THE EFFECT OF CLIMATE AND ATMOSPHERIC POLLUTION ON CORROSION*

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The results of routine observations on the corrosion of the small reference specimens of ingot iron and of zinc exposed at the atmospheric testing stations of the Corrosion Committee all over the world are presented and discussed. The data, which relate to more than 20 sites and to up to 20 separate annual tests at each, provide a good indication of the effect of climatic differences on atmospheric corrosion.

In Great Britain, where for most of the year the climate is sufficiently humid to promote corrosion, the determining factor for its severity is the sulphur pollution of the air. Tests made in collaboration with the Fuel Research Station at 16 sites where the atmospheric pollution is measured have shown an almost perfect correlation between the amount of sulphur dioxide taken up from the atmosphere by lead peroxide pollution gauges and the rate of corrosion, both for steel and zinc.

In the absence of sulphur pollution, corrosion at the sites overseas is generally slight; in dry climates it is negligible. For example, tests at Delhi indicate that the resistance of the Delhi pillar to corrosion is to be attributed to the mildness of the corrosive conditions there rather than to any superiority of the iron itself.

Corrosion on surf beaches in the tropics may, however, be exceptionally severe. At Lighthouse Beach, Lagos, Nigeria and at Kure Beach, N.C., U.S.A., the rates of corrosion for steel are about five times greater than those in the most corrosive industrial atmospheres in Great Britain. The severe corrosion at these places is associated with the salt spray from the sea, and the rate of corrosion falls off rapidly with increasing distance from the surf line.

Preliminary tests on specimens exposed at different heights on the Sutton Coldfield television mast suggest that the effect of distance from the ground is secondary to the natural variations in rates of corrosion from one year to another.

Some details of experimental technique are discussed. Work, in which American investigators have collaborated, has confirmed that at low copper contents variations of a few hundredths of one per cent. in copper content have a marked effect on the corrosion-resistance of ingot iron. Because of the increasing difficulty in controlling the copper content of different batches of ingot iron, the small reference specimens used in the Corrosion Committee's most recent tests have been made of copper–steel instead of ingot iron. The copper–steel now in use contains about $0\cdot3\%$ of copper; minor deviations from this figure should not affect the corrosion rate within the experimental error. It has also been found that, although it is advisable to stir the inhibited hydrochloric acid solution (Clarke's solution) used for derusting iron or steel specimens after exposure, failure to do so does not impair the accuracy of the results, at least for ingot iron or copper–steel.

Introduction

The Corrosion Committee of the British Iron and Steel Research Association has always exposed small reference specimens at its atmospheric corrosion stations at home and overseas to indicate the relative corrosiveness of the various atmospheres. Two materials, one ferrous and the other non-ferrous, are used. For a long time the ferrous material was ingot iron, but for reasons given later, copper–steel has recently been substituted; the non-ferrous material is zinc. Duplicate specimens of both are exposed bare in a vertical position. The period of exposure is generally one year, but a few tests have been made over five years. After exposure the specimens are replaced by a new set, and their losses in weight are determined.

The results obtained give a good indication of how the corrosiveness of the atmosphere varies in different parts of the world, for they relate to more than 20 corrosion stations at which up to 20 annual observations have been made. Their interest is enhanced by the results of similar tests made in the United States with the collaboration of American investigators.

With the object of correlating the intensity of atmospheric corrosion with atmospheric pollution, sets of reference specimens have been exposed for one year at 16 sites in this country where routine determinations of sulphur pollution are made. The Fuel Research Station collaborated in this experiment.

Subsidiary tests have been made at Delhi to elucidate the reasons for the resistance of the iron pillar to corrosion, and on specimens exposed at different heights on the Sutton Coldfield television mast of the British Broadcasting Corporation to ascertain whether the distance from the ground has any influence on the rate of corrosion. The effect of stirring the inhibited hydrochloric acid solution (Clarke's solution) used for removing rust from the ferrous specimens at the end of the tests has also been studied.

Experimental procedure

The experimental procedure is simple. The specimens measure 4 in. × 2 in.; the thickness is nominally $\frac{1}{8}$ in. for ingot iron and copper–steel and $\frac{1}{20}$ in. for zinc. Small holes are drilled at the four corners of the specimens and are used to attach them by means of wire or string to a suitable frame or stand. When in position the specimens hang vertically and are freely exposed, generally at about 5 ft. from the ground. For some purposes, e.g. on the Sutton Coldfield mast,

it has been found more convenient to secure the specimens by means of a single bolt, suitably insulated, passing through a central hole. All tests are made in duplicate, so that the present standard set of specimens consists of two copper–steel specimens and two zinc specimens.

The ingot iron or copper–steel specimens are cut from hot-rolled material. Before exposure the millscale is removed from them by pickling in hydrochloric acid; the pickled iron or steel is thoroughly rinsed in hot water and allowed to dry under its own heat. The zinc specimens are cut from bright-rolled sheet of electrolytic quality and are exposed without any surface preparation other than a thorough degreasing with carbon tetrachloride.

Table I

Units conversion table

Mils	Ingot iron or copper–steel, oz./sq. ft.	Zinc, oz./sq. ft.
0·1	0·07	0·06
0·2	0·13	0·12
0·3	0·20	0·18
0·4	0·26	0·24
0·5	0·33	0·30
0·6	0·39	0·36
0·7	0·46	0·42
0·8	0·52	0·48
0·9	0·59	0·54
1·0	0·65	0·60

After exposure the rust is removed from the iron or steel specimens by treatment with Clarke's solution (see Methods of cleaning) and the zinc corrosion products are removed by means of cold dilute acetic acid. The losses in weight of the specimens are then determined. These are expressed as oz./sq. ft. and are also converted into the equivalent average depth of metal corroded per face in mils (0·001 in.). The unit used in this report is mils per face; this may be reconverted into oz./sq. ft. by reference to Table I.

