PhD Thesis

CONTAMINATION OF POTABLE WATER BY CORROSION OF

TIN-LEAD SOLDERED JOINTS

by

R J OLIPHANT

August 1983

5919183

ProQuest Number: 27696236

All rights reserved

INFORMATION TO ALL USERS

The quality of this reproduction is dependent upon the quality of the copy submitted.

In the unlikely event that the author did not send a complete manuscript and there are missing pages, these will be noted. Also, if material had to be removed, a note will indicate the deletion.

ProQuest 27696236

Published by ProQuest LLC (2019). Copyright of the Dissertation is held by the Author.

All rights reserved.

This work is protected against unauthorized copying under Title 17, United States Code
Microform Edition © ProQuest LLC.

ProQuest LLC.
789 East Eisenhower Parkway
P.O. Box 1346
Ann Arbor, MI 48106 – 1346

All the great struggles of history have been won by superior will-power
wresting victory in the teeth of odds or upon the narrowest of margins.

Winston S Churchill*

* History of the Second World War, Volume III
Published by Cassell and Co Ltd 1959
Quoted with permission of the publishers

SUMMARY

This work was undertaken as part of a contract from the Department of the Environment to investigate the potential of materials used in plumbing systems to contaminate the supply. Particular attention was paid to soldered joints as these will constitute the major source of lead contamination in the future.

This report describes a galvanic corrosion cell for measuring corrosion rates of solder in potable waters and the work to establish that its corrosion behaviour reflected that of an authentic soldered joint.

The work has established that more than a quantitative difference exists between the galvanically mediated corrosion of lead and that of the freely corroding metal. Qualitative differences also occur that are of significance to the Water Industry's treatment approach to reduce lead contamination problems.

The test cell was used to investigate the effect of various water quality parameters on corrosion rates. The parameters found to stimulate corrosion were low pH and high chloride and nitrate concentrations.

Sulphate, silicate and zinc were all found to reduce corrosion. Zinc was discovered to be an inhibitor from an investigation into the effect of flux residues. The material used contained zinc chloride as the active ingredient.

Carbonate hardness and orthophosphate were both found to be without effect on corrosion rates. This was surprising, especially as the latter is successfully used to overcome contamination problems from lead pipe.

Using the corrosion rates measured in this work, attempts were made to quantify the contamination risk from soldered joints. The general conclusion was that only by limiting the area of solder exposed in the bore of the tube could a significant long term problem be avoided. As this depends upon the individual skill of the person making the joint, the only sure way of avoiding contamination is to specify lead free solders.

ACKNOWLEDGEMENTS

I wish to thank the Department of the Environment, who financed this work, for giving permission for the final report to be submitted as a PhD thesis to the University of Surrey.

I also wish to express thanks to the analytical section at the WRC, for the lead analyses and the information on the techniques used. Similarly to my supervisors, Dr R F Stokes (WRC), Dr R Walker and Professor M B Waldron (University of Surrey), for useful discussion on many of the points raised by this work. Also to members of the research staff at the University, Mrs G Gibbs, Mr R West, Mr J Watts and Mr S Greaves, for their work on the identification of various corrosion product films. Finally my thanks to the members of the drawing office for the diagrams and photographs, and to the many secretaries who typed the manuscript, for their perseverance in the production of this thesis.

CONTENTS

PAGE

SUMMARY

ACKNOWLEDGEMENTS

1. INTRODUCTION	1
1.1 THE HISTORY	1
1.2 THE PROBLEM	3
1.3 THE CONTRACTS	4
2. LITERATURE SURVEY	
2.1 PHYSICAL AND MECHANICAL PROPERTIES OF SOFT SOLDERS	6
2.2 CORROSION OF LEAD, TIN AND SOLDER IN AQUEOUS MEDIA	7
2.2.1 Corrosion of lead	8
2.2.2 Corrosion of tin	8
2.2.3 Corrosion of soft solders	9
2.3 REPORTS OF LEAD CONTAMINATION FROM SOLDERED JOINTS	10
2.4 EXPERIMENTAL METHODS FOR STUDYING CORROSION IN AQUEOUS SOLUTIONS	12
2.4.1 Electrochemical potential measurements	13
2.4.2 Linear polarization techniques	17
2.4.3 A-C impedance techniques	21
2.4.4 Bimetallic corrosion techniques (galvanic couples)	23
2.5 LABORATORY WORK ON CONTAMINATION PROBLEMS FROM SOLDERED JOINTS	26
2.6 CORROSION INHIBITORS IN AQUEOUS SOLUTIONS	31
2.6.1 Mechanisms of inhibitor action	31
(a) Acid solutions	31
(b) Near neutral solutions	32
2.6.2 Corrosion inhibitors used in potable water supplies	36
2.7 WATER TREATMENTS USED TO OVERCOME LEAD CONTAMINATION PROBLEMS	38

