity of the extract. The results obtained with some alkaline materials are given in Table 10. It is seen that when the substance is mixed with water, a higher alkalinity is obtained. The experiments were next repeated after incorporating a certain amount of sodium chloride into the water used for preparing the extract, to find out if corrosion is prevented under these conditions also. It is seen from Table 11 that the substances which raise the alkalinity cannot make

TABLE 10 — RESULTS OBTAINED WITH ALKALINE ADDITIVES TO MAKE CEMENT EXTRACT INHIBITIVE

Substance	Amount added (% by wt of cement)	Alkalinity, *N* Substance mixed with	
		Cement	Water
Control (cement extract alone)	—	—	0·06
Trisodium phosphate	0·5	—	0·06
	1·0	0·07	0·06
	1·5	0·09	—
	2·0	0·095	0·10
Sodium carbonate	0·5	—	0·08
	1·0	—	0·11
	1·5	—	0·14
	2·0	0·18	0·20
Sodium hydroxide	0·5	—	0·08
	1·0	—	0·12

TABLE 11 — RESULTS OF EXPERIMENT WITH FURTHER ADDITION OF NaCl TO THE EXTRACTS SPECIFIED IN TABLE 10

Substance	Nature of the extract	
	Without NaCl	With 0·25% NaCl
Control (cement extract alone)	Corrosive	—
0·5% trisodium phosphate	Corrosive	—
2% trisodium phosphate	Inhibitive	Corrosive
2% sodium carbonate	Corrosive	—
3% sodium carbonate	Inhibitive	Corrosive
1% sodium hydroxide	Inhibitive	Corrosive

TABLE 12 — PERFORMANCE OF THE INHIBITOR SYSTEM DEVELOPED FINALLY

Details of test	System	Visual observation
500 hr in salt fog chamber	(a) Control	More than 10 rust spots
	(b) New inhibitor system	No rust spots
Immersion in synthetic sea water for 30 days	(a) Control	Innumerable rust spots
	(b) New inhibitor system	No rust spots

the extract inhibitive, when sodium chloride was also incorporated along with the substance. The effect of addition of alkaline substances on the setting properties, compressive strength and bonding strength of concrete was also studied and it was found that additions of alkaline substances in the amounts required to prevent corrosion affect the various physical characteristics adversely. (The initial setting times for the control, addition of 1-3% sodium carbonate and of 1-3% trisodium phosphate are 65, 5 and 15 min respectively, compared to the setting time specified in the ISS of not earlier than 30 min.) Hence, in subsequent experiments, mixtures of various inhibitors and alkaline substances were considered so as to get an additive which, while not affecting the physical characteristics of concrete, prevents corrosion when chloride is present to the extent that can be introduced through cement, sand, jelly and natural water.

The performance of the inhibitor system that was finally developed in the various tests mentioned above is shown in Table 12. The new inhibitor for prevention of reinforcement corrosion in concrete is covered by Indian Patent Application No. 109784 dated 18 March 1967.

Protective Surface Coatings for Concrete

The accelerated test described elsewhere (Rajagopalan, K. S. & Chandrasekaran, S., unpublished work) simulates as well as accelerates the conditions of exposure of concrete structures. So, various coatings to concrete were screened by this method. It was found that most of the coatings mentioned in literature are unable to prevent reinforcement corrosion by permeation of the salt solution through the concrete. However, the results obtained with some modified formulations based on cement, bitumen, wax, etc., seem to be promising. Tests with these coatings are in progress.

Protective Coatings Based on Portland Cement

When immersion tests in synthetic sea water were conducted to examine the efficiency of the various additions that have been suggested in literature, only ammonium stearate-glue mixture seemed to be the most effective of all the systems[10] examined. The protection given by this system was further tested under more accelerated condition in a salt fog chamber. The results are given in Table 13. It is seen that the inhibitor system is not effective, even though it is better than the coating without the inhibitor. Apart from the poor corrosion performance, the adhesion and hardness of the coating systems mentioned above were also very poor.

TABLE 13 — RESULTS OF 75 HR TEST ON SALT FOG CHAMBER

System	Visual observation
Cement slurry without inhibitor	Numerous rust spots
Cement slurry+0·01% ammonium stearate+0·1% glue +0·01% water glass*	>15 big rust spots
Cement slurry+0·1% ammonium stearate+0·5% glue +0·1% water glass*	12-22 big rust spots
Cement slurry+0·1% ammonium stearate+1% glue +0·15% water glass*	10-13 big rust spots

*Since it was earlier seen that bonding was not good in the case of ammonium stearate-glue system, water glass was added with the idea of improving the bonding.

TABLE 14 — COMPARISON OF THE PERFORMANCE OF THE NEW COATING DEVELOPED WITH SOME COMMONLY KNOWN PROTECTIVE SCHEMES

Test	Protective scheme	Performance
300 hr in salt fog chamber	New scheme	Good
	4 coats of bituminous paint	Good, but paint softens and is easily removed
	2 coats of red lead+ 2 coats of red oxide	Good
Immersion in 10% sodium hydroxide soln for 5 days	New scheme	Good
	4 coats of bituminous paint	Good, but bulging all over the surface
	2 coats of red lead+ 2 coats of red oxide	Paint dissolves
Immersion in 10% ammonium sulphate soln for 15 days	New scheme	Good
	4 coats of bituminous paint	Good
	2 coats of red lead+ 2 coats of red oxide	Good
Immersion in hot water (70-90°C) for 7 days	New scheme	Good

TABLE 15 — COMPARISON OF THE PERFORMANCE OF THE NEW COATING WITH THAT OF PORTLAND CEMENT SLURRY COATING

Protective coating	Protection against corrosion (300 hr in salt fog chamber)	Abrasion resistance and adhesion
Portland cement slurry coating	Uniform and heavy rusting of steel base	Easily removed when scrapped with a sharp tool
New protective coating	Steel base unaffected	Hard to remove by brushing or scrapping

The performance of a new protective coating based on cement slurry and inhibitor mentioned earlier is compared with those of some commonly known protective schemes for steel structures in Table 14. This new protective scheme can be applied by brushing or spraying. It is seen from Table 14 that the new protective coating is resistant to chloride, alkaline medium, sulphate and high temperature. The performance of the new protective scheme is compared with that of cement slurry coating in Table 15.

The new coating is based entirely on indigenously available raw materials and it does not incorporate any toxic constituents. Any removal of coating can be rectified easily by touching up the exposed portion. Apart from reinforcement, a few more fields of application for the new coating are: corrugated steel sheets, pipelines, temporary bridges made of steel structures, electric poles, etc. The new coating is covered by Indian Patent Application No. 112440 dated 28 September 1967.

Summary

The results of an investigation into the cause of corrosion of reinforced brickwork (RB) and reinforced concrete construction (RCC) are presented. The alkalinity of cement and concrete, and the chloride and sulphate contents in building materials were studied. The alkalinity decreases from a maximum of $0\cdot15N$ for aqueous extracts of cement for a water-cement ratio of $0\cdot7:1$ to $0\cdot04N$ at higher water-cement ratios. The highest alkalinity obtained from extracts of cement-sand mortar or 1:2:4 concrete is $0\cdot06N$. While sand and stone aggregate are normally free from chloride, significant amounts of chloride (maximum $0\cdot05\%$) can be extracted from cement and natural water can contain up to $0\cdot95\%$ chloride. More of sulphate is extracted from cement than chloride. The soluble chloride and sulphate react with cement and their concentrations are brought down to one-fifth and one-sixtieth respectively.

The rate of permeation of water and diffusion of salt through lime concrete, which is used in RB constructions, is very much larger than that for 1:2:4 concrete, which is itself quite appreciable. The higher water permeation and diffusion of salts through lime concrete can explain the higher incidence of reinforcement corrosion in RB constructions.

The shift of potential from positive to negative direction in the case of steel embedded in $0\cdot1N$ NaCl solution is attributed to the breakdown of the passivity of steel in the alkaline environment provided by concrete. An elegant method of studying the breakdown of passivity of steel in alkaline solutions by the introduction of chlorides and sulphates has been developed. The method, which consists in passing a chosen value of anodic current through the steel-solution interface and observing the potential-time characteristics, has been very useful in quickly determining the tolerable limits of chloride and sulphate in a very large number of solutions. Below the tolerable limit, the potential goes to oxygen evolution potential and remains at this value. Above the tolerable limit, the potential goes to oxygen evolution, but falls back in less than 5 min. With this method it has been observed that extracts of fresh cement are corrosive, but extracts of set cements are non-corrosive. This is explained by the fall in the concentration of soluble chloride and sulphate by reaction with cement. It is shown by this method that the alkalinity produced in cement concrete by the liberation of free lime and free alkali during setting can tolerate only 130 ppm of chloride or 2750 ppm of sulphate. Beyond 100 ppm of chloride and 550 ppm of sulphate, $0\cdot04N$ alkaline solution becomes corrosive.

The total amounts of soluble chloride and sulphate in raw mix of 1:2:4 concrete as well as in set concrete were calculated for the minimum, average and maximum amounts of soluble chloride and sulphate present in fresh building materials. The amounts of available chloride and sulphate in capillary water in set cement concrete were also calculated. Assuming an average porosity for water permeation of 10%, it is shown that only when the minimum and average amounts are present, the alkalinity obtained in concrete (1:2:4) is adequate to keep the capillary water inhibitive. Even when the average amounts of chloride and sulphate are present initially, gradual diffusion of the salts into the concrete in industrial and marine atmospheres can change the conditions around the reinforcement from inhibitive to corrosive.

An inhibitive mixture, which ensures that the environment around reinforcement can remain inhibitive, even at the maximum concentrations of chloride and sulphate that can be obtained in practice, has been developed. Waterproof coatings to concrete which can prevent diffusion of chloride and sulphate have also been studied.

Acknowledgement

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Corrosion of Metals in Buildings

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FAULTY design has been reported to be a major factor leading to the corrosion of steel and iron in buildings[1]. For example, the corrosion of steel window frames is most intense on the horizontal members where moisture collects outside either as rain or dew and inside as condensed steam. The danger that water will be trapped in the joints can be greatly reduced by careful use of putty to seal the cracks and to bevel the edges of the steel sections so as to facilitate drainage. Yet more often than not this simple step is omitted.

Two rolled steel joists carrying the floor of a refrigeration chamber were placed so closely together that they could not be reached for painting. Heavy condensation of moisture led to dangerous rusting on the inner surfaces of the joists. The steel work had to be replaced after a premature life of 20 years.

Heavy steel girders which carried the roof of a concert hall below and supported an esplanade above (Fig. 1) became dangerously corroded when, because of war damage, cracks developed in the concrete on the top and water penetrated into the enclosed roof space. The entry of water above the ends was made easier by the fact that a gutter ran immediately above the ends of the joints. Another source of weakness was a hollow cast iron baluster built-in-section. Water entered this at the joints and seeped through porous brickwork to the concrete below. The remedy adopted after the corroded steel work was replaced was to redesign the roof in such a way that the surface water was carried clear; special attention was at the same time paid to the waterproofing of concrete.

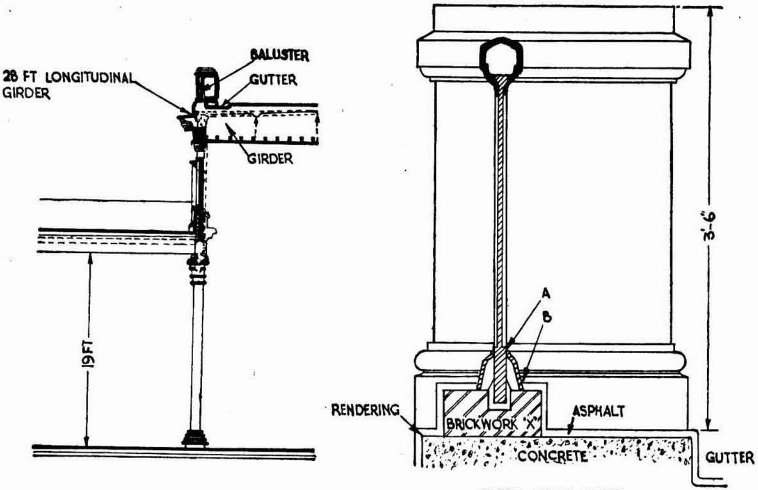
Another factor responsible for serious corrosion in buildings is inadequate initial protection of steel or subsequent neglect in maintenance. A simple example of this is a corroded girder bracket, which had been screwed to the eaves without painting the surface next to the wood and the contact with wood tended to corrode bare steel.

Some lavatory cisterns made from 16 gauge sheet steel and finished with vitreous enamel had failed prematurely due to corrosion. Investigations showed that the real cause of corrosion was the damage to the coating during transport, loose fittings, such as brackets and unions, having been poorly packed and carried loose inside cisterns causing mechanical damage to vitreous enamel.

Failure was observed under the eaves in a house clad with sheet steel, as the eaves were sheltered and evaporation of condensed moisture was retarded. It was necessary to use a special water-resistant finishing paint for this surface in addition to the usual three coats.

Within six months, steel cupboards placed inside domestic kitchens had developed rust both on the flat surfaces and on the edges and bends where the coating was liable to abrasion. The conditions inside the kitchens where besides steam, flue gases from a boiler and from a gas stove were emitted into the air were thus unsuitable for use of steel cabinets.

In majority of instances, reinforcing steel if embedded in good quality dense concrete with



DETAIL OF BALUSTERS

Fig. 1 — Roof design: Section through hall

adequate thickness of cover remains unattacked for long periods. There have been, however, a number of cases where corrosion of reinforcement has been comparatively rapid and progressive. Normally steel in concrete gets protection because of the alkaline nature of concrete. But if concrete is carbonated, this immunity is lost. Steel in aerated concrete is, therefore, more vulnerable to corrosion than steel in dense concrete, both because of easier access to moisture and rapid carbonation of free lime in the concrete.

In a normal reinforced concrete structure, the tensile stress in the steel is comparatively low. But in prestressed concrete the steel is permanently held in tension with a stress equivalent to about 65% of its breaking load. It is necessary, therefore, in prestressed concrete to consider the possibility of stress corrosion. A further difference is that the steel for prestressing is usually thin wire and consequently any corrosion of the wire affects a greater proportion of the working cross-sectional area. The use of steam curing in conjunction with calcium chloride to accelerate the hardening of concrete has been reported to promote corrosion of prestressed concrete.