Routine tests at the Corrosion Committee's exposure stations

Experimental details

The results of the routine observations made on ingot iron and zinc specimens exposed at the testing stations of the Corrosion Committee are given in Tables II and III. During the twenty years concerned five different batches of ingot iron have been used. The composition

Table II

Routine observations at the corrosion stations. Ingot iron and zinc specimens exposed for one year

Site Name	Atmosphere	Rate of corrosion, mils/year							
		Ingot iron				Zinc			
		Number of tests	Max.	Min.	Average	Number of tests	Max.	Min.	Average
Home stations									
Brixham	Marine	6	2·5	1·8	2·1	6	0·09	0·06	0·07
Llanwrtyd Wells	Rural	20	3·8	1·6	2·5	20	0·18	0·08	0·12
Calshot	Marine	18	6·5	1·9	3·1	18	0·19	0·09	0·14
Motherwell	Industrial	11	5·3	2·9	3·8	10	0·19	0·11	0·17
Woolwich	Industrial	9	4·9	3·3	4·0	9	0·17	0·13	0·15
Birmingham	Suburban	6	4·7	3·7	4·1	6	0·16	0·10	0·14
Sheffield (University)	Industrial	12	5·8	2·9	4·5	12	0·35	0·11	0·18
Derby (old site)	Industrial	8	6·2	3·8	5·1	8	0·38	0·23	0·30
Sheffield (Attercliffe)	Industrial	18	7·8	4·2	5·4	18	1·01	0·47	0·62
Sheffield (Brown–Firth Research Laboratories)	Industrial	4	6·6	5·0	5·7	5	0·49	0·37	0·44
Frodingham	Industrial	6	10·4	4·3	6·4	2	0·42	0·37	0·40
Derby	Industrial	5	8·3	6·1	6·8	6	0·31	0·24	0·28
Dove Holes tunnel	Railway tunnel	10	4·4	2·4	3·2	10	3·7	2·6	3·2
Overseas stations									
Khartoum	Dry, tropical	9	0·1	0·0	0·1	9	0·03	0·01	0·02
Nkpoku, near Port Harcourt, Nigeria*	Jungle, tropical	2	0·2	0·2	0·2	3	0·03	0·01	0·02
Abisko, North Sweden	Sub-polar	15	0·3	0·1	0·2	15	0·03	0·01	0·02
Aro, Nigeria	Inland, tropical	7	0·7	0·3	0·5	7	0·09	0·04	0·06
Basrah	Dry, sub-tropical	8	1·0	0·3	0·6	8	0·07	0·03	0·04
Singapore	Marine, tropical	10	0·8	0·5	0·6	10	0·07	0·01	0·04
Apapa, Nigeria	Marine, tropical	16	1·6	0·7	1·1	17	0·11	0·02	0·05
Congella, Durban	Marine, industrial	17	10·4	2·5	4·5	17	0·60	0·12	0·19
Lighthouse Beach, Lagos*	Surf-beach, tropical	2	26·6	22·3	24·4	3	0·60	0·49	0·56

* These sites belong to the Tropical Testing Establishment, Ministry of Supply. The site at Nkpoku is a jungle clearing; that on Lighthouse Beach is at the foot of the radar building (see Table IX)

Table III

Routine observations at the corrosion stations.   Ingot iron and zinc specimens exposed for five years

Site		Rate of corrosion, mils/year			
		Ingot iron		Zinc	
Name	Atmosphere	Five-year tests*	One-year testst	Five-year tests*	One-year testst
Home stations					
Llanwrtyd Wells	Rural	2·2	2·5	0·09	0·11
Calshot	Marine	4·5	3·1	0·13	0·13
Motherwell	Industrial	2·4	3·7	0·18	0·16
Woolwich	Industrial	2·7	3·7	0·16	0·14
Sheffield (University)	Industrial	3·4	4·3	0·20	0·19
Sheffield (Attercliffe)	Industrial	4·7	5·4	0·60	0·61
Dove Holes tunnel	Railway tunnel	2·5	3·2	2·9	3·2
Overseas stations					
Khartoum	Dry, tropical	0·0	0·0	0·01	0·02
Abisko, North Sweden	Sub-polar	0·1	0·2	0·01	0·02
Aro, Nigeria	Inland, tropical	0·3	0·5	0·02	0·06
Basrah	Dry, sub-tropical	0·3	0·5	0·01	0·04
Singapore	Marine, tropical	0·4	0·7	0·03	0·05
Apapa, Nigeria	Marine, tropical	0·8	1·0	0·03	0·04
Congella, Durban	Marine, industrial	3·0	4·8	0·18	0·23

* The number of five-year tests was one, two or three
† Averages for the same years as the five-year tests

Table IV

Analyses of the ingot irons and copper–steel

Material	Thickness, in.	Composition, %							
		Cu	Cr	Ni	C	P	S	Si	Mn
British ingot irons									
B1	⅛	0·038	—	—	0·014	0·008	0·026	—	0·035
B2	⅛	0·064	—	0·05	0·016	0·007	0·038	—	0·036
B3	3/16	0·202	—	—	0·025	0·017	0·049	—	0·030
B4	5/32	0·035	—	0·06	0·03	0·008	0·036	—	0·04
B5	⅛	0·030	0·042	0·047	0·026	0·009	0·047	—	0·043
American ingot irons									
US1	⅛	0·008	(0·005)	0·007	0·02	0·004	0·02	0·002	0·04
US2	⅛	0·039	(0·025)	(0·032)	0·013	0·004	0·025	0·002	0·030
US3	⅛	0·039	—	—	0·017	0·005	0·018	0·003	0·014
US4	⅛	0·039	—	—	0·020	0·005	0·036	Trace	0·032
Copper–steel									
C1	⅛	0·28	Nil	0·10	0·20	0·038	0·052	0·04	0·58

