Corrosion Data

Table 16-1 Dissociation constants of weak elecolytes at 35°C

Reaction	*K*
$H_3BO_3=H^++H_2BO_3^-$	$5.79\times10^{-}$
$H_2CO_3=H^++HCO_3^-$	4.45×10^{-7}
$HCO_2^-=H^++CO_3^{--}$	4.69×10^{-11}
$HCOOH=H^++HCOO^-$	1.77×10^{-4}
$H_2C_2O_4=H^++HC_2O_4^-$	5.9×10^{-2}
$HC_2O_4^-=H^++C_2O_4^{--}$	5.18×10^{-5}
$HCN=H^++CN^-$	4×10^{-10}
$HClO=H^++ClO^-$	5.6×10^{-8}
$HCrO_4^-=H^++CrO_4^{--}$	3.2×10^{-7}
$Cr_2O_7^{--}+H_2O=2HCrO_4^-$	2.3×10^{-2}
$HNO_2=H^++NO_2^-$	4.5×10^{-4}
$NH_4OH=NH_4^++OH^-$	1.81×10^{-5}
$H_2O=H^++OH^-$	1.008×10^{-14}
$H_2O_2=H^++HOO^-$	2.4×10^{-12}
$H_3PO_4=H^++H_2PO_4^-$	7.52×10^{-3}
$H_2PO_4^-=H^++HPO_4^{--}$	6.22×10^{-3}
$HPO_4^{--}=H^++PO^{4---}$	1×10^{-12}
$H_2SiO_3=H^++HSiO_3^-$	1×10^{-10}
$HSiO_3^-=H^++SiO_3^{--}$	1×10^{-1}[illegible]
$H_2S=H^++HS^-$	1.15×10^{-7}
$HS^-=H^++S^{--}$	1.0×10^{-1}[illegible]
$H_2SO_3=H^++HSO_3^-$	1.72×10^{-2}
$HSO_3^-=H^++SO_3^{--}$	6.24×10^{-3}
$HSO_4^-=H^++SO_4^{--}$	1.01×10^{-2}
$CH_3COOH=H^++CH_3COO^-$	1.76×10^{-5}

Table 16-2 Dissociation constants of some weak electrolytes as a function of temperature

Reaction	Experimental Temperature Range, °C	*A*	*B*	*C*
$H_3BO_3=H^++H_2BO_3^-$	5 to 50	−2193.55	3.0395	−0.016499
$HCO_3^-=H^++CO_3^{--}$	0 to 50	−2902.39	6.4980	−0.02379
$HCOOH=H^++HCOO^-$	0 to 60	−1342.85	5.2744	−0.0151682
$HC_2O_4^-=H^++C_2O_4^{--}$	0 to 50	−1539.31	7.1966	−0.021200
$H_2O=H^+-OH^-$	0 to 300	−4470.99	6.0875	−0.017060
$H_3PO_4=H^++H_2PO_4^-$	0 to 50	−1264.51	7.6601	−0.018590
$H_2PO_4^-=H^-HPO_4^{--}$	5 to 50	−1648.88	3.2542	−0.016534
$CH_3COOH=H^++CH_3COO^-$	0 to 60	−1170.48	3.1649	−0.013399

The constants *A*, *B*, and *C*, on being inserted in the equation

$$\log_{10}K=\frac{A}{T}+B+CT$$

will give *K* as a function of *T*, where *T*=deg. Kelvin (deg. C+273.1°). From H.S. Harned and B. B. Owen, *The Physical Chemistry of Electrolytic Solutions*, American Chemical Society Monograph 95, Reinhold Publishing Corp., New York, 1943.

t°C	$H_2CO_3=H^++HCO_3^-$ * *K*	$HSO_4^-=H^++SO_4^{--}$ + *K*	*t*°C	$NH_4OH=OH^-+NH_4^+$ ‡ *K*
0	2.647×10^{-7}	....	18	1.72×10^{-5}
5	3.040×10^{-7}	1.80×10^{-2}	25	1.81×10^{-5}
10	3.430×10^{-7}	....	51	1.81×10^{-5}
15	3.802×10^{-7}	1.36×10^{-2}	75.2	1.64×10^{-5}
20	4.147×10^{-7}	....	100	1.35×10^{-5}
25	4.452×10^{-7}	1.01×10^{-2}	124.8	1.04×10^{-5}
30	4.710×10^{-7}	....	156	0.63×10^{-5}
35	4.914×10^{-7}	0.75×10^{-2}	218	0.18×10^{-5}
40	5.058×10^{-7}	....	306	0.0093×10^{-5}

45	5.139×10^{-7}	0.56×10^{-2}		
50	5.161×10^{-7}	....		
55	....	0.41×10^{-2}		

* H.S. Harned and R. Davis, Jr., *J. Am. Chem. Soc.*, **65**, 2030 (1943).