HISTORY AND DEVELOPMENT OF REINFORCED CONCRETE CONSTRUCTIONS

The use of reinforcement in concrete was first made in 1850, twenty-five years after the invention of portland cement[2]. Lambot in 1850 constructed a small boat of reinforced concrete and in 1855 exhibited the same at the Paris exhibition. In 1861, Monier who was a Parisian gardener, constructed tubs and tanks of concrete surrounding a framework or skeleton of steel wire. In the same year, Coignet proposed constructions of reinforced beams, arches, pipes, etc. In 1867, Monier took out patents on reinforcement consisting of two sets of parallel bars, one set at right angles to and lying upon the other, thus forming a mesh of bars. The work of Monier was followed up by two German engineers, Waysis and Bauschinger, who proved that reinforced concrete is a valuable means of construction and thereby promoted its extensive use in Germany. In France, many systems of reinforcement were invented from time to time, including that of Hennebique, who introduced stirrups and bent-up bars. In England, Hyah built beams of concrete reinforced with metal in various ways in 1877. In between 1884 and 1892, the buildings of the California Academy of Science and the Museum of Leland Stanford Junior University were constructed using reinforced concrete and they were found to withstand the shocks of the earthquake of 1906 remarkably well. Reinforced cement concrete appears to have been first introduced in India in the beginning of this century.

Reinforced concrete has become one of the most widely used materials of construction, because of the ease with which concrete and steel can be fabricated into structural members, utilizing the desirable attributes of both the materials. Concrete is good in compression but weak in tension. Steel is good in tension. If steel bars are embedded properly in the cross-sections of flexural members, the steel can be made to carry the tension, while concrete resists compression as well as protects steel against corrosion. Moreover, because of the adhesion between concrete and steel and because of mechanical interlock between deformations on steel bars and surrounding concrete, the concrete supplies the grip or anchorage required to enable the steel to resist tensile forces. Steel is also used to reinforce concrete compressively in columns and near the compression face of some beams, to resist the diagonal tension that accompanies shear in beams, to serve as ties and spiral reinforcement in columns and to minimize or distribute cracks which tend to form because of temperature changes or shrinkage in concrete.

Concrete to be used in reinforced constructions should be of high quality with less permeability and high mechanical strength. The cement used may be ordinary portland cement or any other suitable cement (high alumina, fly ash, blast furnace slag, supersulphate, etc.). The fine aggregate may be river sand, pit sand or thoroughly cleaned sea sand. The coarse aggregate may be crushed stone (hard sandstone, trap, granite, hard limestone, gravel, cinder, blast furnace slag or hard broken brick). Potable water has been used in making concrete.

In modern practice, steel is used in many a form in combination with cement concrete. Conventional concrete reinforcement is usually in the form of bars (plain, twisted or deformed), wire mesh (welded or woven) or expanded metal fabric (various patented systems). But concrete is also used jointly with a structural steel or cast iron column or steel pipe filled with concrete to form a composite column. Structural shapes, beams and girders are often encased in concrete that serves no structural function beyond that of fire-proofing and protecting the steel members. Steel and concrete are combined in other ways as in the steel-plate-trough type of construction (Truscon-Floretyle-American system) sometimes used for floor and bridge slabs. Peculiar shapes like deck reinforcements are also sometimes employed.

Types of Construction[3,4]

The conventional solid-slab beam and girder floor consists of a series of parallel beams supported at their extremities by girders which in turn frame into concrete columns placed at more or less regular intervals over the entire floor area (Fig. 2). This framework is covered by a one-way reinforced concrete slab. As the slabs, beams and girders are designed as T-beams, advantage is taken of continuity (Fig. 3a, b); one-way solid reinforced concrete slabs are also used over the steel beams of a steel frame building. In precast constructions, the precast slabs may be supported direct upon walls or placed between rolled steel joists. The sides are grooved to form joggles. Cement mortar is used to grout the joints.

Expanded metal (rib mesh) floor consists of three types. Jack-arch type (Fig. 4) consists of rolled steel joists of the required section placed on the

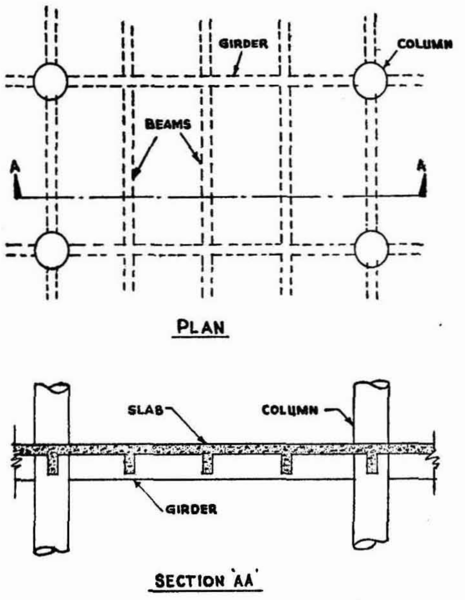


Fig. 2 — Conventional solid-slab beam and girder floor design

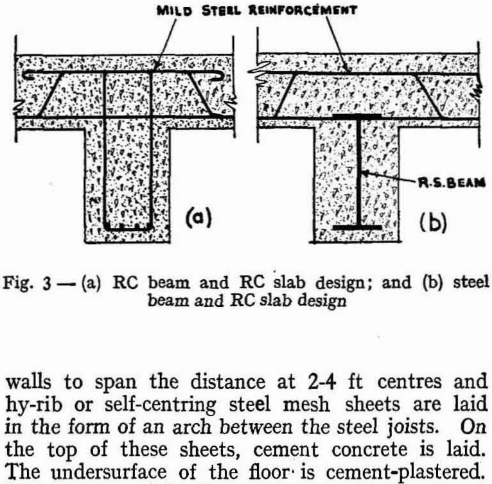


Fig. 3 — (a) RC beam and RC slab design; and (b) steel beam and RC slab design

walls to span the distance at 2-4 ft centres and hy-rib or self-centring steel mesh sheets are laid in the form of an arch between the steel joists. On the top of these sheets, cement concrete is laid. The undersurface of the floor is cement-plastered. Flat floor type (Fig. 5) consists of steel joists placed on the walls at the required spacing and the hy-rib or self-centring steel mesh sheets laid horizontally between the steel joists. The steel sheets rest directly on the top of the lower flanges of the joists. RCC T-ribbed floor (Fig. 6) consists of rolled steel joists replaced by RCC T-ribs and a concrete slab is cast monolithically with these RCC ribs. A flat ceiling of hy-rib or self-centring mesh and cement plaster is provided at the bottom of the T-ribs with the aid of wooden fillet pieces in order to give a better appearance. Floor with RSJ supports (Fig. 7) consists of joists placed on the walls at 2-4 ft centres and on the top of these joists, an RCC slab of the required thickness is cast. The mesh sheets are generally used in the concrete slab. The bottom reinforcement provided in the slab is continuous, which takes up the bottom tension and the top reinforcement consists of strips and takes up top tension. Floor with RSJ encased in concrete (Fig. 8) consists of joists encased in cement concrete and the mesh sheet placed just a little below the top flanges of the steel joists.

Ribbed floor consists of a series of small closely spaced reinforced concrete T-beams framing into beams or girders, which in turn frame into the supporting columns. The T-beams are formed by placing a row of fillers in what would otherwise be a solid slab. The fillers may be special steel pans, hollow clay tile or light-weight concrete tile blocks or ordinary wood forms (Fig. 9a, b). Since the strength of concrete in tension is low and is commonly neglected in design, the elimination of

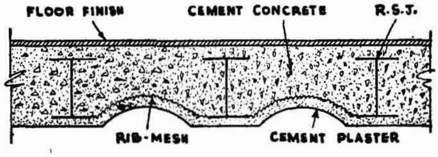


Fig. 4 — Jack-arch floor design

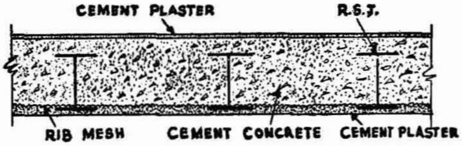


Fig. 5 — Flat floor design

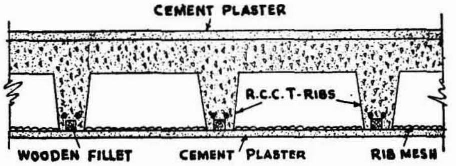


Fig. 6 — RCC T-ribbed floor design

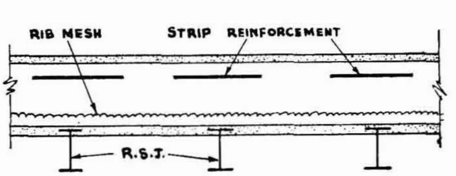


Fig. 7 — Floor design with RSJ supports

much of the tension in a slab by the use of fillers results in a saving of weight with little alteration in the structural characteristics of the slab. Ribbed floors are economical for buildings where live loads are fairly small and the spans comparatively long.

In steel deck floors with concrete slab (Fig. 10), light gauge steel deck is covered with a concrete slab for floors. The deck acts as formwork for the fresh concrete and reinforcement for the hardened slab. This type of construction is fast and the expensive framework is eliminated. Sometimes corrugated sheets are used as decks. Transverse wires are welded to the ridges of the sheet to provide bond between the sheet and the slab and to serve as shrinkage and temperature reinforcement. Ordinary deformed bars are used for negative reinforcement over the supports.

In filler-joist floors (Fig. 11), mild steel joists are spaced at 1·5-3 ft centres and the spaces between the joists are filled with cement concrete. The floor is then finished in one of the usual ways. Sometimes old rails are also used as reinforcement and thus the cost of the reinforcement is reduced. Timber finishing is also done using 2 × 2 in. teakwood bearers at 15 in. c/c and teakwood boarding across the bearers.

Reinforced brickwork constructions — The design of reinforced brickwork structures is based on the same general principles of design and analysis as are adopted for the design of similar RCC structures. Best bricks are selected for the work. But strength of bricks is so variable that we cannot have a universal rule as in concrete work. The concrete for reinforced brickwork consists of well-graded fine aggregate. The bricks should not contain harmful amount of soluble salts.

Fig. 12 shows the construction details of Brebner type RCBW roofs (National Buildings Organization, New Delhi, private communication). The reinforcements are located between bricks and are approximately 12 in. apart. The reinforcement rods vary from $\frac{1}{4}$ to $\frac{3}{4}$ in. diam., depending upon the span length. The reinforcement rods are usually given a covering of cement-sand mortar or concrete (0·75-1·5 in. thick). Over the brickwork, cement concrete of 1 : 2 : 4 or 1 : 1·5 : 3 ratio is applied to the extent of 2 in. A distance of 2 in. is usually specified between brick to brick and this space is also filled up with cement concrete. Over cement concrete, 3-4·5 in. thick lime terracing made of lime : surkhi : brick ballast in the ratio 1·5 : 1·5 : 5 or 1 : 1 : 3 is laid (for taking up compression). Mud-phuska (puddled clay mixed with chopped straw) varying in thickness (0·75-4 in.) is provided over the lime concrete to serve as thermal insulator. Mud-phuska is sometimes followed by a single layer of brick tiles laid in cement mortar. Lastly a waterproof coat of bitumen is given. In the underside of the terrace, a 0·5 in. layer of lime plaster (lime : surkhi : sand of 1 : 2 : 2 ratio) is applied. The lime terracing and the subsequent mud-phuska are given a slope of 1/40th to 1/60th so as to facilitate easy drainage. In RCCB constructions (Fig. 13) hollow tiles are used in place of brickwork. Another type of construction uses a combination of cement concrete and brickwork without much extra cost.

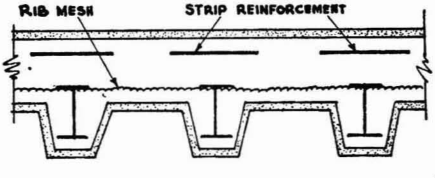


Fig. 8 — Floor design with RSJ encased in concrete

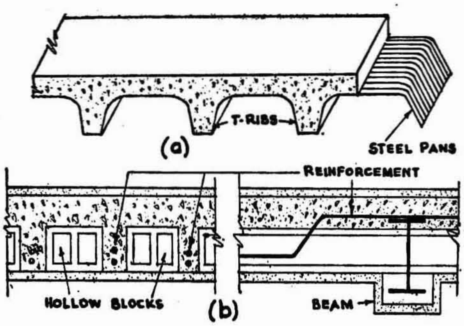


Fig. 9 — Ribbed floor with (a) steel tiles and (b) hollow clay blocks

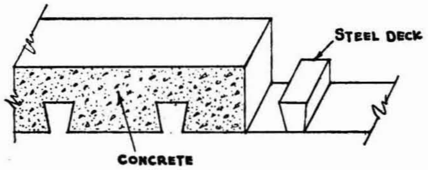


Fig. 10 — Steel-deck floor with concrete slab

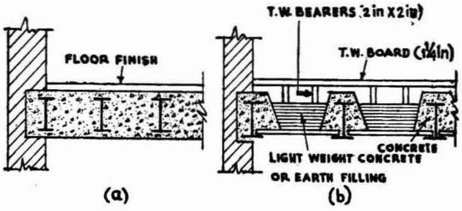


Fig. 11 — Filler-joist floor

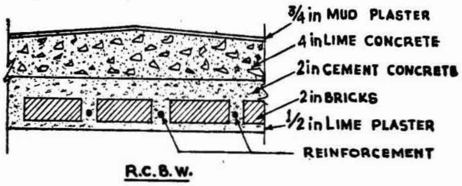


Fig. 12 — Brebner type RCBW roofs

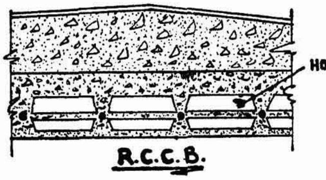


Fig. 13 — RCCB construction

Concrete (1·5 in. thick) on top takes the compression. The ribs are designed as T-beams. Bricks may be laid in 1:6 cement mortar. Rods are well surrounded by mortar or concrete. Similarly, there should be sufficient cover at the bottom. The rods in no place should touch bricks.

REINFORCEMENT CORROSION AND ITS PREVENTION

The corrosion of iron and steel in contact with concrete is of much greater importance than all other cases of corrosion of metals. This is not merely because the amount of metal involved is greater, but also because metal which is corroded is load bearing and the durability of the structure may depend upon the control of this corrosion. It is reported[5] that the world consumption of concrete during 1963 was of the order of 3000 million tons and the steel required as reinforcements in so much concrete can be expected to amount to several million tons. It was estimated[6] that in the United Kingdom, 330,000 tons of steel were used as reinforcements in concrete in 1957. A substantial proportion of the 6 million tons of steel produced in this country must also be going towards reinforcement in concrete.

Any corrosion of the reinforcement results in the formation of rust which occupies a volume about 2·2 times that of the iron from which it is formed[7]. This corrosion product has literally no place to go, so that it produces large internal pressures[8] (as high as 1 ton per sq in.[6]) in the structure and cracks the concrete. After a crack has been formed in this way, the steel corrodes even more rapidly, leading ultimately to complete failure of the structural member involved. Furthermore, the resulting brown rust stain on the structure is most unsightly. According to Halstead[6], a brown stain first appears on the reinforced concrete surface. At this stage, there is no evidence of cracking. Later, a fine crack appears coincident to the steel underneath the surface. The crack widens with time and eventually the concrete over the reinforcement is spalled off and the reinforcing steel is exposed to the atmosphere. The deterioration does not always follow this pattern exactly. Often the brown stain is absent. However, the result is always the same. By the time the crack appears, the steel has corroded. When the crack has widened to the point where spalling of concrete is imminent, the probability is that the reinforcing steel has been appreciably reduced in section with the associated loss of structural strength.