The figures in brackets were determined spectrographically.   Spectrographic examination for other elements in US1 and US2 yielded no significant results

of the ingot iron has differed somewhat from batch to batch; this is shown by the analyses given in Table IV, which also includes data for other materials mentioned in this report.   Moreover, during the war years some deviation from the standard thickness, ⅛ in., proved unavoidable. These variations in composition and thickness have had some effect on the corrosion of the specimens, the magnitude of which can be gauged from Fig. 1.   Here are recorded the rates of corrosion for each year at Calshot, Sheffield (Attercliffe) and Llanwrtyd Wells, both for ingot iron and for zinc.   The higher rate of corrosion of ingot iron B4 is immediately apparent.   Ingot iron B3 has generally shown a slightly lower rate of corrosion, presumably because of its higher copper content.   Differences in the behaviour of the other batches of ingot iron cannot be determined with certainty, but in general the use of different batches of iron has not seriously impaired comparisons between the various sites, although some of the individual observations have been affected.

In view of the variation in the copper content of ingot iron, it was decided in 1950 to change over from ingot iron to steel containing 0·2–0·3% of copper, which would place it above the range within which small variations in copper content have a critical effect on the rate of corrosion. The analysis of the copper–steel now in use is given in Table IV.   It contains 0·28% of copper and 0·10% of nickel.

Tests on some of the new copper–steel specimens have been completed and, in Table V, the results are compared with corresponding figures for ingot iron.   At exposure stations in Great Britain the rate of corrosion of the copper–steel is roughly 0·7 times that of an ingot iron containing 0·03% of copper.   The same ratio was observed in a separate test at Sheffield in which both

ingot iron B5 and the copper–steel were used (see Table XIII and Methods of cleaning).

Discussion of results

It will be seen from Table II that the corrosiveness of the atmosphere varies appreciably from one site to another. In Great Britain the ratio of the highest and lowest rates of corrosion observed for ingot iron exceeds 3 : 1; at the overseas sites it exceeds 200 : 1. The corresponding ratios for zinc are about 10 : 1 and 30 : 1, respectively.

The most corrosive site with respect to ingot iron is the present one at Derby. This is only about 40 yards from the main railway line, as compared to 200 yards for the old Derby site, which is no longer in use. It is an interesting fact, however, that the rate of corrosion of zinc was substantially the same at the old Derby site as at the present one.

The highest rate of attack on zinc is observed at the main Sheffield corrosion station, which is adjacent to the Attercliffe goods yard. The conditions here are more than twice as corrosive towards zinc than at Derby. The attack on zinc exposed on the roof of the Brown–Firth

FIG. 1. *Rates of corrosion from year to year of ingot-iron and zinc specimens (the scale for zinc is ten times that for ingot iron)*

Research Laboratories, about half a mile away, is appreciably lower than at Attercliffe, although the effect on ingot iron is practically identical at the two sites.

The least corrosive site in this country for both metals is Brixham, but it should be noted that this site is mainly used for tests on paints, in which other factors, such as the amount of sunshine, come into account. Excluding Brixham, Llanwrtyd Wells is the least corrosive home site. It is noteworthy that the conditions at Calshot, a marine atmosphere, are not markedly more corrosive to the reference specimens in one-year tests than those in the rural atmosphere of Llanwrtyd Wells. Llanwrtyd Wells is characterized, however, by a heavy rainfall, 55 in. per year, as compared to 26 in. per year for Calshot.

The conditions inside the Dove Holes Tunnel were abnormal, because the specimens were not exposed to rain and the air was full of smoke and steam from locomotives. Under such conditions iron and zinc corrode at practically equal rates.
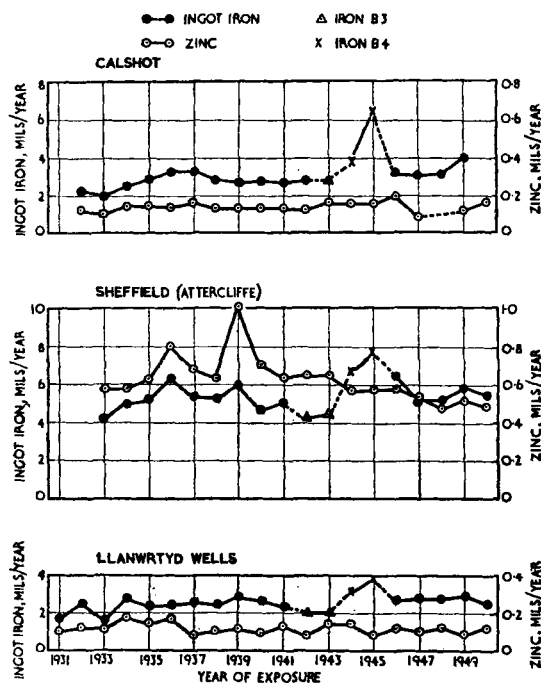
Table V

Routine observations at the corrosion stations. Copper–steel specimens exposed for one year