3. EXPERIMENTAL	41
3.1 DETAILS AND MANUFACTURE OF THE GALVANIC CELL	41
3.2 THE OPERATIONAL PROCEDURES WITH GALVANIC CELLS - THE CORROSION TRACE	42
3.2.1 Corrosion under static conditions	43
3.2.2 Corrosion under flowing conditions	43
3.2.3 Modified method for flowing conditions	44
3.2.4 The corrosion trace	44
3.3 POLARIZATION MEASUREMENT - EVANS DIAGRAMS	45
3.4 REMOVAL OF CORROSION PRODUCT FROM ANODIC SURFACES	46
3.5 MEASUREMENT OF THE INTERNAL SOLUTION RESISTANCE IN THE GALVANIC CELL	47
3.6 PREPARATION OF TEST SOLUTIONS	47
3.7 EXAMINATION OF CORROSION DEPOSITS	47
3.7.1 X-ray examination	48
3.7.2 Electron Spectroscopy Chemical Analysis (ESCA)	48
3.7.3 Scanning Electron Microscopy (SEM)	48
3.8 METHODS OF LEAD ANALYSIS	49
4. RESULTS	50
4.1 THE PHYSICAL CHEMICAL CHARACTERISTICS OF THE GALVANIC CELL AND THE VALIDITY OF USING THE GALVANIC CURRENT AS A MEASURE OF THE CORROSION RATE	50
4.1.1 Polarization studies	50
4.1.2 Determination of the significance of solution resistance in the galvanic cell	52
4.1.3 Effect of anodic area in determining galvanic current	53
4.1.4 Effect of temperature	53
4.1.5 Effect of flow rate	54
4.1.6 Relationship between the quantity of lead corroded and the galvanic current	55
4.1.7 Relationship between the quantity of lead contaminating the solution and the galvanic current	56

4.1.8	Variability in the results	57
4.1.9	The long term corrosion rates of galvanic couples	58
4.1.10	Comparison of galvanic corrosion rates with those for uncoupled lead	59
4.2	EFFECT OF WATER QUALITY PARAMETERS ON GALVANIC CORROSION	59
4.2.1	Effect of pH	60
4.2.2	Effect of carbonate hardness	61
4.2.3	Effect of chloride	61
4.2.4	Effect of sulphate	61
4.2.5	Effect of nitrate	62
4.2.6	Effect of sodium ion	62
4.2.7	Effect of corrosion inhibitors	
	(a) Effect of silicate	63
	(b) Effect of orthophosphate	64
4.2.8	Effect of flux	64
4.3	MECHANISM OF SOLDER CORROSION INHIBITION IN POTABLE WATERS	66
4.3.1	Production of an insoluble corrosion product layer as a controlling mechanism	67
4.3.1.1	Effect of carbonate hardness at pH6	67
4.3.1.2	Analysis of the corrosion product on solder electrodes	68
	(a) X-ray analysis	68
	(b) ESCA examinations	68
4.3.2	Changing the physical form of the corrosion product as a controlling mechanism	69
4.3.2.1	Precipitation of colloidal material	70
	(a) Effect on corrosion of high orthophosphate concentration	71
	(b) Detection of colloidal species in an aggressive solution by the Tyndall effect	71

4.3.2.2	Change in physical form of the corrosion deposit	
(a)	Examination of corrosion products by SEM	73
(b)	The corrosion of lead when not galvanically coupled	73
4.3.3	Inhibition of the cathodic reaction as a controlling mechanism	74
5.	DISCUSSION	75
5.1	CHOICE OF EXPERIMENTAL METHOD	75
5.2	THE COMPARABILITY, REVEALED BY THE POLARIZATION STUDIES, BETWEEN THE CORROSION BEHAVIOUR OF THE GALVANIC TEST CELL AND THAT OF A SOLDERED JOINT	77
5.3	RELATIONSHIP BETWEEN THE GALVANIC CURRENT AND THE LEVEL OF LEAD CONTAMINATION	82
5.4	VARIABILITY BETWEEN REPLICATES	86
5.5	THE VALUE OF SHORT TERM CORROSION TESTS TO PREDICT LONG TERM CORROSION BEHAVIOUR	87
5.6	COMPARISON OF GALVANICALLY MEDIATED CORROSION OF LEAD AND SOLDER WITH FREELY CORRODING LEAD PIPE	88
5.7	EFFECT OF WATER QUALITY PARAMETERS ON GALVANIC CORROSION RATES	90
5.8	MECHANISMS OF SOLDER CORROSION INHIBITION IN POTABLE WATERS	93
	(a) Effect of silicate	94
	(b) Effect of sulphate	95
	(c) Effect of zinc	97
5.9	ASSESSING THE LIKELIHOOD OF CONTAMINATION FROM SOLDERED JOINTS	98
5.9.1	Corrosion rate	99
	(a) Effect on corrosion rate of area of solder exposed	99
	(b) Long term corrosion rates	100
	(c) Effect of flow rate	100
	(d) Effect of the external resistance	100
5.9.2	Volume of water per joint	101