From the age of the structure and the original diameter of the reinforcing steel in the case of two south coast bridges in Africa, the corrosion rate was deduced as 0·006-0·010 in./year[9]. This rate is considered severe when compared to the atmospheric corrosion rate of bare steel in marine locations.

Reinforcement Corrosion in Different Countries

A survey[10] made in 1916 of numerous concrete structures along the seaboard of the United States revealed that the majority of the reinforced concrete structures subjected to sea water action showed evidence of deterioration or failure due to the corrosion of the embedded reinforcement above the water line. Palumbo[11] has reported a case where a reinforced concrete tank was fissured by the expansion of reinforcement rusting because of seepage of water through the concrete. Loos[12] has cited a typical case of the complete destruction of reinforced concrete structures in Java harbour which were constructed according to the best practice of the time.

In 1929, a large series of tests were commenced in United Kingdom by the Institution of Civil Engineers on the resistance of reinforced concrete to attack by sea water[13]. It was found that the reinforced concrete piles suffered less from the direct attack of concrete and deterioration arose primarily from corrosion of the reinforcement with consequent cracking and spalling of the concrete.

The major portions of the San Mateo Hayward bridge in California Division of Highways consist of a reinforced concrete two-lane causeway, seven miles in length. The structure was built in 1928-29. Starting about 7 years after initial construction, an unexpected maintenance problem developed because of the excessive spalling of the concrete. Investigations[14] disclosed that the spalling of the concrete was the result of accelerated corrosion of the reinforcing steel. Despite initial preventive measures like painting, the afflicted areas of corrosion increased progressively and were to be found in the concrete pilings, caps, diaphragms, main deck beams and occasionally in the underside of the deck.

Failures of sea water structures have been observed in Norway and these have been found to arise from rusting of reinforcement[15]. Schikor[16] has mentioned that steel conduits in moist concrete were completely corroded in a few years. Vollmer[17] found mild corrosion to occur in normal concrete after one year.

The reinforced concrete columns in a new school building in the Middle East[1] developed extensive cracks within a year of construction and in places steel had corroded to a depth of about $\frac{1}{16}$ in. The rusting of the steel that had caused the cracking was found to be due to the high chloride content of the concrete surround. The chlorides were introduced mainly with the mixing water and probably also with the sand which was collected from the seashore.

Within 25 years of the construction of a reinforced concrete band stand at a seaside resort (UK), the concrete became badly cracked due to the corrosion of steel reinforcement[1].

Shermer[18] reported typical corrosion of reinforcing steel in a lumber drying kiln where the concrete was exposed to warm moist air.

In the Union of South Africa, it has been observed[9] that reinforced concrete structures exposed to marine atmospheres deteriorate in a relatively short period. The conditions are particularly severe on the south coast of Natal. Minor sections such as balusters and hand rails of bridges have sometimes disintegrated in 4-5 years. It has been observed that in marine atmospheres, deterioration due to corrosion has occurred even when the workmanship, design and general construction practice are apparently sound.

The majority of reinforced concrete structures on the American coasts subject to sea water action have shown evidence of deterioration due to corrosion[10]. The major cause of deterioration both in Maine and Florida has been rusting of the reinforcement causing cracking of the concrete[19]. In 1959, an investigation[20] by the California Division of Highways showed that 20 out of 66 reinforced concrete bridges in an arid desert had evidence of corrosion of reinforcement within 10 years of service. The investigation indicated high concentration of chlorides (41000 ppm) in soils to be responsible for this.

A 200 ft diam. reinforced concrete tank handling magnesium hydroxide slurry was seriously deteriorated[21]. Reinforcing rods of ¾ in. diam. were completely rusted in some areas. Some 1·25 in. diam. rods had less than 0·25 in. of section in some areas. A concrete fence-post showed severe spalling due to corrosion of the reinforcement in UK[22].

Factors Influencing Reinforcement Corrosion

A concrete is composed of a coarse aggregate forming the bulk of the mix, a fine aggregate filling the voids between cement and water to bond the whole together. The sand or fine aggregate and the cement may together be regarded as a mortar in which coarse aggregate is set. One of the most important factors which vitiate against effective protection of steel appears to be the human factor, namely bad practice or poor workmanship.

Workmanship — Even when the same building materials are used, a dense portland cement concrete may remain almost immune from attack, whereas one of poor quality suffers disintegration and failure within the course of a few years. The resistance of concrete to attack is much diminished by the presence of unfilled patches, segregated layers, etc. The greatest care has to be exercised in each one of the following operations: (i) design of the concrete mixture, (ii) selection and processing of the constituents, (iii) placement of reinforcing steel to assure adequate and uniform depth of concrete cover, (iv) rigid supervision and controls in the production, transportation, placement and compaction of freshly mixed concrete, and (v) curing of concrete.

Permeability — The permeability which measures the capacity to transmit fluids is of the utmost importance, since the passivating action of concrete on steel due to its high *p*H can be maintained only by its physical protection and durability. Hayes and coworkers[23] found that curing a specimen at 79% relative humidity increased its permeability seventy-fold as compared to properly cured specimens. The permeability depends on numerous factors such as water-cement ratio, aggregate size and grading, richness of mix, method of compaction, curing, etc. Furthermore, the permeability of a given concrete section probably is not a constant quantity but varies with time and history.

On examining the history of an affected reinforced concrete bridge (San Mateo Hayward bridge) in California Division of Highways, it was found[14] that high water-cement ratio used at the time of construction had resulted in a relatively permeable concrete. In tests on the permeation of salts, it was found that the chloride concentration in concrete adjacent to corroded reinforcement was as great as 0·86% of the dry weight of concrete.

Cover thickness — A minimum concrete cover of 2 in. has been recommended in UK[6]. Even then the reinforcement may be attacked. For the protection of reinforcement, it is probably more important that the concrete should be sufficiently plastic to envelop the steel in a continuous film, even if this involves using more cement than would be necessary merely to provide a given strength. Concrete cover is a factor to be considered with permeability because 2 in. of permeable concrete will yield less protection to steel than 0·25 in. of impermeable concrete[8].

Steel surface — If the surface of steel is contaminated with salt, it is likely to corrode in concrete sooner than clean steel. Actively rusting steel or millscale covered steel is likely to have less corrosion resistance than steel which has been cleaned. All the non-alloy steels used as reinforcement for concrete have low corrosion resistance.

External agencies — Inhibition of corrosion of steel embedded in concrete occurs until the concrete is penetrated by materials which lower the *p*H locally and cause micro and macro differential *p*H cells to operate on the steel surface. Penetration of concrete by salt, water and air takes place at more permeable areas and through cracks. Atmospheric environment in which a reinforced concrete structure is located is, therefore, highly significant.

Materials — Berthier[24] considered the question of reinforcement in portland and slag cement concrete and concluded that there was little difference between the two kinds of concrete as far as providing protection was concerned. The environment provided by the slag cement concrete may be less alkaline, but is probably more stable. Erculisse[25] examined reinforcing steel after it had been embedded in concrete made from coarse slag aggregate, fine slag aggregate and slag cement for 10 years and found no surface attack. He concluded that slag cements are suitable for making reinforced concrete. A comprehensive investigation by the German Reinforced Concrete Committee[26,27] established that the behaviour of reinforcing steel in portland blast furnace cement concrete was no different from its behaviour in normal portland cement concrete. There is a body of evidence to confirm the general conclusion that there is no objection to the use of slag aggregates for reinforced concrete provided the slag meets the requirements of various specifications designed to limit the permissible sulphur content. Similarly, foamed slag, which is used as a light-weight concrete, is satisfactory for reinforced concrete if its sulphur content is not excessive. Clinker aggregates, on the other hand, are not satisfactory. They appear to cause corrosion of reinforcement and are not permitted to be used for making reinforced concrete in UK[28]. The corrosiveness of clinker and boiler slag is probably due partly to the sulphur content and partly to electrolytic effects. Ash from pulverized fuel-stoked boilers does not appear to be objectionable when used in concrete and it is even claimed[29] that its incorporation in a concrete mix should reduce corrosion of reinforcement by lowering the permeability of concrete. The durabilities of concrete prepared from various types of cements are given in Table 1 (ref. 30).

Calcium chloride is widely used for accelerating the setting and hardening of portland cement concrete and an addition of 2% on the weight of the cement is customary. Muller[31] concluded that up to 3·8% of pure calcium chloride could be used in concrete without causing corrosion of reinforcement, provided the concrete remains undamaged. Robson[32] stated that calcium chloride is not objectionable in dense mixes. Another report[6] notes that steel in porous concrete was attacked when 2% calcium chloride was used in the mix. Hamada[33] reached the conclusion that corrosion of reinforcing steel occurs in concrete containing calcium chloride even if the concrete is kept dry. Vollmer[17] noted that reinforcing steel showed slight rust deposits whenever calcium chloride was used. Sokolovich[34] has noted that calcium chloride causes slight corrosion. Pukhalskii[35], in an extensive series of tests, observed the results of adding up to 10% calcium chloride or up to 5% hydrochloric acid to concrete. Corrosion of reinforcing bars was found at early stages and increased as the calcium chloride and hydrochloric acid additions were raised above 2% and 1% respectively. Steel bars were corroded even when they had 25-70 mm concrete cover.

TABLE 1 — RESISTANCE OF VARIOUS TYPES OF CEMENTS

Cement	Inherent resistance to chemical attack		
	Sulphates	Weak acid	Pure water
Ordinary portland cement	Low	Low	Low
Rapid hardening cement	do	do	do
Low heat cement	Medium	do	do
Sulphate resisting cement	High	do	do
Blast furnace slag cement	Medium to high	Medium to high	Medium
Supersulphated cement	Very high	Very high	Low
High alumina cement	do	High	High
Pozzolanic cements	High	Medium	Medium

Electrolytic corrosion — Reinforced concrete may also suffer attack from one source which is without influence on plain concrete, namely electrolysis caused by stray electric currents. In buildings or structures of any type where, through electrical leakages, the reinforcement serves as an earth conveying current, corrosion occurs in damp positions owing to direct electrolytic action. Railways appear to be the chief offenders in this respect. But a case is reported[36] where stray currents in an electroplating plant caused damage. The general opinion appears to be that alternating current does not cause serious corrosion and that the trouble is unusually caused by stray direct currents.

Mechanism of Reinforcement Corrosion

Lewis and Copenhagen[9] set up various types of cells to find out which one is likely to play the more important part in reinforcement corrosion.

Cell 1

Steel | Neutral salt solution of low concentration ‖ Neutral salt solution of high concentration | Steel

Cell 1 corresponds to steel embedded in a section of concrete both permeable and impermeable in parts where local concentrations of sodium chloride could build up. The following theoretical considerations are important: (1) The Nernst equation, $E = E_0 + (RT/NF) \log_e C$, holds for the potential of a metal with respect to its own ions in solution only. (2) In the concentration type cell, the half cell with the lower metal/metal ion concentration becomes the anode. (3) Although variation in salt concentration of a neutral solution can affect the local electrode potential owing to changes in the oxygen solubility of the solution, this effect becomes marked at relatively high salt concentrations only. Thus, it is not expected that type 1 cell will provide any significant potential and that any current produced is, therefore, likely to be small. Figs. 14 and 15 illustrate the results obtained using the experimental half cells of this cell. The single electrode potentials of half cells are recorded in Fig. 14 and the emf's of the cell formed when each half cell is coupled to a 1% sodium chloride half cell in Fig. 15. From Figs. 14 and 15 it is clear that the steady or equilibrium potential reached some 24 hr after immersion does not change significantly with salt concentration and that potential differences are much smaller than those actually observed in corroding reinforced concrete.

Cell 2

Steel | Carbonated cement (low pH) ‖ Alkaline cement (high pH) | Steel

Cell 2 corresponds to the case of steel embedded in concrete having both permeable and impermeable regions where carbon dioxide penetration at one point could lower the pH by carbonation. Although, theoretically, a potential difference of

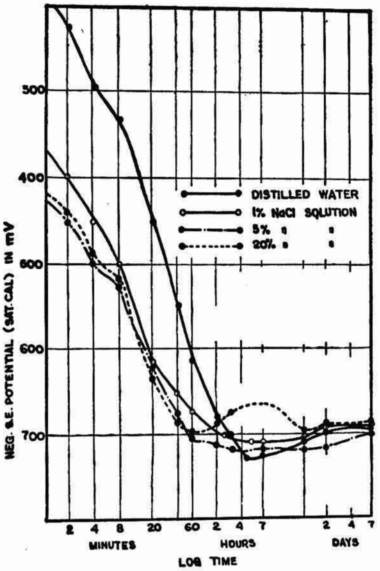


Fig. 14 — Time-potential curves for steel in various neutral salt solutions

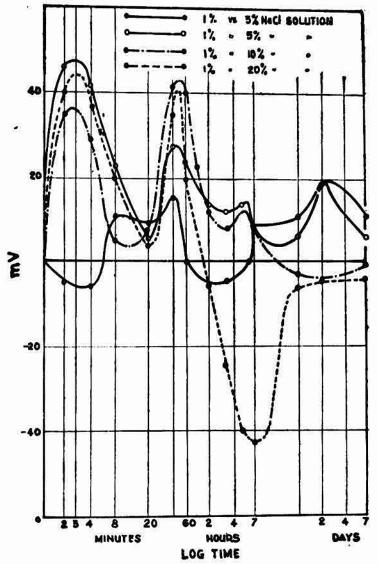


Fig. 15 — Differences in single electrode potentials between steel in 1% NaCl solution and steel in solutions in higher salt concentrations

0·25-0·45 V could be anticipated from this cell, the conductivity of both electrolytes is small. In fact, very feeble currents were obtained. In addition, the carbonate ion present in the anolyte could, under these conditions, act as an anodic inhibitor, thus further restricting the current.

Cell 3

Steel	Carbonated cement + salt	Alkaline cement + salt	Steel

Cell 3 is an extension of cell 2, allowing for salt penetration. The steady potential of steel in aqueous cement extract (uncarbonated) is about −0·260 V (saturated calomel). The steady potential of the other half cell is −0·700 V and, therefore, the expected potential difference of a cell of this nature is −0·440 V. Moreover, the presence of salt reduces the resistivity of the electrolyte and currents of over 3 $\mu a/cm^2$ may flow.

Cell 4

Steel (anode)	Permeable concrete Low *p*H High Cl^-	Less permeable concrete High *p*H Low Cl^-	Steel (cathode)

Cell 4 is the general case, of which cell 3 is the extreme condition and is considered to be the particular cell which is responsible for the corrosion of reinforcing steel in marine atmospheres. This would also have a high potential difference and would lead to significant corrosion.