† H.S. Harned and B.B.Owen, *The Physical Chemistry* of *Electrolytic Solutions*, American Chemical Society Monograph 95, Reinhold Publishing Corp., New York, 1943.

‡ A. Noyes and Y. Kato, *Carnegie Inst.*, *Publ.* **63**, 178 (1907). R.B. Sosman, *op. cit.*, p. 228

Table 17. Spontaneity of common corrosion reactions*

Metal	Solid Product†	Hyerogen-Type‡ Corrosion, $p.H_2=1.0$atm. E (volt)	ΔF per gram atom Metal, gram cal	Oxygen-Type§ Corrosion, $p\cdot O_2=0.21$ atm. E (volt)	ΔF per gram atom Metal, gram cal
Mg	$Mg(OH)_2$	+1.823	−84,000	+3.042	−140,000
Al	$Al(OH)_3$(?)	+1.48	−102,600	+2.70	−180,700
Mn	$Mn(OH)_2$	+0.60	−27,600	+1.81	−83,200
	$Mn(OH)_2$	+0.256	−17,700	+1.50	−10,000
	MnO_2	−0.14	+12,700	+1.11	−101,000
Cr	$Cr(OH)_3$	+0.47	−32,500	+1.69	−117,000
Zn	$Zn(OH)_2$(?)	+0.417	−19,200	+1.636	−75,200
Fe	Fe_3O_4	+0.082	−5,000	+1.30	−80,000
	$Fe(OH)_2$	+0.049	−2,300	+1.27	−58,500
	$Fe(OH)_3$	−0.07	+4,700	+1.15	−80,000
Cd	$Cd(OH)_2$	−0.013	+600	+1.1206	−55,600
Co	$Co(OH)_2$	−0.098	+4,500	+1.12	−51,700
Ni	$Ni(OH)_2$	−0.17	+7,800	+1.05	−48,500
Pb	PbO(red)	−0.250	+11,500	+0.97	−44,600
Cu	Cu_2O	−0.413	+9,500	+0.80	−18,600
	$Cu(OH)_2$	−0.604	+27,800	+0.615	−28,300
	CuO	−0.537	+24,800	+0.680	−31,500
Hg	HgO	−0.926	+42,600	+0.293	−13,600
	Hg_2O	−0.951	+21,970	+0.268	−6,200
Ag	Ag_2O	−1.172	+27,000	+0.047	−1,100

* R. Brown, B. Roetheli, and H. Forrest, *Ind. Eng. Chem.*, **23**, 350 (1931) probably were the first investigatiors to attempt a summary of this type. They also used the terms *Hydrogen Type* and *Oxygen Type* in the same (cf. definitions below). For a more detailed discussion of these data, see J.C. Warner, *Trans. Electrochem. Soc.*, **83**, 319 (1943).

† Except when the formula is followed by(?), the data are quite certainly for the formation of the solid corrosion product as indicated. The formulas given do not, in any case, attempt to indicate the extent of hydration of the solid phase.

‡ The data in the column under "Hydrogen-Type Corrosion" are for reactions of the type

$$M(s)+2H_2O(l)=M(OH)_2(s)+H_2(g,\ 1\ \text{atm.})$$

or

$$M(s)+H_2O(l)=MO(s)+H_2(g,\ 1\ \text{atm.})$$

where s=solid, l=liquid, and g=gas.

The potentials given are the reversible potentials for the galvanic corrosion cells, in which the anode and cathode reations add up to the overall corrosion reactions, thus:

$$\begin{array}{l} \text{Andode: } Zn(s)+2OH^- = Zn(OH)_2(s)+2e^- \\ \text{Cathode: } 2H_2O(l)+2e^- = 2OH^- + H_2(g,\ 1\ \text{atm.}) \\ \hline \text{Total: } Zn(s)+2H_2O(l)+Zn(OH)_2(s)+H_2(g,\ 1\ \text{atm.}) \end{array}$$

A positive value for E or a negative value for ΔF corresponds to a spontaneous reaction. This follows the convention

$$\Delta F = -nFE$$

where F=Faraday (96, 501 coulombs), E=emf, and n=number of electrons (equivalents) taking part in the reaction.