5.9.3	Choice of temperature	101
5.9.4	The calculations	101
5.9.5	Consequences	104
6.	CONCLUSIONS	108
REFERENCES		
APPENDICES		
TABLES		
FIGURES		
PHOTOGRAPHS		
PUBLISHED PAPERS		

1. INTRODUCTION

This work concerns the contamination of potable water by lead arising from the corrosion of tin-lead soft solders used in capillary fittings to join copper tubes. Soft solders are characterised as having melting points below 427°C (800°F)⁽¹⁾ and in the United Kingdom have compositions specified by a British Standard⁽²⁾. Alloys with melting points above 538°C (1000°F) are known as brazing alloys, the low temperature brazing alloys often being termed 'hard solders'. Soldering and brazing share the characteristic that the alloy used as the filler material in the joint has a melting point lower than that of the metal sections being joined.

1.1 THE HISTORY

The earliest example of soldering, at present known, are hard soldered objects (silver with copper) from the Royal Graves of Ur in Mesopotamia of ca. 3,400 BC⁽³⁾. Soft soldering appeared sometime before 2,500 BC. The Greeks and Etruscans were producing soldered articles by the sixth century BC.

Isaiah (ca. the period 900-500BC) contains a reference to soldering, i.e. soldering, CH.41 v.7, but this is believed to be misleading, it having arisen from a 1611 AD metaphorical translation of the Hebraic work 'devek', which means to bond, join or fasten⁽⁴⁾. The word 'solder' comes from the Latin *solidare*, to make firm. In the Norman French, and later English derivatives, the 'l' was frequently dropped so that the 19th century English word was pronounced 'sodder' (which is still the term used in the United States today). The word was never limited solely to metallurgy, it being employed metaphorically to mean to bind, fasten or make solid (its original meaning). Thus Isaiah does not appear to be the earliest literary record concerning solders for, although his carpenter, goldsmith and 'he that smootheth with the hammer' were indeed soldering, they seem to have been using nails⁽⁴⁾.

The earliest indubitable reference to soft-soldering appears in the poem by Lucretius⁽⁵⁾ (ca. 90-50 BC) where he talks of joining copper to copper using tin. References also appear in Pliny's Natural History (76AD). The *Mappae Clavicula*⁽⁶⁾ (ca. 825 AD) is one of the earliest formularies, i.e. collection of useful chemical recipes, to contain information on solders. It describes a 'tin glue' made by mixing two parts tin to one of lead. A technical manual on soldering, describing how to make organ pipes and leaded lights, was written about 1025AD in North Germany by a monk using the pen-name Theophilus⁽⁷⁾. It includes the first mention of the use of a soldering iron, which was indeed at that time made of iron and not copper.

Soft soldering has been used in the plumbing trade from earliest times. The Romans made their water pipes by bending sheet lead over a mandrel and securing the seam with soft solder⁽³⁾, precisely the method used to make organ pipes⁽⁴⁾. The arms of the Worshipful Company of Plumbers, granted in 1588, contain two soldering irons⁽⁴⁾. Since 1700 soft soldering has been used in ever more diverse trades. James Watt employed a 'white-iron man' or tinsmith to make valves for his improved version of the steam engine⁽⁴⁾, and much later it has found use in electrical equipment and hence the modern electronics and communication industries.

Lead pipe, made in the Roman manner, continued to be the standard way of making water pipes for many hundreds of years⁽⁸⁾. By the time an extrusion process had been patented to provide seamless pipes, by Joseph Bramah in 1797⁽⁹⁾, cast iron had begun to replace lead for water mains⁽¹⁰⁾. Lead, however, continued to be the usual material for service connections and internal plumbing until immediately after the Second World War, when the price became prohibitive^(8,10).

Copper pipes for domestic water services, made from sheet metal, were first used in 1810⁽¹⁰⁾. After 1850 heavy gauge pipes, joined by screw threads, were being used in hospitals and similar institutions. The extrusion of copper alloys was introduced by A.G. Dick in 1894⁽⁹⁾. In 1910 light gauge tube first appeared, using either fine thread or rubber ring jointing. In

1921 the Liverpool Corporation started to use light gauge pipes for both internal and external services. In 1936 the first British Standard for copper pipes was published⁽¹⁰⁾. About the same time, capillary (soldered) and compression fittings for joining copper pipe appeared, and the British Standard covering these⁽¹¹⁾ had its first issue in August 1939⁽¹²⁾.

1.2 THE PROBLEM

Symptoms developed by a man engaged in metal extraction and now attributed to acute lead poisoning had been described by Hippocrates⁽¹³⁾ in 370 BC. In the United Kingdom it was not until 1831 that an association was made between the occupation and health of lead miners⁽¹⁴⁾. The whole problem of industrial lead poisoning was reviewed by Legge and Goadby⁽¹⁵⁾ in 1912, from which statutory legislation followed.