Cell 5

Steel	High oxygen availability	Low oxygen availability	Steel

The above differential aeration cell will oppose the *p*H cell potential. But being of a smaller emf, it will be of less importance and cell 4 will dominate.

Finley[8], commenting on the corrosion cell action as explained by Lewis and Copenhagen, proposed the following mechanism based on differential aeration cells. The differential oxygen concentration cell can arise in two ways: (1) there is a difference in the solubility of oxygen in solutions of different dissolved salt content, and (2) there is greater availability of oxygen in those areas of lower water saturation due to a higher permeability to air. He proposed the following mechanism: In the spray and splash zone of concrete structures, sea water is deposited on the surface of the concrete in varying amounts. The amount deposited depends on such physical factors as relative location of the structural members, wave action, prevailing wind direction and wind force. The water either adheres to the surface, runs off or evaporates, depending on the relative humidity, exposure to sun and wind, inclination of the surface to the horizontal and height above the water line. The concrete absorbs water. The water that evaporates leaves salts behind. Their distribution on the surface of the concrete is unequal. The salts diffuse by capillary action into the pore space of the concrete. The dissolved salt content of the pore space water increases in proportion to the amount of salt that was deposited on the surface and will not be the same throughout a member. Increasing salt content decreases the solubility of oxygen. Air diffuses into the pores and oxygen dissolves in the capillary water, the oxygen concentration being greater where the salt content and water saturation are lower. Galvanic cells arise with anodic areas of

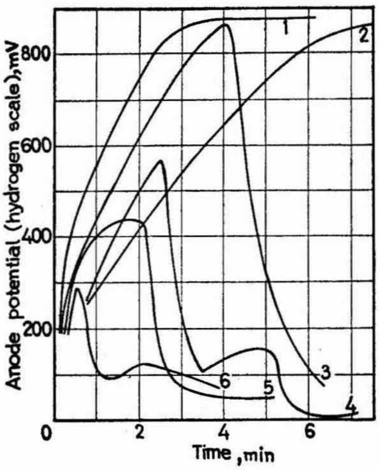


Fig. 16 — Anodic polarization of steel in saturated $Ca(OH)_2$ solution at constant current density [Current density, 10 μa/cm^2; NaCl conc. in solution: (1) nil; (2) 0·0165%; (3) 0·0495%; (4) 0·066%; (5) 0·099%; and (6) 0·132%]

high salt-low oxygen and cathodic areas of low salt-high oxygen. Thus, the differential aeration cells in concrete are much the same as those found on pipelines alternately passing through dry and marshy areas. According to Antonino[37], differential oxygen concentration is possibly one of the prevalent causes of corrosion. Water filling the cracks becomes saturated in time with calcium hydroxide provided by the concrete and this serves as the cell electrolyte. With chlorides present, corrosion is intensified.

Stratful[14] has explained the corrosion of reinforcing steel as being due to unequal concentrations of sea salts, which produce corrosion cells of the differential concentration type. He has explained the mechanism of failure of San Mateo Hayward bridge to be a combination of one or more of the following suggested possibilities: (1) continuous accumulation of sea salts by condensation and evaporation of sea water; (2) the current density of the existing corrosion cells causing additional concentration of certain ions, such as chlorides about the anodic area; or (3) by an increase in the moisture content.

Electrochemical Measurements

Potential measurements in calcium hydroxide solutions and cement extracts had shown that noble potentials are obtained at *p*H 12 and the steel is passive[38]. The same result was observed in mild steel embedded in mortar. However, it was also observed[9] that when sodium chloride was dissolved in these solutions, the potential became more positive for some time and then became negative or started falling to a more negative value from the beginning. In such cases, rust spots were also observed on the steel specimens, indicating breakdown of passivity.

Current density curves obtained by Baumel and Engell[39] showed that steel in 0·1*N* sodium hydroxide and in saturated calcium hydroxide solution is passive and thus corrosion resistant. Steel electrodes embedded in sand saturated with calcium hydroxide solution showed the same behaviour.

To determine the critical concentration of sodium chloride in saturated calcium hydroxide required to initiate corrosion of immersed steel, polarization curves were drawn by Lewis[40], using both the techniques of Hancock and Mayne[41] and Baumel[42]. The results are presented in Figs. 16 and 17; it is seen that the critical concentration is approximately 0·05% of sodium chloride concentration by weight. However, when sodium chloride is added to cement, the formation of insoluble complexes, such as $3CaO.Al_2O_3.CaCl_2.10H_2O$ will have the effect of reducing the effective concentration of chloride ion. The extent to which the effective chloride concentration is reduced by the formation of complexes

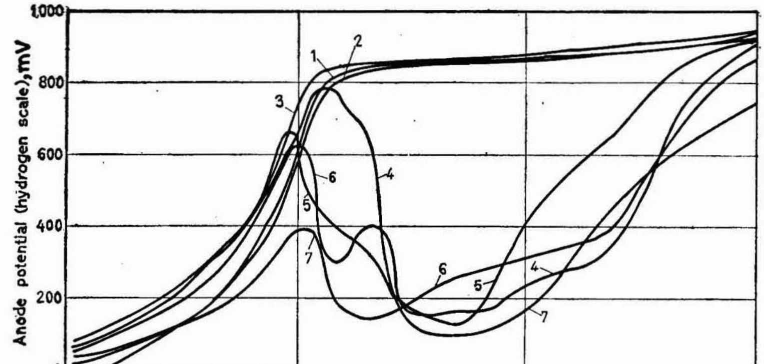


Fig. 17 — Anodic polarization of steel in saturated $Ca(OH)_2$ soln [NaCl conc. in soln: (1) nil; (2) 0·02%; (3) 0·03%; (4) 0·04%; (5) 0·06%; (6) 0·08%; and (7) 0·10%]

TABLE 2 — EXTENT OF REDUCTION OF CHLORIDE ION CONCENTRATION IN DIFFERENT CEMENT SAMPLES ON ADDING SODIUM CHLORIDE

Sample No.	Total NaCl (on cement) %	Available NaCl (on cement) %	Available NaCl (total) %
1	5·87	4·92	83·8
2	5·11	4·10	80·2
3	4·22	3·52	83·4
4	3·51	2·68	76·4
5	2·81	2·10	74·7
6	2·00	1·32	66·0
7	1·00	0·55	55·0
8	0·54	0·26	48·2
9	0·04	0·01	25·0

was determined by analysis of available and total chloride on hydrated cement samples to which sodium chloride had been added before hydration. The results are given in Table 2. The available chloride is taken to be the chloride which is soluble in water at 20°C during an extraction lasting 2 hr, while total chloride was determined by extraction with nitric acid. Polarization curves, obtained by the method of Hancock and Mayne, for steel in water extracts of hydrated cement samples (given in Table 2) showed that the critical addition of sodium chloride to cement before the corrosion of steel can start is approximately 0·54%, which corresponds to an effective concentration of soluble or available sodium chloride of 0·26%.

Tests have been carried out on submerged mild steel in calcium hydroxide solution and cement mortar extracts in the presence and absence of salts and under varying degrees of aeration with a view to determining the *p*H required for inhibiting the corrosion of reinforcing steel in concrete[43]. The quantity of rust was determined by the weight loss method. In calcium hydroxide solutions, in the absence of salts, corrosion decreases with increase in *p*H until inhibition sets in. In the presence of salts, no gradual effect was observed, but inhibition could be obtained at high *p*H. The *p*H level required for inhibition increases with the degree of aeration, both in the presence and absence of salts. At the point of complete inhibition, aeration ceases to have any effect.

Reinforced mortar specimens made with Mediterranean Sea water were tested by Shalon and Raphael[44]. The *p*H necessary for the inhibition under different storage conditions and the *p*H values of mortars and cement pastes made with sea water and fresh water were measured. For calcium hydroxide solutions, *p*H values of >12 gave complete inhibition. For solutions containing calcium hydroxide+salts, higher *p*H values were required. Reinforcing bars were corroded in all sea water-mixed specimens stored in moist air. They showed little or no corrosion when continuously stored in sea water or tap water.

In the presence of a large admixture of calcium chloride, the combined effect of water and oxygen that penetrate the concrete intensifies the action of corrosive elements on the surface of steel. The maximum amount of calcium chloride that may be added without risk of corrosion was found to be 2% by weight of cement.

Kaesche and Baumel[45] have evolved a current-voltage method for testing the aggressiveness of admixtures of unknown composition. In this method, the anodic current-voltage curve of a reinforcement bar is constantly investigated. A reinforcement bar is severely corroded if it proves to have one of the steep current-voltage curves, shown in Fig. 18, for the case of concrete containing calcium chloride. It will be corroded very little if the current-voltage curve shows flatness, characteristic of the passive state. For this purpose, a so-called concrete electrode is prepared as shown in Fig. 19.

Kaesche and Baumel[45] studied the effect of additives on the corrosion behaviour of steel in concrete by current-voltage curves by the method described by Kaesche as well as current-time curves at a constant electrode potential. An investigation of 12 commercial additives by these methods showed that only additives containing chloride when added to the concrete in fairly large quantities, have an adverse effect on the corrosion behaviour of the reinforcement. Satisfactory and lasting corrosion protection of steel in concrete or mortar is ensured only if the whole surface of the steel is coated with

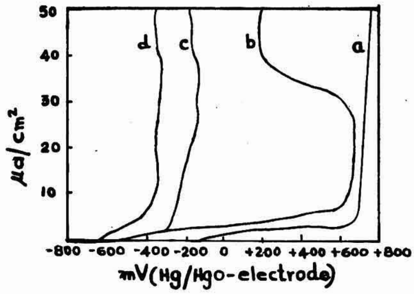


Fig. 18 — Current-voltage curves for concrete containing different amounts of $CaCl_2$ [$CaCl_2$ content: (a) nil; (b) 1%; (c) 2%; and (d) 4%]

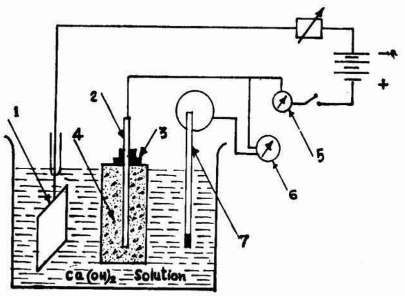


Fig. 19 — Concrete electrode [(1) Pt electrode; (2) steel bar; (3) insulating varnish; (4) concrete; (5) microammeter; (6) valve microvoltmeter; and (7) reference electrode]

cement gel. The actual effect of the gel is that it functions as a largely invariable water reservoir which constantly provides an alkaline film of liquid on the steel surface and maintains the steel in a passive condition. An adequate cover of dense concrete or mortar is necessary to protect the cement gel in the immediate vicinity of the steel from destruction by chemical influences of external origin.

Stray direct currents through concrete cause corrosion of reinforcing rods and lead to cracking of the concrete[46]. Corrosion starts when the critical anodic potential reaches the value at which the passive film on the reinforcing rods is disrupted. Direct current also causes mechanical cracks as a result of the pressure exerted by the corrosion product and gas evolution. Rapid formation of cracks occurs at current densities $\geqslant 37$ ma/sq dm, and the presence of salts accelerates this process. Tests made on the effect of a 25 V dc potential applied to iron rods cast in concrete cylinders showed that (1) increasing the thickness of concrete cover reduced the rate of electrolytic corrosion but did not effectively eliminate it so as to prevent cracking; (2) admixtures were not effective; and (3) the asphalt membrane waterproofing covering provided an effective means of eliminating electrolytic corrosion. Alternating current of industrial frequency flowing through reinforced concrete structures does not significantly corrode reinforcements, provided chlorides are absent.

The anodic corrosion of steel in reinforced concrete under the influence of external electric currents was investigated by Maraghini and Ginnari[47] based on constant current density measurements. Slag cement and pozzolana cement also were studied along with portland cement. For slag cement, the corrosion is fairly slight up to 600 coulombs/cm^2. Beyond this limit, the cement cracks, corrosion proceeds more rapidly and the current output increases considerably. The addition of increasing amounts of chloride to the slag cement results in a gradual decrease of the number of coulombs required to produce failure. Pozzolana cements behave similarly, but failure occurs at about 200 coulombs/cm^2. No such limit has been observed for portland cement.

A typical field investigation — An investigation involving surface potential and electrical resistance measurements conducted by Stratful[14] on San Mateo Hayward bridge gave the following results: (i) On the basis of salt content in a concrete cell, a potential difference of 0·45 V could exist. (ii) The electrical resistivity of concrete at 0% deterioration or where uncracked appears to be in excess of 60,000 Ω cm. Resistivity measurements made on the concrete in anodic areas gave, in general, a good indication of the degree of deterioration in these areas. The resistivity of concrete decreases as the deterioration increases. (iii) If corrosion cell ratio* is greater than $0{\cdot}5\times10^{-5}$, the concrete is likely to crack at the anodic area.

PREVENTIVE MEASURES

Broadly all methods of prevention can be classified as follows[48]: (i) methods based on modification of design and procedure; (ii) methods based on modification of environment; (iii) methods based on modification of metal; and (iv) methods based on protective coatings.

The prevention of corrosion in buildings has been approached from each one of these different ways. The importance of satisfactory design was emphasized earlier. The need to avoid contact between dissimilar metals which are widely separated on the potential scale was stressed with the help of examples. Crevices afford lodgement of moisture and corrosive deposits from the atmosphere. Corrosion of reinforcements has been prevented by giving an adequate thickness of concrete cover. This may also be considered as a solution based on proper design. Addition of inhibiting agents to cement slurries and ensuring that sufficient alkalinity is generated when concrete becomes wet as well as the avoidance of chloride contamination of building materials may be considered as examples of modification of environment. Bitumen paints and epoxy coatings have been suggested for the protection of reinforcements. Here, a protective coating is employed. Though alloy steels are too expensive to be considered as substitutes for steel in building construction, stainless steel is made use of occasionally in the reinforcement of thin walling slabs where the depth of cover is insufficient to conform to the recommendation for normal reinforcement[49]. However, the choice finally lies in only one or two remedies which are most economical, practically feasible and as free from drawbacks as possible.

Corrosion of reinforcing steel is due primarily to the penetration of moisture, chlorides and air to the steel surface. Preventive methods must either prevent the penetration of these materials or render the reinforcement passive to their action. The most desirable solution to the problem is to keep out the salt and to assure that it stays out. Since concrete itself is a powerful inhibitor of corrosion, any procedure purporting to prevent corrosion must reinforce the protection already provided and attempt to minimize the effects of extraneous attacking agents.