§ In the columns under "Oxygen-Type Corrosion" the data are for reactions of the type

$$M(s)+H_2O(l)+1/2O_2(g,\ p=0.21\ \text{atm.}) = M(OH)_2(s)$$

or

$$M(s)+1/2O_2'(g,\ p=0.21\ \text{atm.}) = MO(s)$$

The data have been calculated for these reactions with O_2 at a partial pressure of 0.21 atmosphere because this is approximately the partial pressure of O_2 in dry air under a total pressure of one atmosphere.

Table 18. Galvanic Series for High Purity Metals (69 Days in Sea Water at Key West, Florida)

Metal	Metal Purity (%)	Median Potential (Volts) SCE Reference
(Cathodic)		
Palladium	99. 99+	+0. 308
Platinum	99. 99+	+0. 295
Titanium	Iodide(zone refined)	+0. 200
Tantalum	99. 9	+0. 195
Gold	99. 97+	+0. 175
Columbium	99. 9	+0. 110
(Niobium)		
Zirconium	99. 9	+0. 010
Silver	99. 95	−0. 025
Nickel	99. 99+ (zoner refined)	−0. 038
Siver	99. 999	−0. 115
Copper	99. 99+ (zone refined)	−0. 141
Nickel	99. 99− (zone refined)	−0. 172
Tantalum	99. 99+ (zone refined)	−0. 172
Molybdenum	99. 9	−0. 173
Vanadium	99. 99+ (zone refined)	−0. 209
Tungsten	99. 9	−0. 240
Bismuth	99. 9	−0. 248
Indium	99. 999(specrographic grade)	−0. 368
	Rerun	−0. 525
Tin	99. 999(spectrographic grade)	−0. 671
Iron	99. 9+ (elecrolytic grade)	−0. 749
Alumium	99. 99+ (zone refined)	−1. 472
(Anodic)	99. 99+ (ingot)	−1. 455

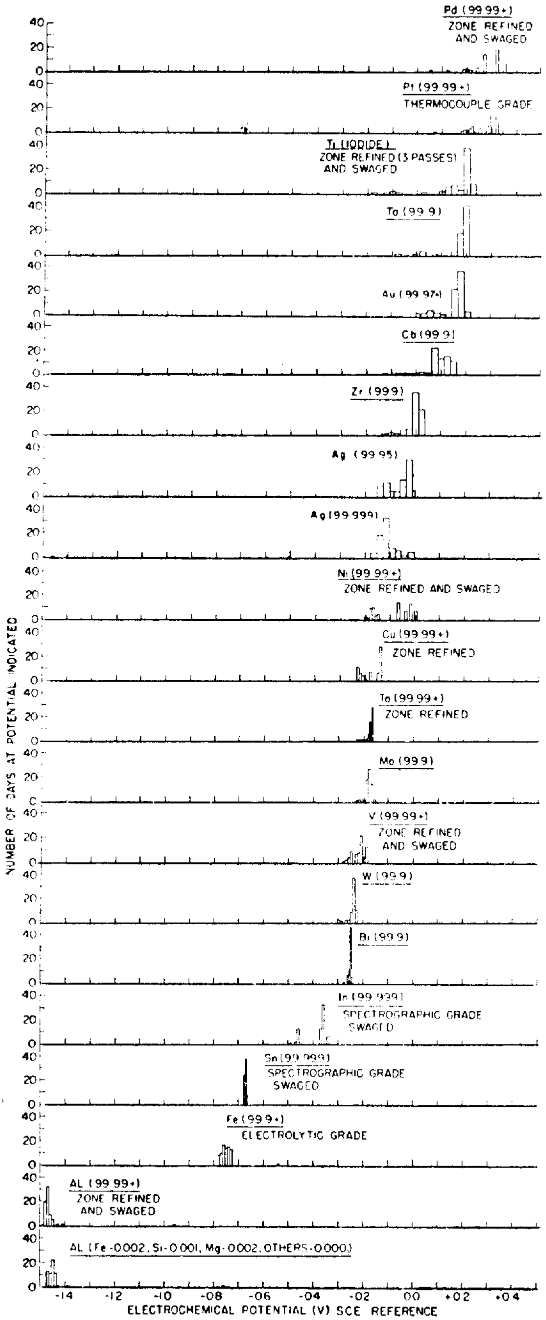

Fig. 1 Histograms of the eletrochemical potentials for high purity metals exposed 69 days in quiescent sea water at Keywest, Florida