Site	Rate of corrosion, mils/year Copper–steel	Rate of corrosion, mils/year Ingot iron[†]	Ratio copper–steel/ingot iron
Home			
Brixham	1·4	1·8	0·8
Llanwrtyd Wells	1·7	2·5	0·7
Birmingham*	3·0	4·5	0·7
Sheffield (Attercliffe)	3·8	5·5	0·7
Sheffield (Brown–Firth Research Laboratories)	3·8	(5·7)	(0·7)
Derby	4·3	(6·8)	(0·6)
Overseas			
Nkpoku, near Port Harcourt, Nigeria	0·2	(0·2)	(0·9)
Apapa, Nigeria	1·2	(1·1)	(1·1)
Congella, Durban	3·2	(4·5)	(0·7)
Lighthouse Beach, Lagos	15·1	(24·4)	(0·6)

* Exposed for nine months

† Figures in brackets do not refer to the same year but are averages over earlier years (cf. Table II)

The atmosphere at Lighthouse Beach, Lagos is exceptionally corrosive to ingot iron and copper–steel, which soon become covered with thick scaly rust (Fig. 2). The rate of attack on zinc at this exposure site is no greater than that found at Sheffield (Attercliffe), although the corrosive environments are completely different.

The rates of corrosion at Congella, near Durban, are comparable with those observed in moderately industrial atmospheres in Great Britain. Otherwise the rates of corrosion at the overseas sites are low and in some places negligible, e.g. Khartoum. This is due mainly to the absence of sulphur pollution; at some of the sites, of which Khartoum again is an example, the atmospheric humidity is also low.

The results of the five-year tests (Table III) place the sites in much the same order of corrosiveness as those of the one-year tests (Table II). Except at Calshot, the rate of corrosion of ingot iron is less over the longer period. The rate of corrosion of zinc is substantially the same over one year and over five years.
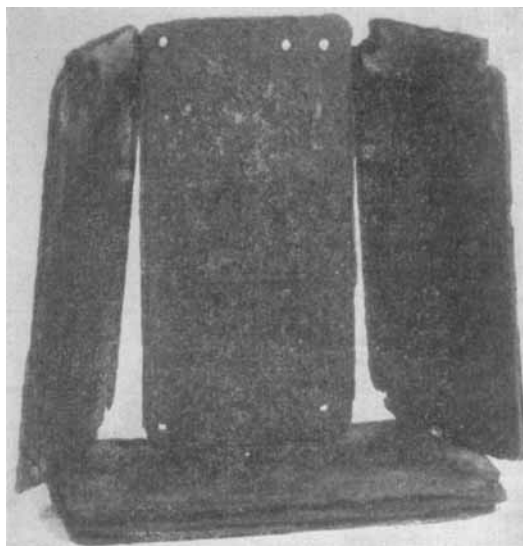
FIG. 2. *Corroded ingot-iron specimens from Lighthouse Beach, Lagos, Nigeria (one year's exposure). (The photograph shows a pair of specimens, one lying flat with the scaly rust still attached, the other vertical with the rust scales flanking it)*

Correlation of atmospheric corrosion and atmospheric pollution

The effect of atmospheric pollution on atmospheric corrosion has long been a subject for interesting discussion. In order to place the relationship between these variables on a more rigorous quantitative basis, arrangements were made in 1951 to expose sets of reference specimens of copper–steel and zinc at 16 sites where routine determinations of the sulphur dioxide in the atmosphere are made by means of the standard lead peroxide instrument.[1] The Fuel Research Station, Department of Scientific and Industrial Research, collaborated in this research by selecting four groups of four sites each, representing slight, moderate, heavy and severe pollution, respectively.

A set of reference specimens (two copper–steel and two zinc) was exposed for one year beside the lead peroxide instrument at each site. The lead peroxide cylinders used for the sulphur dioxide determinations are changed monthly and their sulphate contents are found by analysis. In Table VI the averages of the 12 monthly sulphate determinations are compared with the corrosion rates of the specimens over the whole year.

Table VI

Correlation of rates of atmospheric corrosion of copper–steel and zinc with sulphur pollution in the atmosphere

Degree of pollution and exposure site	Sulphur pollution, standard units*		Rate of corrosion, mils/year Copper–steel		Zinc	
		Average		Average		Average
Slight						
Godalming, Surrey	0·23		1·67		0·042	
Loggerheads, Cheshire	0·50		2·22		0·086	
Hornchurch, Essex (N. Ockendon)	0·52		2·26		0·065	
Teddington	0·82	0·52	2·49	2·2	0·083	0·07
Moderate						
Hornchurch, Essex (Suttons Lane)	0·92		2·46		0·127	
Leicester (Westcotes)	1·04		2·42		0·111	
London (Ravenscourt Park)	1·23		2·68		0·142	
London (Victoria Park)	1·28	1·12	2·97	2·6	0·175	0·14
Heavy						
Barking (Greatfields Park)	1·60		2·95		0·190	
Huddersfield (Ravensknowle Park)	1·94		3·25		0·212	
London (East Greenwich)	2·20		3·98		0·230	
Salford (Ladywell)	2·31	2·01	4·14	3·6	0·331	0·24
Severe						
Sheffield (Hunshelf Bank)	3·58		4·21		0·506	
Manchester (Monsall)	3·60		4·36		0·416	
Sheffield (Sewage works)	3·66		4·26		0·439	
Billingham (Council offices)	5·24	4·02	7·06	5·0	0·476	0·46

* Wt. in mg. of SO_3 absorbed per day by 100 cm.² of the lead peroxide surface of the gauge