Design Aspects and Quality of Concrete

The first precaution is to avoid the more aggressive locations where possible. If advantage could be gained by utilizing the natural shelter provided by some topographical features, this factor should merit serious consideration by surveyors and planners[9]. The design should exclude potentially dangerous features which allow water collected on the structure to flow over concrete surfaces instead of being thrown clear. Rain water from pools collected on the structure will leach out hydroxides from the concrete and accelerate carbonation. Most authorities agree that provision of adequate concrete cover to steel is essential. A 3 in. minimum has been mentioned[50]. But a 2 in. minimum is generally considered essential[9].

$$\text{*Corrosion cell ratio} = \frac{\text{Max. surface potential difference between anodes and cathodes}}{\text{Av. specific electrical resistance in the anodic area}}$$

Great care should be taken that the materials used in construction are free from salt[9]. Water both for mixing and for aggregate washing and sand or aggregate used should be tested for salt. If salt is present, the aggregate should be well washed. Salt-contaminated water should be rejected as unsuitable for construction work. Any additives for use in the mix should be carefully examined and should be avoided if they contain chloride. The use of shrinkage aggregates and porous aggregates must be avoided. Ideally, the steel used should be clean and free from rust or millscale when the concrete is placed. Since this is generally regarded as an impractical recommendation and since rusty steel is reputed to result in a greater bond strength than clean steel, the only precaution which need be taken in the matter of steel is that before placing the concrete, the steel should be protected from marine atmospheric corrosion. If this is not possible, the steel should be well washed with fresh water when in position in the shutters to remove any salt deposits from its surface. The resistance of the concrete under marine conditions may be increased by preferring slag-containing cement or sulphate-resisting cement in place of ordinary portland cement.

Concrete Permeability

Many materials are recommended, usually under proprietary names for incorporating in mortars and concretes with the object of making the concrete less permeable to water[51]. Particular mention may be made of materials like sodium and potassium silicates, diatomaceous silica, sodium, potassium and ammonium soaps, vegetable oils and resins. They are added either to the water or direct to a concrete mix or sometimes premixed with cement. The stearates are probably the materials used in proprietary compositions. These stearates are water repellent and reduce the capillary forces by which water is drawn through a mortar or concrete.

Surface Coatings on Concrete

There are also a large variety of materials which are applied to the surface of concrete either to waterproof the surface or to render it immune to attack by chemical agencies. The surface treatments may be classified[52] as (i) treatment with aqueous solution of sodium silicate, drying oils or mineral oils in volatile thinner; (ii) thin surface coatings of bituminous, coal tar and chlorinated rubber paints, resin lacquers and wax coatings; (iii) thicker surface coatings of bitumen or bitumen rubber emulsions, emulsion pastes with fillers; (iv) linings of asphalt mastic, rubber mastic, plastics, clay tile and other inert materials. Thinner surface coatings have limited resistance to abrasion and limited life. Thicker lining is given if long life is needed. A protective coating made up of phenols from oil-shale acids 50%, formalin 30% and water 20% applied in double coat to concrete is reported to reduce water penetration[53]. Coatings of tar and pitch have often been applied to protect reinforced concrete from deterioration in sea water, but their effective life is too short and in some places they only hide the damage that is taking place[54]. The impregnation of concrete piles with hot bitumen under reduced pressure has been used extensively by the Los Angels harbour board with effective results[54]. Epoxy resin coating has all the advantages of an ideal surface coating on concrete, but is costly[55]. A 10 or 12 mil coating of a thin film of plastic paint over the entire structure is reported to be very effective[56]. Industrial vinyl copolymer resin paints were found to provide satisfactory waterproof coatings for concrete[57]. It is important that the coatings be applied as soon as possible after the curing of concrete. Once salt is present in the concrete, the effectiveness of the coating may be reduced[9].

Coatings to the Reinforcement

Various passivating treatments for reinforcing steel have been suggested, such as pickling in hydrochloric acid followed by treatment with phosphoric acid[58] and treatment with a hydrolysable silicate or hydrated silica[59]. Simple preliminary coating of steel with a dense mortar is recommended to counteract acid fumes[60]. The application of coatings of cement-containing paints with waterproofing admixtures[61] or of slurries of lime and cement with casein or bone-glue[62,63] is also recommended as an anti-corrosive measure. Bitumen paints are said to protect reinforcement from calcium chloride in concrete, but some paints of this type prevent the formation of bond between the steel and concrete[33]. Combinations of inhibiting agents in cement slurries are also proposed, notably sodium dichromate[64], sodium carbonate, sodium phosphate[65] and sodium benzoate[32,66]. A thin layer of portland cement containing 2% K_2CrO_4 is coated on steel bars before their use in concrete[64]. In some cases, the reinforcing rods are treated with a mixture of mineral material (concrete, quartz and sand or slaked lime) which contains $BaCrO_4$ in amounts $<1\%$ (ref. 67). The sulphate present in the concrete reacts with $BaCrO_4$ and soluble chromate is formed which passivates the iron. A method is described[68] for protecting ordinary reinforcements by phosphatization; phosphatization was conducted in a 3% solution of Fe and Mn phosphates at 96-98°C for 40-50 min. Then the surface was passivated with an 80% solution of $K_2Cr_2O_7$ at 80-90°C for 18-20 min and further coated with a lacquer at 18-25°C for 2-3 min. In another method[69], steel bars were immersed in a solution of 10-80 kg bitumen with high drop point and 90-20 kg synthetic resin in approximately 300 g hydrocarbon solvent containing 10-50% of a finely dispersed alkaline earth hydroxide. The resulting coating was elastic and highly resistant. But all these methods do not appear to have made much headway for the reason that if a coating is introduced between steel and concrete, the bonding strength of steel to concrete is affected.

Inhibition in Concrete[9]

The steel surface carrying a film of γ-Fe_2O_3 can act as an efficient cathode. If a non-conductive film of other oxides or hydroxides as produced by cathodic inhibitors, e.g. calcium carbonate, aluminium oxide, magnesium hydroxide, etc., could be deposited, the cathode efficiency would be markedly reduced. Unfortunately, adding soluble aluminium, zinc or magnesium compounds would result in their hydroxides being precipitated by the alkalinity in the concrete throughout the mass and not selectively where they are required. Anodic inhibitors such as alkalies, phosphates and chromates are effective only when present in sufficiently high concentrations and are otherwise dangerous, because of localized corrosion. When high concentrations are used, the properties of concrete may be affected adversely. Further, the solubility of inhibitor should be such that while sufficient inhibitor is in solution, it is not so great as to allow leaching out to take place. From these considerations, it is clear that until more fundamental work is done, the use of conventional inhibitors cannot be recommended.

Cathodic Protection

Berthier[24] recommended cathodic protection of reinforcing steel and Whalley[70] quoted a case of the successful use of magnesium anodes to prevent further corrosion of reinforcement exposed to brackish water.

To ensure continuous economic protection, the cathodic metallic circuit should be electrically continuous, if interference effects and anodic spots are to be avoided[9]. But the operations involved are generally too extensive to be practicable. Sacrificial anodes with their limited forcing potentials are unlikely to be satisfactory. Due to extreme variability in the electrical resistivity of concrete under different conditions (100 Ω cm to 100,000 Ω cm), impressed current systems would require extensive anode arrangements if reasonable current spread is to be obtained. Furthermore, the acids produced at the anode could cause chemical attack on concrete and the alkali produced at the steel surface may also affect concrete. From the above considerations it follows that cathodic protection generally could not be applied economically and is not a practical solution.

Electrolytic Corrosion

To decrease electrolytic corrosion of reinforced concrete, it is recommended to avoid direct electrical grounding through concrete and to use underground protective coating on concrete. The use of high quality concrete does not prevent corrosion[71]. Increased cover thickness can only reduce the rate of attack. The only remedy seems to be the insulation of steel or concrete. In this connection, asphalt and steatite have been suggested[72].

Corrosion of Non-ferrous Metals in Buildings[73]

A country house with lead valley gutters was re-roofed with wood shingles. It was subsequently reported that lead had become useless. It was typical of new, cedarwood shingles that they contain acids which are only slowly washed out by rain. Such acids intensify attack which would in any case occur slowly owing to vegetable growth on the roof. The lead had suffered severe channelling and perforation. This could have been avoided if a thick good coating of bituminous compound extending well underneath the edge of the roof covering had been given to the lead. Lead is subject to attack by lime and by portland cement mortar and concrete. Hence, a heavy coating of bitumen is called for when it is coming into contact with lime, mortar or concrete.

Like lead, zinc is likely to corrode in both alkaline and acidic conditions. So, it may also be attacked when in contact with or embedded in lime, portland cement mortar or concrete and also acid plasters when damp. It is, therefore, desirable to give at least a coating on zinc when embedded in plasters and mortars. Contact with brickwork is generally harmful. Some salt in the brick and alkalies in the mortar may promote corrosion. Zinc coated steel is a traditional material for conveying and storing industrial and domestic fresh water. Zinc suffers a pitting type of attack in hot water. The effluent from wash basins and domestic sinks is not aggressive to zinc. The use of cleaners like bleaching powder with high chloride content can, however, lead to failure of zinc pipes. Galvanized wire fencings sometimes present depressingly rusty appearance. Much of this could be avoided provided a really effective zinc coating was given. In one length of fencing in a rural area, it was noted after 4 years that every alternate strand of wire was rusting, evidently because one coating was much thinner than the other. Zinc soakers (Fig. 20) were used on a roof abutting against a parapet wall. Corrosion had occurred on the zinc face in contact with the brickwork. There was no damp-proof course below the coping of the parapet wall, so that the brickwork would often be in a damp condition. Zinc soakers should at least have been protected by a good quality bitumen coating where it was in contact with the brickwork, since it was to be expected that salts in the brickwork and alkalies in the mortar would promote corrosion of zinc.

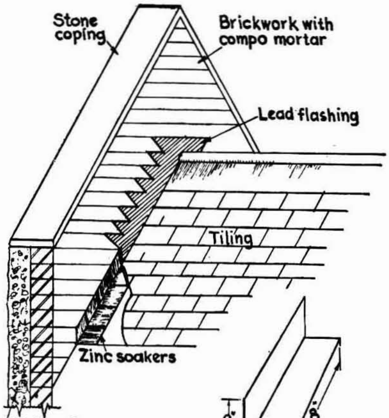


Fig. 20 — Zinc soakers at junction of roof with abutment wall

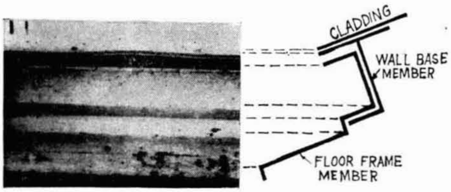


Fig. 21 — Perimeter frame of aluminium bungalow showing early stages of corrosion

Copper is used as roofing and as tubing and also for architectural metal work, such as window frames, hand rails, etc., and in electrical wiring. Generally, copper is not affected by contact with other building materials, such as wood, cement, concrete and plaster. But acid cements, plasters and also coke breeze can give rise to corrosion in wet or damp conditions. Copper should not be buried in these materials, unless adequately protected. While ordinary concrete has no deleterious effect on copper, foamed concretes which contain foaming agents of nitrogenous nature can lead to stress corrosion cracking.

Unlike the other metals discussed, aluminium has been used on a large scale for structural purposes. The major structural use of aluminium alloys has been for temporary and permanent bungalows erected after the last war. The construction of prime perimeter frame of one type of bungalow showing earlier stages of corrosion is given in Fig. 21. Extensive laminar corrosion of these structural units has been the main feature of these bungalows, occurring mainly in the exposed faces and in the crevices produced by adjacent surfaces. Severe loss of strength and prominent bulging of the exterior wall-cladding have resulted. Complete dismantling of three identical bungalows selected in various conditions from three widely separated sites in England has shown that corrosion also exists on contact surfaces not visible on cursory examination. The alloy was used in the as-extruded, solution heat-treated and fully heat-treated conditions. Recent work has shown that the destructive effect of layer corrosion can be reduced by extended ageing and metal spraying. However, the lesson to be learnt from this experience of prefabricated bungalows is that materials for building are meant to last for a long time and newer products should have a reasonable test period before receiving widespread application. Condensation troubles have also been experienced in aluminium bungalows. Water gets into the underside of a metal sheet roof in several ways. Water vapour from the inside of the structure is one obvious source. Where the roof is not insulated, drips from the condensed moisture produced affect the ceiling below. Adequate ventilation or isolation of the roof cavity is the simplest answer here. Aluminium reacts vigorously with wet concrete mix and is attacked by the alkalinity in the concrete. Therefore, it should not come

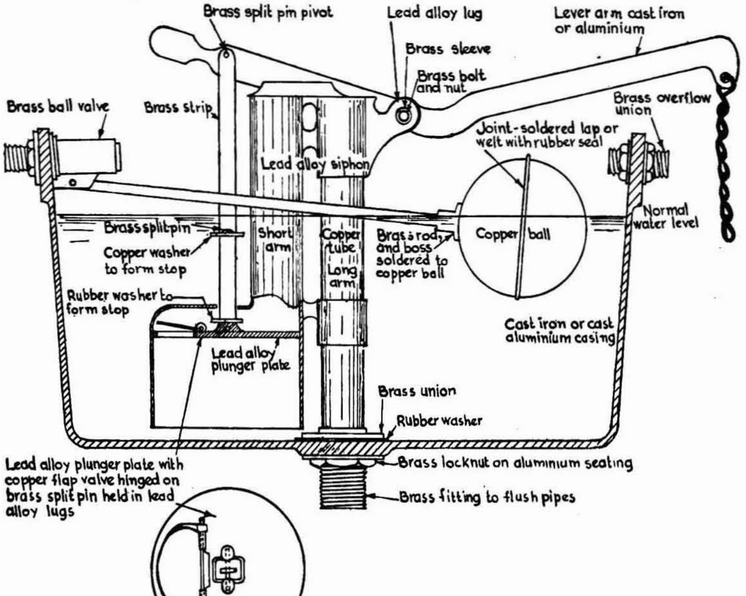


Fig. 22 — Variety of metals in flushing cistern

into direct contact with concrete. Aluminium rain water pipes have also been used to cope with bathroom and kitchen wastes. Cases of rapid failure have been reported which indicate that this is a dangerous practice. Several instances of corrosion of cast aluminium alloy flushing cisterns were reported when they were introduced. A variety of metals and alloys had been used for the components of the cistern as indicated in the diagram (Fig. 22). Undoubtedly, this has played a part in accelerating the corrosion of aluminium.

Work done in the CECRI[74-80] on reinforcement corrosion and its prevention will be discussed in the subsequent paper.