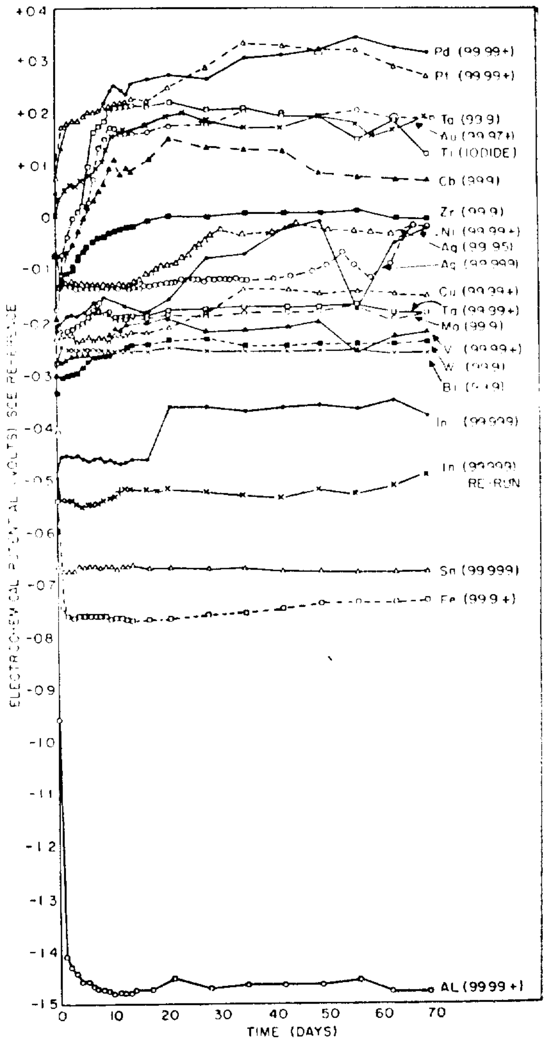

Fig. 2 Electrochemical potentials vs time graphs for high purity metals exposed 69 days in quiescent sea water at key west, Florida

Table. 19-1 Paints used for atmospheric tests The paint code names are also used for immersion and other tests

Priming paints

Code	Description
UNMOD PTP	Pretreatment primer (unmodified), to 'Bakelite' formula W.P.I.
MOD PTP	Pretreatment primer (modified), to the 'Bakelite' modification of formula W.P.I.
ZN CHROME	Zinc chromate in a linseed in a linseed-tung phenolic medium, to D.E.F. specification No. 1039
CA PLUMBATE	Calcium plumbate in oil to B.S. 3698: 1964 Type A
CL RUBBER	Chlorinated rubber sealer (unpigmented)
RED OXIDE	Red oxide in oil, to B.S. 2524: 1954
AL BITUMEN	Aluminium in a blown bitumen solution
RED LEAD A	Red lead in oil to B.S. 2523: 1594 Type A
ZN RICH EPOXIDE	Zinc-rich in an epoxy-polyamide medium, to the 'Shell' formula. TB/RES/154/1

Finishing paints

Code	Description
MIO	Micaceous iron oxide in a long-oil tungpgenolic medium, to B.T.C. Specification No. 35, items 61, 62 and 63
RT ALKYD	Rutile titanium dioxide in a long-oil alkyd medium, to D.E.F. 1156
AL BITUMEN	Aluminium in bitumen (as primer above)
AL TUNG	Aluminium in a tung-phenolic medium to C.S. 2686
C-T EPOXIDE	Coal-tar epoxide paint No. 834 to the 'Shell' formula TB/RES/136/1

Table 19-2 Condition after 5 years' exposure of the painted bare steel specimens in the atmosphere

Condition of paint
- A In good condition
- B Beginning to fail (should be repainted)
- C Overdue for repainting
- D Failed (some loss of basis sleel)