Ingelson has reviewed the long and involved story of the growth of awareness of the problem of lead pick-up arising from the carrying of corrosive water in lead pipes, plumbosolvency⁽¹⁶⁾. By the end of the nineteenth century the concentration of lead above which poisoning could arise was believed to be 1.4 mg l^{-1} ⁽¹⁷⁾. Since that time the 'safe level' has been gradually reduced so that by 1970 it stood at a recommended 0.1 mg Pb l^{-1} , not exceeding 0.3 mg Pb l^{-1} after 16 hours standing in contact with lead pipe⁽¹⁸⁾. Work on the effects of low lead levels over long periods of time, so called sub-clinical effects, suggested that even lower levels were required⁽¹⁹⁾. In the standard for drinking water, issued by the Commission of European Communities in 1980⁽²⁰⁾, a level of $0.05 \text{ mg Pb l}^{-1}$ for a sample of running water was given as the maximum admissible concentration. It also included the rider that, in cases where samples "either frequently or to an appreciable extent exceed 0.1 mg Pb l^{-1} , suitable measures must be taken to reduce the exposure to lead on the part of the consumer".

More information on the changes in standards for lead in water in recent years is given in the Water Research Centre Technical Report 43⁽²¹⁾. Justification for a $0.05 \text{ mg Pb l}^{-1}$ standard is discussed and the different sources of the daily body burden of lead evaluated. The latter indicates

that water containing 0.05mgPb l^{-1} would constitute 40% of the daily body uptake of lead. At 0.1mgPb l^{-1} water is the major source at 55% while at higher levels the percentage increases even more steeply. The Department of the Environment, aware of the possible difficulty of meeting the proposed EC standard, financed a survey of houses of Great Britain in 1977 to determine the scale of the problem⁽²²⁾. This showed that 9% of houses had a first draw sample (i.e. after standing overnight) in excess of 0.1mgPb l^{-1} and 20% were in excess of 0.05mgPb l^{-1} . On average 4.3% of the households would have a daytime sample (i.e. one taken at random during the day without prior flushing) in excess of 0.1mgPb l^{-1} . The results for Scotland considered on their own, however, gave a figure of 21% for random daytime samples in excess of 0.1mgPb l^{-1} , indicative of the corrosive soft supplies commonly found there. The effect on the final lead concentration of the various individual factors has been assessed using regression analysis on the survey results⁽²³⁾.

Evidence has been presented of a correlation between water lead concentrations and blood lead levels⁽²⁴⁻²⁶⁾. The presence of lead in the blood has been shown to affect the activity of the enzyme delta amino laevulinic acid dehydratase (δ -ALAD), which is involved in the conversion of laevulinic acid to porphobilinogen in the normal haem synthesis⁽²⁴⁾. Lead has also been cited as a causative agent in various disorders including hyperactivity⁽²⁷⁾, decreased intelligence^(28,29), hypertension⁽³⁰⁾, mental retardation⁽³¹⁾ and renal failure⁽³²⁾. The apparent correlations between soft water and cardiovascular problems⁽³³⁾, and infant mortality⁽³⁴⁾, have been associated with the presence of lead in the water.

1.3 THE CONTRACTS

Prior to 1980 there was no statutory limit on the substances present in drinking water. The 1973 Water Act laid down that a water supply would be "wholesome,"⁽¹⁷⁾ without any definition of the legal meaning of the word. Water undertakings complied with this part of the act by adopting the World Health Organisation European Standards for drinking water⁽¹⁸⁾.

In the mid 1970's the EC started work on a directive for drinking water and about the same time the Department of the Environment (DoE) placed two research contracts with the Water Research Centre (WRC). The first concerned the development of strategies to comply with the statutory lead level that would be in the EC directive, either by water treatment and/or pipe replacement. The second contract concerned technical support for the committee redrafting the Model Bylaws⁽³⁵⁾.

The work reported here was carried out under the second contract from the DoE. With the ban on the use of lead pipes in new plumbing systems, tin-lead soldered joints now constitute one of the few remaining potential sources of lead contamination still allowed. Further, it was considered that work on contamination arising from soldered joints was necessary to complement the much larger project at the WRC on lead pipes.

2. LITERATURE SURVEY

2.1 PHYSICAL AND MECHANICAL PROPERTIES OF SOFT SOLDERS

Soft solders not only have low melting points but also low mechanical strengths. They are used to provide continuity, either physical, electrical or even thermal, between structures fabricated in materials with much higher melting points and strengths. Tin is the essential element in solders, because of its ability to wet many of the metals required to be joined, e.g. copper, iron, nickel, zinc, and their alloys. The other elements found in solders, either singly or in combinations, include lead, antimony, silver, cadmium and zinc. The compositions of many of these alloys are covered by a British Standard⁽²⁾, and their physical and mechanical properties, as well as their uses, have been reviewed in the literature^(36,37,38).