Summary

The common types of reinforced concrete constructions are described and the instances of reinforcement corrosion reported from different countries are reviewed. It is shown that the factors responsible for reinforcement corrosion may be grouped as (i) faulty workmanship; (ii) permeability to water, water vapour and salts; (iii) inadequate cover thickness; (iv) rusting of reinforcement before embedding in concrete; (v) corrosiveness of some building materials; (vi) calcium chloride added to accelerate setting and hardening of concrete; and (vii) stray electric currents. It is indicated that two types of cells are likely to operate with significant current flow in RCC structures, viz. (i) cell set up by differences in salt concentration and *p*H, and (ii) cell set up by differential aeration. For electrochemical measurements, both potential-time curves at constant current density and current-voltage have been successfully employed. For the examination of structures *in situ*, surface potential and electrical resistance measurements have been successfully used in identifying the RCC bridges which are likely to suffer early corrosion.

Several examples of corrosion arising from improper design are cited and the importance of correct design in preventing corrosion stressed. The various types of materials which are used to make concrete waterproof and the various types of waterproofing coatings on concrete which are currently employed are mentioned. The treatments given to steel reinforcement to prevent corrosion and the attempts made to introduce corrosion inhibitors in concrete are discussed. Instances of corrosion of non-ferrous metal parts used in the construction of buildings because of inadequate appreciation of their behaviour in contact with building materials are cited.

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REVIEWS

INVARIANT MEANS ON TOPOLOGICAL GROUPS AND THEIR APPLICATIONS by Frederick P. Greenleaf (Van Nostrand-Reinhold Co., New York), 1969. Pp. x+113. Price $ 3.00

The book deals with the notion of Banach invariant means. Section 1 gives an account of invariant means and measures on discrete groups and semigroups including Von Neumann's basic work on the subject. Section 2 deals with invariant means on locally compact groups, including Day's notions of weak and strong invariance. Section 3 deals with many interesting applications and describes methods to solve contemporary problems in a form accessible to the non-experts as well. At the end of the book, the following three appendices are appended: (1) Non-uniqueness of invariant means; (2) The Ryll-Nardzewski fixed point theorem; and (3) The equivalence of various types of invariant means.

The book is based on the lectures which the author had given at Berkeley in the Spring and Fall quarters of 1966. It is meant both for graduate students and for working mathematicians. It gives recent developments in an illuminating manner and draws attention to some unsolved problems. The bibliography is complete and even refers to some of the unpublished work.

In the opinion of the reviewer, the book is an extremely useful addition to the library.

P. L. BHATNAGAR

LECTURES ON INTEGRAL EQUATIONS by Harold Widom (Van Nostrand-Reinhold Co., New York), 1969. Pp. vi+124. Price $ 3.50

Besides the introduction which sets out the main topic of the book, namely the investigation of the integral equation

$$\int_x K(x, y)f(y)dy = \lambda f(x)+g(x)$$

it contains the following 6 chapters: (I) Banach spaces; (II) Completely continuous operators; (III) The Fredholm theory; (IV) Hilbert space theory; (V) Applications to ordinary differential equations; and (VI) Singular integral operators.

The above list of chapters is enough to suggest that the entire treatment of the book is modern and it is meant for graduate students as well as research workers in the subject. Chapters I, II and IV present the general theory of operators on Banach and Hilbert spaces and provide the necessary background knowledge for the actual theme of the book. Chapter III outlines the original approach of Fredholm, Chapter V gives the applications of the theory of self-adjoint integral operators to certain ordinary differential equations, and Chapter VI discusses some special type of singular integral equations using the technique of Fourier transforms.

In the opinion of the reviewer, the book under review is a very welcome addition to the very few books so far written on this subject.

P. L. BHATNAGAR

LECTURE SERIES IN DIFFERENTIAL EQUATIONS: Vol. 1, edited by A. K. Aziz (Van Nostrand-Reinhold Co., New York), 1969. Pp. viii+199. Price $ 4.50

The book consists of the following four parts, each consisting of two or three lectures given by various authors during the year 1965-66 under the title "Lecture Series in Differential Equations" sponsored jointly by the Air Force Office of Scientific Research, the Joint Graduate Consortium (American, Catholic, George Washington, Georgetown and Howard Universities) and the University of Maryland:

Part I: Control Theory — (1) Linear control processes and mathematical programmes by George B. Dantzig; (2) The Lurie problem on nonlinear controls by Solomon Lefschetz; (3) The Bang-Bang principle by Lawrence Markus.

Part II: Dynamical Systems — (1) The Mantner phenomenon and geometric flow theory by Louis Auslander; (2) Dynamical properties of transformation groups by Walter Gottschalk.

Part III: Boundary Value Problems — (1) Periodic solutions of nonlinear equations of evolution in infinite dimensional spaces by Felix E. Browder; (2) Some linear and nonlinear boundary value problems for evolution problem by J. L. Lions; (3) Intersection theoretic principles for the existence of critical points and fixed points by J. T. Schwartz.

Part IV: Differential Operators — (1) Estimates for singular integral operators by A. P. Calderon; (2) Formally normal ordinary differential operators by E. A. Coddington; (3) On pseudo-differential operators by L. Nirenberg.

The book is written for the use of graduate students as well as the research workers in the field of control theory and differential equations. The treatment is rigorous, lucid and clear, but presupposes a good knowledge of matrix theory, the usual theory of ordinary differential equations, modern mathematical analysis and modern algebra.

The reviewer hopes very much that the Indian universities will be able to adopt the point of view presented in this book in revising their syllabi on ordinary differential equations in order to make these courses more purposeful and modern.

P. L. BHATNAGAR

GUIDE BOOK ON NUCLEAR TECHNIQUES IN HYDROLOGY, prepared by the Working Group on Nuclear Techniques in Hydrology of the International Hydrological Decade (International Atomic Energy Agency, Vienna), 1968. Pp. 214. Price US $ 5.50

The scope of this guide book is to give the hydrologist a general picture of the several nuclear techniques applicable to hydrological problems. The hydrologist is thereby enabled to choose the best suited technique for a given hydrological problem.

The book is divided into five sections. The first section is of an introductory nature, while the remaining four sections deal with the hydrological problems associated respectively with the atmosphere, surface water, sub-surface water and interrelationships among these. In the introductory section, the basic concepts about radioactivity, the interaction of radiation with matter and the methods for measurement of radiation are given in a popular style with a view to giving a background knowledge of the subject to the engineers and thus to make them understand the physics of operation of the various techniques.

The available techniques are classified under three groups: (a) environmental isotopes, (b) artificial isotope tracers, and (c) application of sealed radioactive sources. The first group of isotopes occur in the atmosphere, in rocks and minerals of the earth, in surface waters and ground waters. By a direct measurement of the natural isotopic content the analysis could be conducted. An outline of the techniques using environmental isotopes is given in each section. In the case of artificial isotopes, the radiations in which the hydrologist is likely to be concerned produce ionization in gases through which the radiation passes. Radioactive tracers are useful in the application of the well-known tracer techniques in which dyes and salts are used as tracers for water.

The various subjects in the book are dealt with in a clear and comprehensible manner. The diction is good and the subheadings are concise and clear. The availability of an authoritative and practical guide book of this kind is bound to give satisfactory solutions for various problems faced in such diverse fields as soil physics, irrigation, corrosion, oil drilling, etc. The book would be a valuable asset as a technical guide to hydrologists and should find a place in the shelves of the libraries of the various research institutions concerned with hydrological and allied problems.

BIGUANIDES — THE CHEMISTRY OF BIGUANIDES by F. Kurzer & E. D. Pitchfork (Springer-Verlag, Berlin), 1968. Pp. 375-472. Price £ 8.50

In view of the versatile reactivity and utility of biguanide and its derivatives and the closely related S-triazines as analytical and complexing agents, drugs, dyeing agents, textile chemicals, insecticides and in photography and several other fields, the chemistry of biguanides has assumed an important place in applied research. Consequently, much of the work is covered under patents and is inaccessible to an average worker. Thus, the present review by Kurzer and Pitchfork is a timely and welcome publication.

The publication is divided into several small convenient sections and covers about 80 pages. With the extensive references included (763) it will serve as a useful reference manual. The structure, methods of synthesis and chemical reactions have been discussed briefly, but the scope of the material presented is of necessity limited by the severe limitations of space imposed on a monograph of this size. Useful physico-chemical data such as dissociation constants and UV spectral data of several compounds have been compiled and an attempt has been made to correlate these. The section on chemical properties is the longest as it is expected to be, but a certain amount of repetition could have been avoided. Reactions of biguanides with orthoesters and amidines have been left out.

On the whole, this small monograph is a critical presentation of the chemistry of biguanides and will serve a useful purpose on the shelf of an organic chemist working in this field.

The printing and get-up are good.

R. H. SAHASRABUDHEY

PHYSICAL PROPERTIES OF STEROID CONJUGATES by S. Bernsteen, J. P. Dusza & J. P. Joseph (Springer-Verlag, Berlin), 1968. Pp. xii+212. Price £ 12.00

The book under review is primarily a compilation of the characterization data of the conjugates obtained from 147 important steroids. The conjugates selected are the sulphates and the glucopyranosidouronic acids and organic and inorganic salts derived from both. Some derivatives of different types have also been included in a limited number of cases. In addition to the usual data, supplementary informations have been supplied, wherever available, on spectral and chromatographic behaviour, countercurrent distribution, electrophoresis and optical rotatory dispersion. The data supplied will be very useful to pharmacists, who use steroid conjugates in many of their formulation, but not so much to organic chemists, who normally use more conventional derivatives for characterization. A formula index of the parent steroids has been provided in the beginning and a reference catalogue at the end. The paper, printing, binding, etc., are excellent and the general get-up is delightful. The authors and the publishers deserve appreciation for bringing out this small compilation.

S. C. BHATTACHARYYA

ORGANIC COMPOUNDS OF LEAD by Hymin Shapiro & F. W. Frey (Interscience Publishers Inc., New York), 1968. Pp. xiii+486. Price $ 18.00

The present book is the second in a series of monographs on " The Chemistry of Organometallic Compounds ", being published under the editorship of Prof. Dietmar Seyferth. A number of excellent reviews on the subject by E. Krause and A. Von Grosse (1937), by R. W. Leeper, L. Summers and H. Gilman (1954), by H. Shapiro (1959), by H. Shapiro and F. W. Frey (1967), by L. C. Willemsens (1964), and by L. C. Willemsens and G. J. M. van der Kerk (1965) already exist in the literature.

The book has been written with a view to providing a comprehensive account of the current state of knowledge about organolead derivatives with reference to their synthesis, properties and structure. Tetraethyllead, the most exploited organolead compound, has also the credit of being the first organometallic compound to be used industrially in 1922 by T. Midgley (Jr) and T. A. Boyd. Although the methyl analogue is beginning to be used in larger quantities since 1960, tetraethyllead remains the most widely employed and successful antiknock agent for internal combustion engines. Although more than 1200 organolead compounds have been synthesized by now, tetraalkyllead derivatives continue to remain the centre pieces in the chemistry of organolead compounds, and justifiably claim the major attention in the present book also.

The first five extremely brief chapters, dealing with the nature of bonding, synthetic methods, physical and chemical properties and physiological and toxological behaviour of organolead compounds, appear to be rather perfunctory. They could have been preferably combined in a single chapter in which the status of organolead chemistry might have been discussed in the light of recent advances in the chemistry of organometallic compounds, particularly of group IV elements.

The next ten chapters deal with various classes of organolead compounds separately. The sixth chapter dealing with tetraalkyl and tetraaryllead derivatives is the longest of all. Later chapters cover the hexaalkyl and hexaaryl, dialkyl and diaryl-, cyclopentadienyl-type and unsaturated organolead compounds. The eleventh to fifteenth chapters deal with a variety of organolead salts, organofunctional lead compounds, heterocyclic and optically active compounds and organolead-organometal compounds in general. All these areas of organolead chemistry have been relatively less investigated and the authors might have profitably indicated some directions in which fruitful investigations could be carried out. The last two chapters, naturally, deal with analysis of organolead compounds and their industrial applications; these are exceptionally well written.

Much of the data in each chapter throughout the book have been summarized in tables which are coupled with adequate references, covering right up to the beginning of 1967. The literature coverage appears to be really comprehensive and would be of great advantage to those who use the book as a source of reference material.

A perusal of the large number of references given in the book clearly indicates that the majority of the investigations in the field of organolead chemistry have arisen out of industrial need. It is in this direction that the book would be a most welcome addition to the existing literature in the field.

A more critical survey could have certainly made the book of greater utility to graduate students and research workers in the field of organometallic chemistry, particularly of non-transition metals. Even so, all those interested in any aspect (academic or industrial) of organolead chemistry would find the book a very convenient source of useful information.

The printing and get-up of the book are excellent. The figures and illustrations are well drawn and beautifully represented. The reviewer could not detect any serious printing mistakes, a few which came to his notice are:

Page 203 (bottom): b.p. of $(CH_2CH)_4Pb$ is 50° at 4 mm

Page 238 (bottom half): b.p.s of $(CH_3)_3PbOSi(CH_3)_3$ and $(C_2H_5)_3Pb.OSi(C_2H_5)_3$ are 65° and 100° at 1 mm

Page 373 (upper half): NaX has been left out from the products in the equation.

R. C. MEHROTRA

PUBLICATIONS RECEIVED

A PROGRAMMED INTRODUCTION TO GAS-LIQUID CHROMATOGRAPHY by J. B. Pattison (Heyden & Sons Ltd, London), 1969. Pp. xv+303. Price $ 4.95

PRINCIPLES OF APPLIED BIOMEDICAL INSTRUMENTATION by L. A. Geddes & L. E. Baker (John Wiley & Sons Inc., New York), 1968. Pp. xiii +479. Price $ 13.50

IMMUNOCHEMISTRY AND THE BIOSYNTHESIS OF ANTIBODIES by Felix Haurowitz (Interscience Publishers Inc., New York), 1968. Pp. xvii+301. Price $ 10.95

BREEDING ASIAN FIELD CROPS by John Milton Poehlman & Dhirendranath Borthakur (Oxford & IBH Publishing Co., Calcutta), 1969. Pp. 385. Price Rs 18.00

MOLECULAR GENETICS edited by H. G. Wittmann & H. Schuster (Springer-Verlag, Berlin), 1968. Pp. viii+341. Price $ 12.00

NOTES & NEWS

Highly stripped heavy ions

A group of scientists at AVCO-Everett Research Laboratory is trying to use an electron cloud to make a source of highly stripped heavy ions for nuclear physics experiments. As in the case of an electron-ring accelerator, the AVCO device uses external magnetic fields to control the motions of an electron cloud and then uses the electrostatic fields generated by these electrons to trap the ions and strip them.

Because of the great interest in making super heavy elements, many experimenters would like to obtain a beam of uranium ions. If the AVCO device works, it can make 10^{11} ions of U^{60+} per second from a source about 40 cm in diameter (compared to useful currents of at best U^{11+} or U^{12+} from the presently available ion sources), which could then be accelerated in a 2 m diam. cyclotron to an energy that would exceed the coulomb barrier of a uranium target. In the expected reaction a gigantic compound nucleus would then fission asymmetrically and produce a new super heavy element.