Cause of failure
- (R) Rust
- (E) Chalking and/or erosion

Paint scheme (for paint code sec **Table 1**)		tatford	Shoreham	Osu*
		Industrial	Industrial/marine	Tropical/surf
A15	UNMOD PTP, ZN CHROME, 2 coats MIO	A	C(R)	C(R
		A	B(R)	C(R
A19	2 coats RED LEAD A, 2 coats RT ALKYD	A	B(R)	D(R
		A	C(R)	D(R
A20	ZN RICH EPOXIDE, 2 coats C-T EPOXIDE	A	B(R)	C(R
		A	B(R)	C(R

Note: A20 is identical with S11 *$4\frac{1}{2}$ years' exposure at Osu

Table 19-3 Condition after 5 years' atmospheric exposure of paint schemes applied over sprayed metal coatings

Condition of paint
A-In good condition　B-Beginning to fail(should be repainted)　C-Overdue for repainting　D-Failed(some loss of of basis steel)
Cause of failure
Bl-blisters　Cr-cracing　Cp-corrosion products　Fl flaking　R-rust

	Paint scheme (for paint code see **Table I**)	'Normal' schemes								Variants																			
										One less finishing coat						Metal-sprayed, then left damp overnight				Metal-sprayed, then weathered for 6 months before priming				6 months' weathering after priming					
		Stratford Industrial			Shoreham Industrial marine			Osu+ Tropical surf		Stratford Industrial			Shoreham Industrial marine			Stratford Industrial		Shoreham Industrial marine		Stratford Industial		Shoreham Industrial marine		Stratford Industrial		Shoreham Industrial marine		Osu+ Tropical surf	
		Al	Zn	All-oy	Al	Zn	All-oy	Al	Zn	Al	Zn	All-oy	Al	Zn	All-oy	Al	Zn	Al	Zn	Al	Zn	Al	Zn	Al	Zn	Al	Zn	Al	Zn
A1	3 coats AL BITUMEN									CCp CCp	BCp BCp		CCr A	CCr BBl															
A2	2 coats AL TUNG	A A																											
A3	2 coats MIO	A A			A A															A A		A A							
A4	2 coats RT ALKYD	A A			A A															A A		A A							
A5	UNMOD PTP 3 coats MIO	A A	A A		A A	A A				A A	A A	A A	A A	A A	A A	A A		A A						A A	A A	A A	A A		
A6	UNMOD PTP. 3 coats RT ALKYD	A A	A A		A A	C*Cr C*Cr				A A	A A	A A	A A	CCr CCr	A A	A A		A A					C+Cr C+Cr	A A	A A	BBr A	CCr CCr		
A7	ZN CHROME, 2 coats MIO	A A	A A		A A	CBl BBl		A A	DCp DCp							A A	A A	A A	BBl BBl	A A	A A	A A	A A	A A	A A	A A	CBl CFl	A A	D D
A8	ZN CHROME. 2 coats RT ALKYD	A A	A A		A* A*	CCr BCr		BFl BFl	DCp DCp	A A	A A		A A	CCr CCr		A A	A BCr	A A	CFl CCr	A A	A A	A* A*	C*Cr C*Cr	A A	CFl CFl	BBl BBl	CCr CCr	B B	D D
A9	CL RUBBER. 2 coats MIO	A A	A A		A A	BBl BBl		A A	CCp CCp							A A	A A	A A	BBl BBl					A A	A A			B B	D D
A10	CL RUBBER. 2 coats RT ALKYD	A A	A A		A* A*	CCr CCr		BFl BFl	DCp CCp							A A	A A	A A	BCr BCr			B+Bl B+Bl		A A	A CFl			B B	D D
A11	RED OXIDE. 2 coats MIO	A A	A A	A A	A A	CCr BBl	A A									A A				A A		A A		A A		A A			
A12	RED OXIDE. 2 coats RT ALKYD	A A	A A		BBl BBl	CCr CCr										A A				A A		A A		A A		BCr BCr			
A13	MOD PTP. 2 coats MIO					BBl BR			DCp CCp																		BBl BBl		D D
A14	MOD PTP, 2 coats RT ALKYD					BBl A			DCp DCp																		CCr BCr		D D
A15	UNMOD PTP. ZN CHROME. 2 coats MIO		A A			A A			CCp DCp																				
A16	UNMOD PTP, ZN CHROME. 2 coats RT ALKYD		A A			CCr CCr			DCp CCp								A A				A A		CCr CCr						
A17	CA PLUMBATE, 2 coats MIO		A A														A A				A A				A A				
A18	CA PLUMBATE, 2 coats RT ALKYD		BBl A														BBl BBl				A BBl				A A				