Correlation coefficients have been calculated between the corrosion of copper–steel, the corrosion of zinc and the sulphur pollution. The method used was Spearman's ranking method. The 16 sites were arranged in order of (a) increasing corrosion of copper–steel, (b) increasing corrosion of zinc and (c) increasing sulphur pollution. If $d_1, d_2, \ldots d_{16}$ are the differences between the rankings of the individual sites according to the two variables to be correlated, then the correlation coefficient is equal to $1 - 6\Sigma d^2/(16^3-16)$, 16 being the number of observations. The values for each pair of variables are:

Corrosion of copper–steel versus sulphur pollution	..	0·98
,, ,, zinc versus sulphur pollution	..	0·97
,, ,, copper–steel versus corrosion of zinc	..	0·95

The correlation between sulphur pollution and corrosion is high, both for copper–steel and zinc. This demonstrates beyond question that the sulphur dioxide concentration in the air is the determining factor for the intensity of the corrosion of these metals in Great Britain. The connexion between atmospheric corrosion and atmospheric pollution is immediately evident from the simple diagram shown in Fig. 3, which represents average values for each group of four sites at the same pollution level. Another interesting feature brought out by this diagram is that, whereas the rate of corrosion for zinc is roughly proportional to the sulphur pollution of the atmosphere, the rate of corrosion for copper–steel increases relatively more slowly with increase in sulphur pollution. Consequently, as a general rule, the ratio of the corrodibility of copper–steel to that of zinc decreases as the corrosiveness of the atmosphere increases. This point will be considered further in the General discussion (p. 94).

Sundry tests

Tests at Delhi

In view of frequent references to the freedom from corrosion of the iron pillar at Delhi, a set of specimens was exposed there in July, 1950, with the kind assistance of Major H. B. Deshpande, J.P. As the two zinc specimens were lost, the tests were repeated on a fresh set of specimens for another year (July 1951–July 1952). The results are given in Table VII.
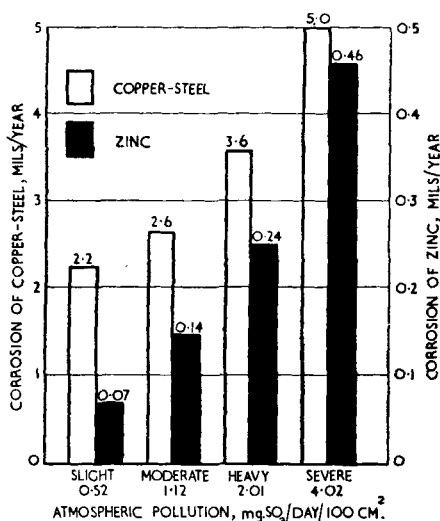

FIG. 3. *Correlation of atmospheric corrosion and atmospheric pollution. (The scale for zinc is ten times that for copper–steel)*

Table VII

Corrosion at Delhi

Period of exposure	Rate of corrosion, mils/year	
	Copper–steel	Zinc
1950–1951	0·23	Lost
1951–1952	0·17	0·006

The observed rate of corrosion of copper–steel at Delhi, about 0·2 mil per year, is much lower than the rates observed at the home sites, which range from 1·4 to 4·3 mils per year (Table V), and is of the same order as the rate in the least corrosive of the overseas atmospheres. The value for zinc at Delhi, 0·06 mil per year, is comparable with the figure obtained at Khartoum, where corrosive attack is at a minimum. Indeed, the zinc specimens returned from Delhi retained considerable reflectivity.

It may be concluded that the atmosphere at Delhi is only mildly corrosive and that the resistance of the pillar to corrosion is due primarily to this factor rather than to the composition of the iron itself. Meteorological observations at New Delhi confirm this view. The records show that throughout most of the year the relative humidity of the atmosphere lies well below 70%, which, as W. H. J. Vernon has shown, is the critical humidity for the rusting of iron.

Effect of height

A preliminary investigation of the effect of height on corrosion was made by exposing sets of specimens at four different heights on the television mast at Sutton Coldfield. The results of tests over a year are given in Table VIII. They suggest that the variation of the corrosiveness of the atmosphere round this mast with height is small.

Tests in Nigeria

To assist the Tropical Testing Establishment, Ministry of Supply, in their study of corrosion in the tropics, 24 pairs of single ingot iron and zinc specimens were supplied to them in 1950 for exposure in Nigeria. Tests were made at several sites either for a full year, or during the wet or dry seasons of the same year; each season is about four months long. The wet season speci-

Table VIII

Effect of height of exposure on the corrosion of copper-steel and zinc

Height above ground level, ft.	Rate of corrosion, mils/year Copper-steel	Zinc
30	2·7	0·19
200	2·8	0·24
400	2·6	0·23
580	2·2	0·23

mens and those for the whole year were put out at the same time. Several pairs of specimens were exposed at increasing distances from the surf line on Lighthouse Beach, Lagos, where there is a continuous salt spray from the sea. The salt spray travels up the beach for a distance that depends on the wind direction. Rough estimates of the concentration of salt in the air were obtained by hanging a wet cloth across the wind for a few hours and measuring the salt collected.

The results of the experiments are given in Table IX. Although they relate to single speci-mens only, they suffice to suggest several interesting general trends. For example, at Lagos corrosion is extremely severe near the surf line but decreases rapidly on moving inland. This decrease is confirmed by the results obtained at the Corrosion Committee's two exposure stations in Nigeria, Apapa and Aro (Table II). At Apapa, situated on the coast near Lagos but sheltered from the surf by an island, both ingot iron and zinc corrode roughly half as rapidly as in rural districts of Great Britain. At Aro, on the Nigerian uplands, the corrosivity of the atmosphere is even less. It is evident from the figures given in Table IX for the salt content of the air that the decrease in corrosion with increasing distance from the sea is associated with a decrease in the sea salt blown inland from the surf. As would be expected, the rates of corrosion during the dry season are generally less than those during the wet season. The most notable exception is at the high-water mark site on Lighthouse Beach. Presumably here the surf cloud rather than the rainfall is the determining factor.