At first the AVCO group thought of building a complete accelerator, called the heavy ion plasma accelerator (HIPAC), but later the idea seemed promising as a heavy ion source for other accelerators.

In the proposed HIPAC, an electron cloud is contained in a toroidal vacuum chamber by an azimuthally symmetric magnetic field. The electron space charge creates a topologically closed potential well in which ions can be trapped. Because the electron kinetic energy in HIPAC is about 10 keV, the ions will become highly stripped. After sufficient stripping occurs, the magnetic field is lowered, allowing electrons to move towards the wall; this movement reduces the potential well depth. The ions can leave the device through a negatively biased aperture.

The first HIPAC experiments showed containment of 7×10^9 electrons/cm^3 for 1 m sec. At such densities any strong plasma instability could be expected to occur in microseconds. The vacuum is being improved to about 10^{-9} torr and magnetic field duration increased. This experiment should be capable of making highly stripped ions [*Physics Today*, **22** (5) (1969), 58].

New pulse technique for measuring natural point discharge in the atmosphere

A new method of measuring natural point discharges in the atmosphere which dispenses with the need to insert metallic probes into trees has been reported from the Department of Physics, University of Durham. The technique is based on the pulsed nature of the discharge current, caused by space charge quenching of such discharge currents. Though the application of the technique at present involves much labour, its most important application may be in the calibration of less elaborate apparatus.

Observations made over a century on the phenomenon of corona or point discharge of atmospheric electricity at the tips of earthed pointed objects have shown that the average potential gradient near the surface over open ground is about 100 V m^{-1}. The negative bound charge on the earth's surface is neutralized by the atmospheric ion conduction current. Further, during thunderstorms negative charge is carried to the surface of the earth. Since the amounts of positive and negative charges brought to the surface by various processes should according to natural processes very nearly balance, it is felt that the phenomenon of point discharge might be responsible for the major part of the process towards equalization of positive and negative charge transfers to the earth's surface. This makes its measurement a key operation if the charge transfer processes at the surface are to be quantitatively understood.

Till now, estimates of total point discharge to earth over a given area were based on the measurement of current through a metal point mounted on a pole or a tree top. Since a tree has several arrays of pointed edges, the potential distribution could not be assumed to be concentrated at the point of the probe. Further, there was no way to assess the effect of electrodes on the tree.

In the new method, a capacitance electrode is wrapped round one of the top branches of a tree. These electrodes do not have any contact with the tree and the current through them is recorded continuously. Comparative observations made with a field mill and a metal point probe show that with further refinements, the technique will be successful in the measurement of point discharge currents [*Nature, Lond.*, **222** (1969), 654].

Computer-generated 3-D pictures

A rapid and inexpensive two-step process using a computer for making holograms for subsequent 3-D viewing of the subject has been developed at the Bell Telephone Laboratories (BTL), Murray Hill, NJ. This development provides scientists, architects, statisticians and other regular users of a computer with a practical method of converting data stored in a computer's memory into 3-dimensional pictures and graphs. Although the computer production of holograms is not new, the new BTL method is an improvement over the earlier one in that it takes only about 20 sec of the computer time compared to a few hours in the previous process to convert equations, formulae, statistical data, and 3-dimensional (3-D) objects into a form suitable for the making of holograms. Hence this process is rapid enough for making mass production of copies of the hologram. Another advantage of this process is that the holograms can be viewed in ordinary incandescent light and the use of laser light for viewing can be dispensed with. The quality of the holograms made is comparable to that of a standard 3-D hologram.

In the new method, the computer, in the first step, calculates a series of 1 through N adjacent images of the subject stored in its memory. The images, equivalent to ordinary 2-D photographic images of the subject, as seen from the points 1, 2, ... N, are then transferred, one by one, to microfilm by a microfilm plotter connected to the computer. A microfilm frame for each picture is thus obtained.

In the second step, a hologram of the information stored in the microfilm is made within a few minutes by using a simple experimental set-up.

Each view stored on the microfilm is brought in front of the laser in turn. Simultaneously, a mask automatically shifts to expose only the corresponding section of the hologram plate, so that the 2-D views calculated by the computer are stored side by side. The reference beam remains constant for all the views so that all will be reconstructed as a single 3-D subject. Although this composite hologram is made up of a series of small holograms, each derived from a single 2-D view of the subject, the composite reconstructed image from the hologram is 3-dimensional and shows a 360° view of the subject. The viewer can by simply moving his head from side to side in front of the hologram see the object rotating through a full cycle [*Bell Lab. Rec.*, **47** (1969), 126].

Holographic identification of fingerprints

A holographic system that can identify a suspect's fingerprints from 1·5 million filed prints in about 2 min has been devised by the Conductron Corporation of Ann Arbor, Michigan, USA.

The fingerprints are identified holographically using a Fourier transform of filed prints, stored in the form of photographs. The suspect print is photographed and the transparency converted into a hologram. The filed transparencies of prints are compared with the hologram on an optical bench. The reel of filed prints is driven through the expanded and collimated laser beam until a bright spot, signifying the matching of the film print and hologram of the suspect print (i.e. when they are complex conjugates of one another) appears on the screen [*New Scient.*, **42** (644) (1969), 73].

Ultrasonic helium bubble chamber

A new technique for photographing the tracks of nuclear particles traversing a bubble chamber has been evolved at the European Organization for Nuclear Research (CERN) in Geneva. The technique utilizes successfully the ultrasonic excitation of bubble growth along the tracks of ionizing particles, using helium as the operating liquid. All previous attempts to produce bubble tracks ultrasonically have been unsuccessful regardless of the choice of the liquid. The important advantages in using an ultrasonic standing wave system to provide the necessary expansion in a bubble chamber are the replacement of the bulky expansion system by static crystals [thus avoiding (i) the use of complicated moving parts and (ii) the general disturbance of the liquid mass], and the high repetition rate which is potentially possible.

In the conventional bubble chamber, a liquid, such as hydrogen, helium or freon, is held near its boiling point under pressure. Before a charged particle beam is fired into the liquid, the pressure is released by a moving system or a membrane. This causes boiling preferentially along the particle tracks, which are then photographed. The liquid must then be immediately placed under pressure again.

In the ultrasonic bubble chamber (UBC) filled with liquid helium, sound waves of about 1 Mc/s frequency were produced which make the helium sensitive to cause bubble formation whenever a nuclear particle flashes through the chamber. The two significant characteristic features of the UBC are: (i) at sufficiently high amplitudes, bubbles formed in the early half of a cycle will not be completely recompressed in the subsequent half-cycle (since absorption of sonic energy is irreversible) and can then grow to visible size over a number of cycles (50-60 cycles of the sound field corresponding to 600 μsec), and (ii) the bubble density is independent of temperature for a given under-pressure and bubble growth rapidly increases at lower temperatures.

The CERN UBC is essentially a horizontal cryostat composed of 3 cylindrical glass vessels. The inner vessel contains two piezoelectric crystals, the mechanical alignment of which can be adjusted from outside. Ultrasonic standing waves are set up between these crystals by pulsing (at 110 kHz with 700 V rms) them by using a power amplifier. A 25 J flash of about 40 μsec duration in conjunction with a cylindrical reflector and lens system, to produce convergent illumination, is used for photographing the tracks. The apparatus is aligned for operation so that the particle beam passes along the cylindrical axis of the chamber. After the crystals and chamber have been carefully tuned to electrical and acoustic resonance, bubbles are produced in the chamber along the tracks of minimum ionizing pions and protons, and successful operation is achieved in the temperature range 3·4-3·65°K.

The UBC, when perfected, should enable photographs of nuclear events to be taken much more frequently than the one or two times a second usual with most existing instruments with which the debris from nuclear collisions is studied [*Nature, Lond.*, **220** (1968), 1177; *Sci. News*, **95** (1969), 11].

Giant scintillation counter for high energy particles

Hofstadter and his collaborators at Stanford University have explored an overgrown NaI(Tl) crystal as detector of high energy particles (including neutral particles) in the GeV range for the first time. They used NaI(Tl) because it has an excellent scintillation yield, a high density and a correspondingly small radiation length, though for detection of GeV particles the crystals must be huge.

The Stanford detector consists of six separate crystals, whose sizes range from 29 to 33 cm in diam. and 9·5-18 cm in thickness. Each crystal is sealed in a thin aluminium case and viewed radially by four photomultipliers. The six crystals are mounted coaxially to simulate one large crystal

69 cm thick along the beam axis. Energy resolution for an incident electron or gamma ray is 1-2% for the energy range 4-14 GeV. Unlike in some other devices this resolution improves as energy increases (a realistic limit is 0·1%). The NaI(Tl) crystals can also be used to detect strongly interacting particles, but they must have larger diameters and greater lengths. It is claimed that there is virtually no limit to the highest energy detectable by the detector [*Physics Today*, **22** (5) (1969), 58].

Synthesis of theaspirone

A novel synthesis of theaspirone–1-oxa-8-oxo-2,6,10,10-tetramethylspiro [4,5]-6-decene, a volatile fraction of black tea–has been achieved starting from dihydro-β-ionol acetate. Dihydro-β-ionol acetate was transformed to the conjugated diene by bromination with N-bromo succinimide and successive treatment with dimethylaniline. This conjugated diene on photo-oxidation in the presence of eosine in ethanol afforded a peroxide which on catalytic reduction with Lindlar's catalyst afforded a diol, which was oxidized to a ketone. This ketone was also prepared by treating the peroxide with sodium hydroxide. Ether cyclization was effected by heating a dimethylsulphoxide solution of this ketone. Although the resulting ether formed a crystalline semicarbazone, m.p. 208-9°, the ether regenerated from the semicarbazone was shown to be a mixture of two racemic stereoisomers of theaspirone, by gas chromatography.

The spectral data (UV, IR, MS, NMR) of two racemic stereoisomers are found to be almost superimposable. The spectral data of theaspirone coincide with those of the synthetic one [*Tetrahedron Lett.*, No. 22 (1969), 1803].

Mucor rennin, a new milk-clotting enzyme

A new enzyme isolated at the University of Tokyo in crystalline form from *Mucor pusillus* var. Lindt may prove a good substitute for rennin, the milk-clotting enzyme produced only in the stomachs of milk-fed calves [*Biochim. biophys. Acta*, **171** (1969), 138]. The enzyme preparation is found to produce various types of cheese using the conventional cheese manufacturing steps and compares well with rennin in its milk-clotting activity, molecular weight (3000) and optimum *p*H for proteolytic activity. It does not differ much from rennin in its other physical properties: partial specific volume, 0·74; sedimentation coefficient, $2{\cdot}39 \times 10^{-13}$ cm g sec^{-1} $dyne^{-1}$; diffusion coefficient, $7{\cdot}9 \times 10^{-7}$ cm^2 sec^{-1}; and frictional coefficient (f/f_0), 1·33. Although the crystal structure of *Mucor* rennin differs from that of rennin, the new enzyme is available for the manufacture of cheese and hence may facilitate cheese making, which is at present hampered for want of adequate supplies of rennin.

The crude enzyme obtained from the moulds grown on wheat bran by the procedure of Arima *et al.* [*Agric. biol. Chem.*, **31** (1967), 540] is purified by column chromatography over Amberlite CG-50, DEAE-Sephadex A-50 and Sephadex G-100. It is dissolved in 0·1*M* sodium acetate buffer (*p*H 5·0) to make its concentration 2-3%. To this solution is added $(NH_4)_2SO_4$ to 40% saturation and the solution contained in a cellophane tube is dialysed against 0·1*M* sodium acetate buffer (*p*H 5·0) containing $(NH_4)_2SO_4$ of 40% saturation. $(NH_4)_2SO_4$ is added to the outside solution of the cellophane tube dropwise to increase the concentration in the tube gradually. At about 50% saturation enzyme crystals are formed in the tube and are collected after concentration of the enzyme solution in a refrigerator.

A new assay for DNA endonuclease activity

An extremely sensitive method for the assay of endonuclease activity has been reported from the Department of Biochemistry, Case Western Reserve University, Cleveland, Ohio [*J. biol. Chem.*, **243** (1968), 4401]. The new method, which depends upon the liberation of large fragments of DNA of average molecular weight approx. 400,000 from a polyacrylamide gel in which high molecular weight isotopically labelled DNA is entrapped, can be used to examine the kinetics of DNA degradation by deoxyribonuclease I, deoxyribonuclease II and *Escherichia coli* endonuclease I. It can be applied to double stranded DNA, double stranded alkylated DNA and single stranded DNA and hence can find use in purification of as yet uncharacterized endonucleases. The method, however, suffers from the limitation that both strands of a double stranded DNA molecule must be cleaved in order to observe the liberation of DNA from the gel.

This shortcoming in the method has, however, been helpful in assigning mechanisms by which the different endonucleases perform their activity. The observed initial lag in the hydrolysis of DNA by DNAase I and not by DNAase II and *Esch. coli* endonuclease I is indicative of the double hit mechanism, which requires more than one encounter between enzyme and DNA for a break in both strands of DNA, operating in the case of DNAase I, and single hit mechanism, which requires only one encounter between enzyme and DNA — for the hydrolysis of both strands, in the case of DNAase II and *Esch. coli* endonuclease I.

Isotopically labelled DNA is incorporated in a polyacrylamide gel, which is then polymerized in a vertical glass tube (15×1 cm) by aeration with nitrogen for about 60 min. The gel is then transferred to a 10 ml syringe and fragmented by passage through a 50 mesh screen. It is washed with 10 vol. of 0·05*M* Tris-HCl buffer (*p*H 7·2) containing 0·15*M* KCl and $2 \times 10^{-4}M$ EDTA. The average gel preparation contains approximately 186 mμmoles of DNA nucleotide per ml of gel volume after it is packed by centrifugation at 2000 *g* for 5 min. Stock DNA gel suspension is stirred with a magnetic stirrer. To an aliquot of this suspension, divalent metal ions needed for the enzyme activity are added and the reaction is started by the addition of the enzyme and stopped by the addition of 0·5 ml of 0·1*M* EDTA. The supernatant fraction obtained after centrifugation at 2000 rpm for 5 min is collected and its radioactivity determined using a Tracelab low background gas flow counter.

Scanning electron microscopy—A new technique for studying microorganisms

Although scanning electron microscope, which permits the rapid three-dimensional examination of the surfaces of minute objects, has been available for several years, and has been employed in the physical sciences, it has been put to use in biology only very recently. Among the biological objects stereoscanned thus far are the mineralized tissue, pollen grains, exoskeleton of arthropods, foraminifers, actinomycetes and soil microorganisms. More recently [*Science, N.Y.*, **163** (1969), 1064, 1076], E. B. Small and D. S. Marszalak from the University of Illinois, and D. Greenwood and F. O'Gardy from St Bartholomew's Hospital, London, have extended the application of scanning microscopy to the study of the Protozoa and antibiotic-induced surface changes in bacteria respectively.