Notes: Underlined results relate to condition after 4 years(repainting trials)　+Exposure at Osu 4 1/2 years　*Metal coating thickness 2, 4 & 6
Metal coating thickess 2 & 6 mils(all others 4 mils)

Table 19-4 Condition after 5 years' immersion of paint schemes apliped over sprayed metal coatings

Condition of paint
A In good condition
B Beginning to fail (should be repainted)
C Overdue for repainting
D Failed (some loss of basis steel)

Cause of failure
Bl Blisters
Cr Cracking
Cp Corrosion product
E Erosion
Fl Flaking

	Paint scheme (for paint code see **Table 1**)	'Normal' schemes						Variants							
								Metal-sprayed, then weathered for 6 months before priming				Weathered for 6 months after priming			
		Brighton Pier			Avon Dam			Brighton Pier		Avon Dam		Brighton Pier		Avon Dam	
		Half-tide immersion			Full immersion			Half-tide immersion		Full immersion		Half-tide immersion		Full immersion	
		Al	Zn	Alloy	Al	Zn	Alloy	Al	Zn	Al	Zn	Al	Zn	Al	Zn
S1	CL RUBBER—3 coats chlorinated rubber	BCp			A A	A									
S2	MOD PTP—3 coats chlorinated rubber	BCp	A		A	A									
S3	3 coats aluminium/vinyl-copolymer	A			A										
S4	MOD PTP—3 coats aluminium/vinyl-copolymer	A	A	BFl	A A	A A	A A					A	A	A A	A A
S5	ZN CHROME—2 coats MIO	CFl	BCp												
S6	MOD PTP—ZN CHROME—2 coats MIO	A	CFl												
S7	MOD PTP—ZN CHROME—2 coats micaceous iron oxide/polyurethane	A	CFl	A	A A	A A	A A	A	A	CBl CBl	CBl CBl		CFl		CBl CBl
S8	3 coats AL TUNG	A			A A										
S9	3 coats AL BITUMEN	A	BCp		A A	A A	A A								
S10	MOD PTP—3 coats BISRA paint No. 655	CE	CE					CE	CE			CE	CE		
S13	2 coats C-T EPOXIDE	A	BBl	BFl				CFl	CFl						

Notes: The chlorinated rubber systems in S1, S2 and S12 (**Table 24**) were the same
The aluminium/vinyl copolymer systems in S3 & S4 were the same
BISRA 655 (in S10) is aluminium/basic lead sulphate/iron oxide in a linseed-tung-phenolic medium

Table 19-5 Condition after 5 years' exposure of the painted bare steel specimens in the immersion test

Condition of paint
A　In good condition
B　Beginning to fail (should be repainted)
C　Overdue for repainting
D　Failed (some loss of basis steel)

Cause of failure
(R)　Rust
(E)　Chalking and/or erosion

Paint scheme (for paint code sec **Table 1**)	Brighton Pier	Avon Dam
	Half-tide immersion	Full immersion
MOD PTP, 3 coats BISRA 655	C(E)	A
	—	A
S11 ZN RICH EPOXIDE, 2 coats C-T EPOXIDE	A	A
	—	A
4-coat chlorinated rubber system(primer zinc-rich)	A	A
	—	A

Table 19-6 Condition after 5 years of the meatl coatings bare at all sites

Condition of coating
A　In good condition
B　Beginning to fail
D　Failed (Some loss of basis steel)

Cause of failure
(R)　Rust

Metal coating, 4 mil minimum (100 microns)	Stratford	shoreham	Osu*	Brighton Pier	Avon Dam
	industrial	Industrial/marinc	Tropical/surf	Half-tide immersion	Full immersion
Aluminium	A	A	A	B	A
	A	A	A	—	A
inc	A	A	D(R)	D(R)	D(R)
	A	A	D(R)	—	D(R)
Zinc/aluminium alloy	A	A	—	—	—
	A	A	—	—	—

*4½ years' exposure at Osu