Table IX

Results of tests in Nigeria

Site	Distance from surf	Salt content of the air*	Ingot iron (B5) Wet season	Ingot iron (B5) Dry season	Ingot iron (B5) Whole year	Zinc Wet season	Zinc Dry season	Zinc Whole year
Lighthouse Beach, Lagos								
High water mark	50 yd.	11·1	45·9†	45·0†	37·7‡	1·86	1·48	1·51
Top of radar building (17 ft.)	200 ,,	4·2	13·3	9·0	17·7	0·89	0·78	0·58
Foot of radar building	200 ,,	3·1	22·9	3·7	14·9	0·69	0·36	0·57
Top of lighthouse (75 ft.)	400 ,,	5·0	18·9	11·2	—	0·63	1·52	—
Foot of lighthouse	400 ,,	0·8	3·9	2·5	2·2	0·27	0·16	0·11
East Mole								
Fisheries site	1300 ,,	0·2§	2·5	1·7	1·6	—	—	0·02
Port Harcourt								
T.T.E. H.Q. compound	25 miles	—	3·1	2·3	1·9	0·07	0·10	0·02
Nkpoku jungle site, clearing	37 ,,	—	0·8	0·4	0·2	0·11	0·07	0·03

* Collected on a wet cloth, expressed as mg. of sodium chloride/day/100 cm.² of cloth; not determined at Port Harcourt
† Pitted
‡ Perforated at several places
§ At 3000 yd. from the surf

Effect of copper content on the corrodibility of ingot iron

When it became difficult to obtain further batches of ingot iron with a very low and repro-ducible copper content, attention was turned to the extent of the effect of variation in copper content on the rate of corrosion of the iron. Six specimens of each of three different ingot irons, US1, B5 and US2, with the analyses given in Table IV, were exposed at Sheffield on the roof of the Brown-Firth Research Laboratories, through the courtesy of Mr. H. T. Shirley. Two of these irons, US1 and US2, were of American origin and, with the kind collaboration of Mr. F. L. LaQue, of the International Nickel Company Inc., New York, similar tests were made in the U.S.A.

The results of determinations on duplicate sets exposed for one year and five years, respectively, are given in Table X. The figures for Sheffield are average values for six specimens; the agreement between replicates was good. Ingot iron US1 with the lowest copper content (0·008%) corroded much more rapidly than the others. There was little difference in corrosion resistance between irons B5 and US2 containing 0·030% and 0·039% of copper, respectively;

Table X

Corrodibility of ingot irons with various copper contents

Site Name	Atmosphere	Duration of exposure, years	Rate of corrosion, mils/year		
			USI (Cu, 0·008%)	B5 (Cu, 0·030%)	US2 (Cu, 0·039%)
Sheffield	Industrial	1	7·8	5·8	5·5
		5	6·9	4·9	4·8
Kure Beach, N.C. (800 ft. from sea)	Marine	1	—	2·4	3·1
		5*	—	2·0	3·3
Kearny, N.J.	Industrial	1	12·0	7·0	—
		2	9·0	5·3	—
South Bend, Pa.	Semi-rural	1	5·6	3·4	—
		2	5·0	2·7	—
Truitsburg, Pa.	Rural	1	3·3	2·4	—
		2	2·5	1·8	—

* Both specimens perforated at the bottom edge and deeply pitted on one face

the latter was slightly more resistant. In the American tests iron USI also corroded the most rapidly, but irons B5 and US2 were placed in the reverse order.

Similar results were observed in tests at Kure Beach on the four American irons (Table XI), although here the behaviour of iron US4 was anomalous.

Table XI

Sundry tests on ingot iron specimens exposed together for one year at Kure Beach, N.C.

Distance from sea, ft.	Rate of corrosion, mils/year			
	USI (Cu, 0·008%)	US2	US3 (Cu, 0·039%)	US4
80	47·0	35·0	30·0	17·0
800	7·9	2·8	2·8	2·0

It is clear from these experiments that the rate of corrosion of ingot iron is markedly affected by minute variations in its copper content when this is low; very high rates of corrosion may be observed when the copper content of the iron approximates to zero.

Tests in the U.S.A.

In addition to the tests already reported, other tests on British ingot iron have been made in the U.S.A. at three corrosion stations operated by Mr. C. P. Larrabee, of the United States Steel Co., Pittsburgh. The results are included in Table X. A few zinc reference specimens have also been exposed at American testing stations with the results given in Table XII.

Table XII

Results of tests on zinc specimens exposed for one year in the United States (1950–1951)

Site	Type of atmosphere	Rate of corrosion, mils/year
Kearny, N.J.	Industrial	0·15
South Bend, Pa.	Semi-rural	0·07
Truitsburg, Pa.	Rural	0·10
New York City	Industrial	0·24
State College, Pa.	Rural	0·03
Kure Beach, N.C. (80 ft. from sea)	Marine	0·39
Kure Beach, N.C. (800 ft. from sea)	Marine	0·07
Bayonne, N.J.	Moderately industrial	0·17

The general result of these experiments is to show that the rates of corrosion of ingot iron and zinc in similar types of atmosphere are substantially the same in the U.S.A. and Great Britain (Table II). It is also noteworthy that the tests at Kure Beach (Tables XI and XII) reveal the same effect of distance from the sea as those at Lighthouse Beach, Lagos (Table IX).