Tin wets the substrate metals by virtue of van der Waals forces that develop between oxide free surfaces. The latter are produced by using one of a variety of fluxes, ranging from corrosive inorganic halides to mildly reactive wood or gum resins⁽³⁹⁾. The other property of tin is to produce an intermetallic compound with the substrate metal which, although it adds mechanical strength to the joint, can produce brittle failure if the layer becomes too thick. This effect is small with such metals as copper, iron and nickel because of low solubilities and diffusion rates⁽³⁶⁾. The "solderability" of a particular solder/flux/metal system is defined in terms of wettability, or the surface tension between the molten solder and substrate metal, and the time required to make the joint. The former determines how easy it is to obtain a joint free of defects, and the latter the risk of producing a weak joint from intermetallic embrittlement⁽³⁶⁾.

Lead is the second element most commonly used in solders and ranges from 5 to 95% of the alloy composition⁽³⁷⁾. It forms a eutectic with the tin of composition 62%Sn:38%Pb, melting point 183°C. This alloy is called tinmans solder and is particularly useful in soldering electrical connections. Plumbers solder, 40%Sn:60%Pb, has a large solidification range, 183-234°C,

Figure 1, which makes it particularly suitable for the plumbers' traditional wiped lead joint. Alloys of high lead content are used wherever feasible because it is much cheaper than tin.

The shear strength of the most widely used solders are in the range 23-54 MN.m⁻²(36). The highest strengths occur with alloys having high eutectic contents e.g. 60:40Sn/Pb, 50:47.5:2.5Sn/Pb/Sb and 95:5Sn/Ag. Strengths fall with increases in temperature so that above 100°C tin-rich or lead-rich alloys become necessary e.g. 95:5Sn/Sb, 95:5:1.5Pb/Sn/Ag(36). The creep resistance of alloys is an important parameter especially in such applications as high temperature heat exchangers. The creep strengths of alloys containing 40 - 60%Sn are similar and are all increased somewhat by the addition of Sb, Cu or Ag(36). However for substantially higher creep resistances tin-rich alloys of the type 95:5Sn/Ag, 95:5Sn/Sb are required. The fatigue strengths of soldered joints are not easy to define, because creep often accompanies fatigue even at room temperature. This makes the values obtained very dependent upon the frequency of stress reversal and mean stress value. For joints made of tin-lead alloys containing 50-60% Sn, the fatigue strength at 10⁵ reversals, zero mean stress and ambient temperatures, is of the order of 15 MN.m⁻². There seems to be very little variation in this value over the standard composition ranges for solders(36).

2.2 CORROSION OF LEAD, TIN AND SOLDER IN AQUEOUS MEDIA

The present investigation is concerned with a contamination problem arising from a corrosion reaction, rather than with the gross effects of corrosion such as mechanical failure or some other loss of function in the component affected. Further, because the maximum admissible concentration of lead in potable water is so low, see above 1.2, it means that even the excellent corrosion resistances normally found with lead and solders can nevertheless be insufficient, under certain circumstances, to prevent significant contamination of the water.

2.2.1 CORROSION OF LEAD

The Pourbaix diagram for the corrosion of lead in distilled water⁽⁴⁰⁾, Figure 2, indicates the formation of insoluble lead oxides around neutral pH values. This suggests that between pH 5 - 11.5 the metal passivates and corrosion rates will be low. Below pH 5 Pb^{++} becomes the thermodynamically favoured species and, because no insoluble corrosion product is formed, corrosion occurs. Similarly for pH values above 11.5 where the plumbite ion $HPbO_2^-$ becomes the favoured species. The area of passivity can be greatly extended by the presence of anions that have insoluble lead salts, e.g. carbonate, sulphate, etc.⁽⁴⁰⁾ Because most of the common lead salts are insoluble⁽⁴¹⁾, lead will have low corrosion rates in many aqueous environments. Even in some acid solutions rates can be low if the anion produces an insoluble corrosion product e.g. lead in sulphuric acid.

Potable drinking waters have a sufficiently neutral pH and normally contain enough carbonate to result in low corrosion rates with lead. Indeed one of the reasons why lead has been used so extensively for conveying drinking water is that, as well as its ease of working, it has excellent corrosion resistance. The present author has inspected lead pipes that had carried soft water for nearly 100 years in which the corrosion damage was minimal. This same water, however, was classified as "plumbosolvent" and was producing unacceptably high levels of lead in the supply. Thus the corrosion of lead in drinking water, although negligible compared with other metals, is still significant.

2.2.2 CORROSION OF TIN

The Pourbaix diagram for tin⁽⁴²⁾ in pure water, Figure 3, shows an even wider passivation region than is found with lead. Although tin does corrode at low pH values, even here the reaction is slow because of the high hydrogen over-potential. The effect of anions in extending the corrosion resistance of tin is less important than with lead, because rarely is any corrosion product formed other than the oxide. Anions that have soluble tin salts e.g. nitrate, sulphate, chloride and bromide,

produce a pitting attack at breakdown points in this oxide layer. When the tin is electrically coupled to a more noble metal e.g. copper, the intensity of the pitting is increased⁽⁴³⁾.