Small and Marszalak have devised a method which produced life-like results in their study of the protozoans. The technique requires three successive steps: (i) instantaneous fixation of living specimens in osmium tetroxide and aqueous mercuric chloride; (ii) freeze-dry sublimation involving cooling in liquid nitrogen (−180°C), and sublimation to dryness for 5-12 hr in vacuum (5×10^{-2} torr) and cold temperature (−60°C); and (iii) metal coating done in a vacuum evaporator and a thin film of gold and palladium evaporated at a high vacuum (5×10^{-6} torr) on to the specimens rotated 50-100 times/min.

Surface organelles like the pseudopods, flagella and cilia with their numerous patterns and arrays — diagnostic for species identification — can be faithfully preserved, retaining a life-like appearance, and when coupled with the depth of field and the excellent resolution of the scanning electron microscope, they can be seen as never before. Scanning electron microscopy thus permits the rapid examination of spatial relationships of biological structures not obtainable with light microscopy or only laboriously reconstructed from electron microscopic studies, and provides the biologist with a more direct, simpler means.

New synthetic fluid for maintenance of normal activity of isolated tissues

Solutions which are currently in routine use to provide artificial environment for the maintenance of normal functioning of the isolated animal tissues include Sydney Ringer's — advanced as early as 1882 — and several others which are its later modifications. The functioning of these 'Ringer' solutions is based on the assumption of blood plasma as the natural cellular environment which, in fact, is not the case, since the proper environment of cells is interstitial fluid (also called intercellular or tissue fluid) found between the cells and bathing them. The presently employed solutions deviating substantially from the ideal are likely to result in serious alterations of physiological parameters like membrane potentials which are sensitive to ionic concentration changes. In an attempt to solve this problem, A. H. Bretag of the University of Adelaide's Department of Human Physiology and Pharmacology [*Life Sciences*, **8** (1969), 319] has produced synthetic interstitial fluid (SIF) especially for use with isolated rat tissues, although it could be used with advantage as bathing fluid for most types of isolated mammalian tissues. The best available recent data on rat blood composition and relationship between interstitial fluid and plasma were critically evaluated by the author while determining the most probable composition of rat's interstitial fluid.

The SIF is made by dissolving 6·3 g NaCl, 0·26 g KCl, 0·17 g $MgSO_4.7H_2O$, 2·2 g $NaHCO_3$, 0·26 g $NaH_2PO_4.2H_2O$, 2·1 g Na gluconate, 1·0 g glucose and 2·6 g sucrose in 1 litre of distilled, deionized water, equilibrating the solution with carbogen (5% CO_2 in O_2) and finally adding 1·7 ml of 10% $CaCl_2$. In use, the SIF is continuously bubbled with carbogen to maintain the *p*H.

There is likelihood of SIF proving valuable in the perfusion of organs for transplantation and as a basis for a dialysate for use in artificial kidney machines, the solutions currently employed for these purposes having been based on inadequate information.

Indian Institute of Science, Bangalore

The annual report of the Indian Institute of Science, Bangalore, for the session 1967-68 gives an account of its main research activities during the year. A total of 317 research papers were published during the year — 163 in pure sciences and 154 in engineering.

Significant results have been obtained in the areas of vitamins, proteins, cytogenetics and sanitation biochemistry. In the studies concerning the toxic effects of *Lathyrus sativus* (*Khesari dhal*) it has been found that dimethyl sulphoxide when given intraperitoneally to rats which were fed on a diet of *Khesari dhal* produced a lowering of blood ban barrier and resulted in dragging of the hind legs similar to those observed earlier in monkeys. Feeding of orotic acid increased glycogen and citrate levels in rats within 24 hr of feeding, whereas fatty acid level increased only after 72 hr. Glucosamine could reverse fat accumulation without affecting the glycogen and nucleotide levels. Ribonuclease A has been shown to undergo structural alterations both in acidic and mildly alkaline *p*H regions to form stable active forms of the enzyme. It has been demonstrated that differences in the folding of the chain in the S-protein region of the enzyme is responsible for the initial changes in the structure of ribonuclease A in both acidic and alkaline environment.

A new function has been discovered for ubiquinone as a regulatory molecule in controlling the synthesis of cholesterol in the liver, thereby decreasing serum-cholesterol levels, similar to the action of the cholesterol-depressing drug Antromid-S. The regulatory effect of ubiquinone on steroidogenesis manifested only in adult animals and was found to be absent until weanling stage. This offers scope for the therapeutic use of this naturally occurring lipid-quinone.

Using essentially immunological techniques it has been shown for the first time that the placenta of the sheep and cow secrete a follicle stimulating hormone type of material. A large number of polluted water samples were studied and it was shown that a simple test for the enzyme catalase may be usefully applied, particularly for the assessment of organic pollution of water. This catalase activity is largely due to the bacterial development as shown by further experiments with pure cultures of seven bacteria from sewage and soil.

Investigations on the rhizosphere microflora of mulberry (*Morus indica*) revealed that rhizosphere bacteria of the mulberry assist the plant by elaborating plant hormones, which help elongate the root as well as the shoot. It was also observed that the bacteria associated with the leaves of the plant are nitrogen fixing species, and these contribute to the nitrogen nutrition of the plant. The rhizosphere flora bring about better aggregation of the soil and include such species of heterophobic bacteria as are able to attach methionine effectively and promote nitrification to proceed in the soil.

The tubercle bacillus has been found to possess a new enzyme — acetohydroxy acid isomerase — whose activity can be demonstrated in the presence of vitamin C and for the first time vitamin C has been shown to have a definite role in metabolism.

The use of films of plastics like polyethylene and polyvinylchloride as infrared filters is being studied and encouraging results were obtained in this direction. Complexes of Ni(II) halides with antipyrene (Apy), having the composition, $NiCl_2.2Apy$, $NiBr.2Apy$, and $[Ni(Apy)_6]I_2$ and pyridine N-oxide and antipyrine complexes of manganese(III) perchlorate of the composition $[MnL_6](ClO_4)_3$ have been prepared and their structures assigned. Some diphenyl sulphoxide (DPSO) complexes of iron(II) have been characterized. DPSO complexes of TiO^{2+}, ZrO^{2+}, VO^{2+}, UO_2^{2+} and Th^{4+} have been prepared. Total synthesis of a naturally occurring steroid has been achieved. During the attempted synthesis of oestrone, a modified Clemensen reduction of 1-methoxycarbonyl-2-methyl-2-cyano-3-keto-7-methoxy 1,2,3,9,10,10a-hexahydrophenanthrene furnished an interesting dimeric product whose structure was completely elucidated. A urinary steroid could be synthesized for the first time using the neutral product obtained by the hydrogenation of the ketal of *d*-equilenin as the starting material. Total syntheses of 17-β-hydroxy-des-A-androst-9-ene-5-one and 17-β-hydroxy-10*d*-des-A-androstan-5-one have been achieved. A relatively low-cost vapour phase chromatograph useful for classroom demonstration has been developed.

Process development work for the manufacture of acetone, acetylene, cyclohexane and propionaldehyde has been completed and is of industrial relevance.

Studies in solid state physics, spectroscopy, mass spectrometry and nuclear geology, with emphasis on the development of instruments were carried out. Considerable attention was given to the development of modern instrumentation for photoelastic studies, thermal expansion and specific heats of liquid mixtures, nuclear quadrupole resonance, electron nuclear double resonance, dynamic nuclear polarization and for the production of semiconductors. The structure analysis of meso-3,3′-di-(*p*-bromophenyl)-bi-phthalidyl was completed. The structure was defined by three-dimensional least squares procedure with anisotropic thermal vibrations for all the atoms.

Dr V. A. Altekar

Dr V. A. Altekar, Professor of Metallurgy, University Department of Chemical Technology, Bombay University, has been appointed Director, National Metallurgical Laboratory, Jamshedpur.

Born on 4 March 1925, Dr Altekar took his degree in metallurgical engineering in 1946 from the Banaras Hindu University. His research work on the utilization of the lead-zinc ores of Zawar was well received and he was awarded a scholarship by the Colorado School of Mines, USA, for post-graduate work on ' Mechanism of formation of nodular cast iron '. Working under Prof. C. B. Carpenter and Prof. Wichman he obtained his master's and doctorate degrees in metallurgical engineering. He was also assigned many industrial problems. He worked for some time with the US Bureau of Mines and also with a private copper mining and milling company in Arizona.

On his return from USA, Dr Altekar rejoined the Banaras Hindu University and carried out investigations on minerals. In 1957, he joined the Bombay University where in 1962 a chair was specially created in recognition of his outstanding work in the field of mineral processing and chemical metallurgy. In recognition of his contributions to industrial research and education, the Union Ministry of Mines and Metals named him ' Metallurgist of the Year ' in 1968. The award carried a prize of Rs 3000. His paper on ' Selective chlorination of ilmenite in fluidized bed reactors ' was awarded the Kamani gold medal for being the most meritorious paper published by the Institute of Metals (India).

Dr Altekar has done pioneering work on chlorine metallurgical processes like chemical beneficiation of minerals; production and purification of metal chlorides; electrowinning of metals from fused chlorides; studies on the thermodynamic properties of unstable metal chlorides; application of fluidized bed techniques for metallurgical problems in India, etc.

Dr Altekar is intimately connected with various industrial processing and production problems and has conducted a large number of investigations on behalf of public and private sector enterprises. He has been consultant and technical adviser to a large number of firms and is responsible for the designing and commissioning of ore dressing plants for low grade manganese ores, plants for processing bauxite, preparation of project reports on upgrading of ilmenite for export, utilization of sea bitterns, electrothermal smelting of zinc, production of superfine metallic zinc dust from waste, zinc oxide, etc. Dr Altekar has been singly responsible for the successful development of the unique process for the production of high purity zinc, as he not only conceived the idea but also designed and commissioned the commercial electrothermal zinc dust and smelting plant at Thana near Bombay, utilizing entirely indigenous talents, materials and equipment. Initiated in 1966, the project was completed in 1968. Dr Altekar has also been technical adviser to the Hindustan Copper Ltd.

Dr Altekar is the author of a large number of research and technical papers on various facets of metallurgical science and technology and two patents which are concerned with processing and treatment of indigenous ores and minerals like bauxite, ilmenite, manganese ores, chromite, iron ores, etc.; extraction characteristics of aluminium, zinc, manganese, iron, etc.; utilization of metallurgical wastes; use of substitute alloys; basic concepts on reaction mechanism in metal and alloy production; suveys on mineral deposits of the country; production of metallic compounds; and export potentialities of ores and minerals. Dr Altekar has also guided research at post-graduate level.

He is associated with the National Chemical Laboratory as a member of its advisory panel. He is also member, Minerals Advisory Committee of the Maharashtra Chamber of Commerce, and Maharashtra State Industrial Research Committee.

Dr Altekar is one of the pioneers in building up the Indian Institute of Metals, Bombay. Presently a member of the Institute, he was its chairman from 1964 to 1966. He is Vice-President, Society for Advancement of Electrochemical Science and Technology and member, Institute of Indian Foundrymen.

FORTHCOMING INTERNATIONAL SCIENTIFIC CONFERENCES

Date	*Conference*	*Place*
October 1969	International Colloquium on Properties and Nature of Coordination Bonds	Paris
2-5 Nov.	Second International Symposium on Recent Advances in the Study of Atherosclerosis	Chicago
3-8 Nov.	World Congress on Cybernetics	Vienna
4-6 Nov.	International Congress on the Radiation Protection Problems in the Pacific Use of Nuclear Energy Proceedings of the Emission, Diffusion and Retention of the Fission Products	Gif-Sur-Yvelte
5-7 Nov.	Second International Conference on Accelerator Dosimetry and Experience	Stanford, California
10-14 Nov.	Symposium on the Performance of Nuclear Power Reactor Components	Czechoslovakia
18-22 Nov.	International Meeting on Nuclear Desalination	Madrid
19-20 Nov.	International Symposium on Non-destructive Testing of Nuclear Reactor Components	Rotterdam
30 Nov.-4 Dec.	International Conference on the Constructive Uses of Atomic Energy	San Francisco
November	International Rubber Conference	Moscow
7-12 Dec.	International Conference on Global Impacts of Applied Microbiology	Bombay
December	International C-14 and T-3 Dating Conference	Caracas
2-7 Feb. 1970	Second Conference on Nuclear Data for Reactors	Vienna
16-21 Feb.	Symposium on the Handling of Nuclear Science Information	Vienna
18-20 Feb.	International Solid State Circuits Conference	Philadelphia

Announcements

▪ *The Fourth Symposium on Earthquake Engineering* will be held at the School of Research & Training in Earthquake Engineering, University of Roorkee, Roorkee, during 14-16 November 1970. The main topics of discussion at the symposium will be: Structural response and design of structures for earthquake and blast forces; Design of dams and appurtenant works in earthquake zones; Housing in seismic zones and damage during recent earthquakes; Soil and foundation behaviour during earthquakes; Instruments for earthquake engineering and seismological studies; Seismicity, wave propagation and ground motion; Seismo-tectonic studies of seismic regions; and Observation of earthquake damage and determination of iso-seismal and iso-force lines.

Synopses (300 words) of papers intended to be presented at the symposium should be sent by 31 March 1970 to the convener c/o School of Research & Training in Earthquake Engineering, University of Roorkee, Roorkee. The last date for sending full papers (limited to 6000 words) is 30 June 1970.

▪ *The Computer Society of India* will be holding its fifth annual meeting at the College of Engineering, Guindy, Madras 25, during 8-10 January 1970. The programme for the meeting will include a number of invited talks and panel discussions on subjects of topical interest and also technical sessions for presentation of contributed papers. The technical sessions will cover the following areas: (1) Management applications; (2) Computer education; (3) Applications (structural engineering, chemical engineering, electrical engineering and miscellaneous); (4) Systems (hardware and software); and (5) Numerical analysis. An exhibition of books, literature, components, instruments and systems is also being arranged. Further details can be had from Dr S. Natarajan, Convener, Computer Society of India, c/o College of Engineering, Guindy, Madras 25.

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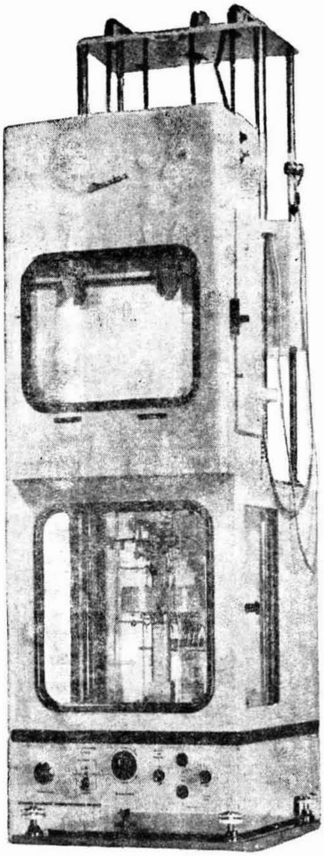

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