Methods of cleaning after exposure

Since the tests continue over many years, it is important that the methods of cleaning corroded specimens after exposure should be such that the personal factor is reduced to a minimum. Some attention has therefore been paid to the methods used for this purpose in the researches under consideration.

Ingot iron and copper–steel (Clarke's solution).—The ferrous specimens are derusted by immersion in Clarke's solution. This consists of 2 parts of antimonious oxide, 5 parts of stannous chloride and 100 parts of concentrated hydrochloric acid. The solution is used cold, and constant agitation is recommended. As some doubt arose whether the solution had been kept adequately stirred when derusting some of the specimens, a test was made to ascertain the possible effect

of this factor. Some ingot iron and copper–steel specimens were descaled in the usual manner by pickling in hot 5% hydrochloric acid, washed, dried and weighed. The specimens were then immersed for 30 minutes in Clarke's solution, the two different materials being treated separately. Half the number of specimens in each batch was derusted in stagnant solution; for the other half the solution was well stirred. After washing and drying the specimens were reweighed. Their losses in weight are given in Table XIII. The losses are small but are significantly greater for the stirred solutions.

After this treatment, all the specimens were pickled for five minutes in hot 5% hydrochloric acid to remove any protective film deposited from the derusting solution. After washing, drying and weighing, the specimens were exposed outdoors at Sheffield (Brown–Firth Research Laboratories) for one year. Then they were derusted in Clarke's solution. During the derusting of half the number of specimens from each batch, the solution was kept stirred and the surfaces were frequently wiped with a rubber 'policeman'. For the other half the solution was stagnant and the surfaces were not wiped. After washing in cold and hot water and drying, the final weights of the specimens were determined, and the losses due to exposure were calculated. It is reassuring to find that the results (Table XIII) indicate that, for the specimens investigated, the efficiency of the derusting process is not impaired if stirring of the solution is omitted.

Table XIII

Effect of not stirring on the derusting of the iron and steel specimens in Clarke's solution

Material	Treatment before exposure		Treatment after exposure				
	Condition of solution	Wt. loss, g.	Condition of solution	Wt. loss after one year (g./specimen)			Rate of corrosion, mils/year
					Pairs	Average	
Ingot iron (B5)	Stagnant	0·036	Stagnant	12·8			
		0·037		12·5	12·6		
	Stirred	0·048		12·7			
		0·063		12·7	12·7	12·7	5·64
	Stagnant	0·041	Stirred	12·4			
		0·046		12·6	12·5		
	Stirred	0·038		13·1			
		0·051		12·5	12·8	12·6	5·62
Copper–steel (C1)	Stagnant	0·051	Stagnant	9·4			
		0·047		9·1	9·2		
	Stirred	0·063		9·0			
		0·068		9·0	9·0	9·1	4·06
	Stagnant	0·041	Stirred	9·2			
		0·040		9·3	9·3		
	Stirred	0·071		9·1			
		0·068		8·9	9·0	9·2	4·07

Zinc.—The standard procedure now in use for the removal of the corrosion products from the zinc specimens is to immerse them for one minute in cold 10% acetic acid and scrub them while immersed with a bristle brush; if a specimen is heavily corroded, it is given a preliminary scraping with a wooden scraper to remove loose corrosion products. After removal from the acetic acid, the specimens are washed in cold and hot water, dried and weighed.

In the past specimens have been left in the acetic acid for a much longer time than one minute. This is unwise, for experiments have indicated that the acetic acid attacks the zinc appreciably when the corrosion products have been removed. Tests to elucidate this point will be carried out as soon as time permits, but it is not considered that any earlier result has been seriously affected.

General discussion and conclusions

Most of the results reported here are derived from the routine exposure of small ingot iron and zinc specimens at the Corrosion Committee's stations. These figures throw a useful light on the conditions prevailing at the various sites, particularly when they are considered in conjunction with meteorological data, and afford a means of assessing the severity of the tests made on the main series of specimens exposed there. Routine exposures of this nature will be continued. They are being supplemented at present by observations of the meteorological conditions at Derby, Brixham, Nkpoku, near Port Harcourt, and Lighthouse Beach, Lagos. In addition observations of the atmospheric pollution at Brixham, Derby and Sheffield (Attercliffe) have recently been commenced, using both the lead peroxide method and the British Standard deposit gauge (B.S. 1747 : 1951).

The following conclusions may be drawn from the results already obtained:

(i) The corrosion of iron or steel and zinc varies considerably from one climate to another.

Minimum values approximating to zero rates of corrosion may be observed in dry unpolluted climates, whereas devastating rates of attack may occur on surf beaches.

(ii) In Great Britain the determining factor for the rate of corrosion is the sulphur pollution of the atmosphere. Almost perfect correlation has been observed between the orders of corrodibility of 16 sites for copper–steel and for zinc and the corresponding figures for sulphur pollution, as determined by the lead peroxide pollution gauge.

(iii) The rate of corrosion of zinc is directly proportional to the sulphur pollution of the atmosphere and remains substantially the same when the exposure period is increased from one to five years.

(iv) The rate of corrosion of copper–steel increases more slowly than that of zinc with increase in the sulphur pollution. It also falls off as the exposure period is prolonged, whereas zinc corrodes at a roughly constant rate.