Because the oxide is the main passivating film formed on tin, the metal has excellent corrosion resistance to distilled water either hot or cold. Similarly, corrosion does not occur with most potable waters. The exceptions to this occur where the carbonate level is low at the same time that chloride, sulphate or nitrate concentrations are high.

2.2.3 CORROSION OF SOFT SOLDERS

The corrosion of solders in soldered joints is very much affected by the geometry of the arrangement and the metal being joined. Normally the area of exposed solder is small so that when the metal being joined is more electropositive than the solder, and the electrolyte being carried has sufficient conductivity, the situation of small anode/large cathode arises and corrosion damage can be severe. Solders are anodic to copper and monel, but cathodic to steel, zinc and cadmium. Where a tin-lead solder is used to join aluminium, a destructive corrosion can occur in the presence of water. This arises from a grain boundary effect in the tin, produced by the diffusion of aluminium into the solder during the fusion process, such that the water produces a severely embrittling intercrystalline attack.

The corrosion resistance of tin-lead solders, in the absence of conditions particularly corrosive to tin, decreases as the proportion of lead in the composition increases. This proportionality is usually not constant across the range. Thus in potable waters the decrease is fairly slow up to a lead content of 70%, however, above this value the resistance falls much more steeply. Preferential corrosion of tin can occur after prolonged contact with solutions of anionic surface active agents⁽⁴³⁾.

A problem particular to soldered joints is corrosion arising from the presence of flux residues. With the active varieties e.g. those based on

acid halides, it is recommended that a workpiece should be washed after assembly, first in water acidified with acid and then in neutral water, to remove the last traces⁽⁴³⁾. Non-aggressive fluxes, based on resins, and others that are only active when hot, are now available to minimise this problem⁽³⁹⁾.

2.3 REPORTS OF LEAD CONTAMINATION FROM SOLDERED JOINTS

Most of the recent literature on lead contamination of potable water has been concerned with the more prevalent problem arising from lead pipes. Many writers, however, have also recognised soldered joints as another potential source of contamination.

Nielsen⁽⁴⁴⁾ reported levels of 10.5mg l⁻¹ cadmium and 2.0mg l⁻¹ lead in water obtained from a laboratory tap at Oslo University, arising from a fitting containing a cadmium based brazing material and tin-lead solder. This led the Danish Corrosion Centre to devise a laboratory test to assess the potential of fittings to contaminate the supply. Under the conditions of this test, water from a tap cock with tin-lead soldered joints picked up in excess of 0.03mg lead in 24 hours. Contamination rates were found, using a slightly simplified test, of 2 µgPb cm⁻² per 24 hours from a 50:50 tin-lead solder, 0.7µgPb cm⁻² per 24 hours from a 2.5% leaded brass and 18µgPb cm⁻² per 24 hours for a 5% leaded gunmetal. It was suggested that these rates would be increased by coupling with more electropositive materials and this was supported by cases of lead poisoning, reported in Sweden, arising from many years of consuming drinking water from a copper tank with soldered joints.

Dangel⁽⁴⁵⁾, in a report on metal pick-up in the distribution system of one of the sources of the Seattle Water Department, found an eightfold increase in lead compared with the concentration at the treatment works, even though no lead pipes were used. Out of a sample of 34 domestic plumbing systems, 3 exceeded 0.1mgPbl⁻¹ on a standing sample. Although "sweat-solder" in copper plumbing was suggested as a possible cause, no attempt was made to verify this.

Karalekas et al⁽⁴⁶⁾, in one of a series of articles concerning lead problems in soft New England waters, gave the results of a survey in which 3.9% of the houses sampled exceeded the lead standard while not having lead pipes. He went on to suggest possible sources of this lead which included badly caulked run lead joints in the mains (he thought this unlikely), tin-lead solders (50:50 alloy was normally used) or leaded bronzes. Although he mentioned the dezincification of brasses, he did not specifically mention leaded brasses as another potential source of the metal.

Britton and Richards⁽⁴⁷⁾, during the period of the present study, reported the case of a plumbing system in a school on the Isle of Arran (Scotland) which had high lead levels, solely from the corrosion of soldered joints, three years after the removal of all lead pipes. Figures as high as 0.7mgPb l^{-1} were achieved on a random daytime sample and many others were above 0.1mgPb l^{-1} . Many of these water samples came from the plumbing in the school kitchens which contained a total of 32 joints.