The behaviour of copper–steel is undoubtedly associated with the fact that the rust layer, when once formed, retards further attack. This is probably true to some extent for ordinary steel. As Copson[2] has shown, the effect is particularly marked for steels containing copper (and certain other low-alloy additions), because of the gradual accumulation of an insoluble basic copper sulphate in the rust. On the other hand, the constancy of the corrosion rate of zinc with time is to be attributed to the ready solubility of its corrosion product.

The closer approximation to direct proportionality between the corrosion rate of zinc and the sulphur pollution is no doubt connected with the fact, observed by Schikorr,[3] that in sulphur-polluted atmospheres, zinc and other non-ferrous metals corrode according to their chemical equivalent, i.e. the amount of metal attacked is chemically equivalent to the sulphate taken up from the atmosphere. For iron, on the other hand, the amount of metal corroded is many times greater than that corresponding to the formation of iron sulphates.

(v) Although the mechanisms discussed in the previous paragraph (iv) do not explain certain anomalies observed between various sites, e.g. the two at Derby or two of those at Sheffield (see Discussion of results), they provide an adequate reason for the most important experimental fact, namely that as the sulphur pollution increases, the ratio of the corrosion of iron to that of zinc in the same atmosphere decreases. Moreover, because the rates of corrosion themselves increase with the sulphur pollution, it is generally true that this ratio is lowest in the most corrosive atmospheres. As is evident from Fig. 4, there are certain exceptions to this generalization, notably at sites where the rates of corrosion are low because of lack of pollution (say, below 0·1
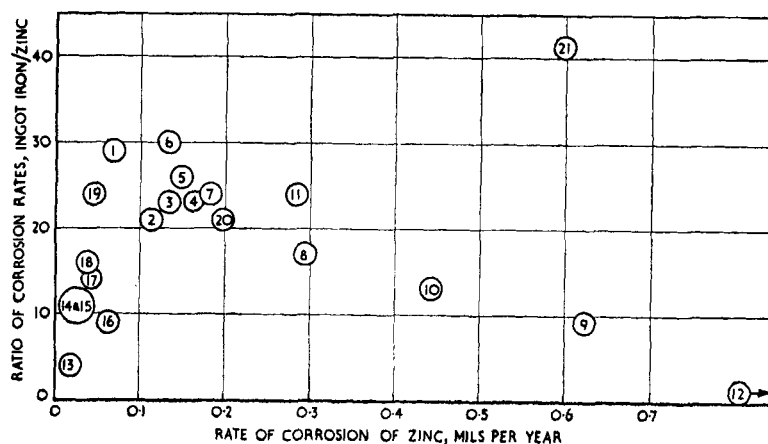

FIG. 4. *Ratio of the rates of corrosion of ingot iron and zinc in different atmospheres*

Key to exposure stations

Home		Overseas
1. Brixham	7. Sheffield (University)	13. Khartoum
2. Llanwrtyd Wells	8. Derby (old site)	14. Nkpoku, near Port
3. Calshot	9. Sheffield (Attercliffe)	Harcourt
4. Motherwell	10. Sheffield (Brown–Firth	15. Abisko
5. Woolwich	Research Laboratories)	16. Aro
6. Birmingham	11. Derby	17. Basrah
		18. Singapore
		19. Apapa
12. Dove Holes tunnel*		20. Congella, Durban
		21. Lighthouse Beach, Lagos

* In the Dove Holes tunnel, where the rate of corrosion of zinc is 3·2 mils/year, the ratio is 1

mil/year for zinc), or at Lighthouse Beach, Lagos, where the corrosion is due to sea salt spray rather than to sulphur pollution of the air.

This variation in the ratio of the corrodibilities of iron and zinc has the interesting practical consequence that under conditions of high sulphur pollution it may become uneconomical to use zinc for the protection of unpainted steel parts, and a more profitable result may be achieved by increasing the thickness of the steel section. These conditions are unlikely to arise in the open air, but they may exist in (steam) railway tunnels, and they held good for certain anti-glare structures erected during the war over pig-beds and coke ovens, from which abnormally high amounts of sulphur acids were emitted when the iron or the coke was quenched.

(vi) Tests made in the neighbourhood of the iron pillar at Delhi indicate that the noted resistance of this pillar to corrosion is due to the mildness of the local atmospheric condition rather than to any superiority of the iron itself.

(vii) Preliminary study of the variation of corrosion with height above the ground, made by exposing specimens at different levels on the Sutton Coldfield television mast, suggests that the effect of this factor on the rate of corrosion is less than the variation that might be expected from one year to another.

(viii) Tests in Nigeria have shown that steel is heavily corroded on a surf beach, but that corrosion decreases rapidly on proceeding inland. Rusting at a site half a mile from the surf line was less than one-tenth of that at a site 200 yards from it.

(ix) Further evidence of the importance of traces of copper in iron or steel in determining the rate of atmospheric rusting has been obtained in collaborative tests with American investigators. As the copper content of ingot iron cannot be controlled with the necessary degree of accuracy, copper–steel is now used instead of ingot iron for the ferrous reference specimens in the Corrosion Committee's tests. The copper–steel contains about $0\cdot3\%$ of copper; small differences in this copper content will not affect its resistance to corrosion within the experimental error.

(x) Failure to stir Clarke's solution when derusting ingot iron or copper–steel does not affect the efficiency of the derusting process.

References

1 'The Investigation of Atmospheric Pollution', 1948, The Fuel Research Station, Department of Scientific and Industrial Research (London : H.M.S.O.)

2 Copson, H. R., *Proc. Amer. Soc. Test. Mater.*, 1945, **45**, 554

3 Schikorr, G., *Arch. Metallk.*, 1948, **2**, (7), 223