In their report Britton and Richards⁽⁴⁷⁾ also mentioned previous work⁽¹¹⁰⁾ in Glasgow on the galvanic corrosion of lead pipe at its junction with copper. The latter arose either when short lengths of copper had been inserted to repair the lead pipe, or where they formed part of the internal plumbing of the property. The authors suggested that, if the water was cuprosolvent, copper in solution might plate out on the lead by simple metal exchange and produce local galvanic cells along the whole length of the lead pipe. In their earlier paper⁽¹¹⁰⁾, they suggested that a copper to lead sequence, i.e. lead downstream of a copper section, produced more incidences of high lead levels than the reverse, i.e. when the copper was just prior to the kitchen or dietetic tap and downstream of any lead pipe. In their survey of 195 households in Glasgow, 69 were identified as having at least one copper section upstream of lead pipe. Of these, only 38% (26) yielded satisfactory water samples whereas the figure was 89% for all the other properties⁽⁴⁷⁾.

These authors also reported⁽⁴⁷⁾ work on lead profiles along the length of the service pipe, obtained by taking sequential small volume samples from the tap. Many of these profiles showed unusually high lead levels in the

sample taken from around the lead/copper junction, e.g. samples from the house of one of the authors⁽⁴⁸⁾ gave a lead concentration of $\sim 0.73\text{mgPbl}^{-1}$ at the bimetallic junction whereas the average figure along the rest of the lead pipe was only $\sim 0.17\text{mgPbl}^{-1}$.

A case was reported in Manchester of high lead levels arising from soldered joints⁽⁴⁹⁾ in an eight storey building. The long internal runs of copper pipe in such systems result in the water having long residence times during which warming occurs. That this was happening was supported by the high copper figures also found. Lead levels were as high as 0.4mgPbl^{-1} with many of the other water samples having values in excess of 0.1mgPbl^{-1} . This was not an isolated incidence, similar problems had occurred with infrequently used outlets in plumbing systems that had been in service for more than 16 years.

2.4 EXPERIMENTAL METHODS FOR STUDYING CORROSION IN AQUEOUS SOLUTIONS

In essence, corrosion experiments entail exposing the material of interest under defined conditions followed by the application of some technique to assess the consequence. Where a specific practical problem is being investigated, the exposure conditions most appropriate e.g. environment, temperature, time, etc. are usually obvious. Similarly, of the various methods available for assessing the outcome, e.g. weight loss, pit depths, corrosion rate, loss of mechanical strength, etc. one may be more immediately pertinent to the problem under consideration.

For an investigation into the contamination of potable water from lead solder, aqueous environments covering the range of compositions found in public water supplies, and a temperature found in domestic plumbing systems, are most appropriate. Both static and flowing water conditions are of interest. The most relevant method of assessing the outcome of such exposure, determining the concentration of lead contaminating the test water, is not specifically a corrosion technique at all. Of the corrosion techniques available, those that give the cumulative corrosion damage e.g. weight loss, or the average corrosion rate e.g. weight loss over time, are of limited interest. Techniques that yield corrosion rates at a specific

point in time are more useful, because they can be used to estimate contamination levels. Thus, in this instance, electrochemical methods are the most useful corrosion techniques for supplementing information available by chemical analysis.

The electrochemical techniques used in corrosion experiments include:-

- (a) Electrochemical potential measurements,
- (b) Linear polarization,
- (c) AC impedance,
- (d) Bimetallic (galvanic) couples.

2.4.1 Electrochemical potential measurements

Electrochemical potential is at best an ambiguous guide to corrosion rates. The potential adopted by a metal in an aqueous environment is that at which the total corrosion current produced by the various anodic reactions is balanced by all the current consuming cathodic reactions occurring on the same metal. The electrochemical potential may increase (become more positive) because of an increase in the cathodic reaction rates, which will result in nett increase in corrosion rate, or because of an increase in anodic polarization, which corresponds to a decrease in corrosion rate.

The electrochemical potential is an indication of the chemical reactions occurring at the surface of the electrode and a major shift in its value may denote a change in these of consequence for corrosion. This is often the case for metals that show an active/passive transition e.g. stainless steels. The production of a protective oxide layer greatly reduces the anodic (corrosion) reaction and hence is accompanied by a large increase in the electrochemical potential e.g. +400mV in 20% H₂SO₄ for the martensitic steel 431S29, BS970 0.12%C, 15-18%Cr, 2-3%Ni(50). This phenomenon

can be used in reverse when studying the conditions for film breakdown e.g. the stress corrosion cracking of austenitic stainless steels in boiling saturated MgCl_2 solution studied by Hoar et al⁽⁵¹⁾.

Certain types of corrosion problems result in potential values markedly different from that normally assumed by the metal and so can be used to indicate the presence/absence of such problems. Thus copper undergoing pitting in natural waters assumes potentials of the order 50-150mV above the value in the absence of attack and this has been used to determine the conditions under which this type of corrosion occurs⁽⁵²⁾. This has been studied in detail by Lucey⁽⁵³⁾. The pitting of aluminium in natural waters is similar and has been studied by Wranglen⁽⁵⁴⁾.

The change of potential over time has been used as a measure of susceptibility to corrosion. May⁽⁵⁵⁾ studied the corrosion of 70:30 brass in seawater by determining the length of time required for a scratched surface to reform its oxide layer and the potential to rise back to its original value. More recently Pourbaix⁽⁵⁶⁾ developed a test for the air-weathering of low-alloy steels which involved alternate immersion in water and exposure to air. The potential of the specimens when in the water is monitored over 12 days and the alloys that develop a protective patina achieve electrochemical potentials approximately 200mV higher than those with non-protective rusts.

Pourbaix has also used electrochemical measurements to predict the likely corrosion behaviour of metals in a wide range of aqueous solutions. The results are usually presented as Potential-pH Equilibrium diagrams, commonly called Pourbaix diagrams, and those for lead and tin in pure water are shown in Figures 2 and 3 respectively.

Details of the construction of these types of diagrams can be found in the literature^(57,58). In brief, from thermodynamic considerations of all the chemical interactions possible with the metal/water system, the most stable species, and the range of potential and pH over which it remains such, is determined. The lines, demarcating areas where different species

are the most stable, correspond to the chemical reactions that convert one species to the other. The reactions that involve a change of oxidation state, but no pH term, give horizontal lines on the diagram, e.g.

Those that involve a pH effect, but no change in oxidation state, give vertical lines, e.g.

Reactions involving both a change in oxidation state and a pH term give oblique lines, e.g.

The region of stability of pure water is marked by two parallel lines across the diagram. For aqueous corrosion the species of interest and their interactions lie between these two lines.

Three different types of zone are distinguished on a Pourbaix diagram. A zone of corrosion is where the stable species is the aquo ion so that the metal spontaneously corrodes. The aquo ion concerned is not necessarily cationic, amphoteric metals such as lead and tin have a zone of corrosion at high pH values because of a stable anionic species. A zone of immunity occurs on the diagram where the metal is the most stable species. In this region not only does the metal not corrode, its cationic or anionic species tend to be converted to the free metal. The third zone is a zone of passivity where the stable species is an insoluble salt of the metal e.g. an oxide or hydroxide. If this insoluble salt forms a corrosion product layer on the metal surface, it can be expected to retard the transport of material and hence greatly reduce the reactions occurring. The effectiveness of a particular layer at minimising corrosion rates depends on its solubility in the solution concerned, its adherence to the metal surface and its permeability to ions and electrons. The physical form of the deposit is often important.

The position of the demarcation lines between the different zones depends on the concentration of the metal ion being considered. Pourbaix defined the areas by taking an arbitrary figure of 10^{-6} g ion l^{-1} at equilibrium. Thus in a zone of corrosion the concentration of the metal aquo ion is 10^{-6} g ion l^{-1} or more. In a zone of immunity the concentration of any anions or cations is less than 10^{-6} g ion l^{-1} . In a zone of passivity the ions with which the precipitated salt is in equilibrium are similarly 10^{-6} g ion l^{-1} or less.

The Pourbaix diagrams for both lead and tin, Figures 2 and 3 respectively, suggest that in potable waters both metals have low corrosion rates because of the formation of a passivating film, Section 2.2. These diagrams, however, have their limitations as a predictive tool. They are based on thermodynamic data, which are necessarily concerned with equilibrium conditions, whereas the interest in corrosion is usually the rate of reaction which is a kinetic factor. Also, it is impossible to predict how slow the corrosion reaction is in a zone of passivity. If the salt that is the stable species is formed indirectly, e.g. the corrosion of the metal occurs first and is subsequently followed by precipitation of the metal ions produced, the corrosion product may be formed out of contact with the metal surface and hence cannot stifle the reaction.

The presence of other anions and cations can also greatly alter the size and shape of the various zones, Section 2.2. Finally, a concentration of 10^{-6} g ion l^{-1} of lead represents a concentration of $206 \mu g l^{-1}$, which is more than four times the current EC limit for potable drinking water, so that this level of dissolution of the passivating film is significant. Thus, because of the interest in contamination, the area of "passivity" in the Pourbaix diagram for lead in potable waters needs to be restricted even further.

2.4.2 Linear polarization techniques

Work by Tafel⁽⁵⁹⁾, on the evolution of hydrogen on various metal surfaces by the application of an electric potential, established the empirical equation that now bears his name.

$$\eta_{\pm} = \mp a \pm b \log i \quad \dots 2.1$$

where η is the applied voltage

i is the corrosion current density

a and b are constants.

By considering the kinetics of the anodic reaction that occurs on a metal surface when its potential is increased to above that of its rest potential, it can be shown⁽⁶⁰⁾ that the current density is given by the relationship:

$$i_a = i_0 [\exp [(1-\beta)\eta_a F/RT] - \exp (-\beta\eta_a F/RT)] \quad \dots 2.2$$

where i_a is the anodic current density

i_0 is the exchange current density at the rest potential

η_a is the applied anodic overpotential

β is the symmetry factor

and the other terms have their usual significance.

The exchange current density is numerically equal to both the anodic and cathodic current densities at the rest potential and the former, in the absence of any other oxidisable species, equals the corrosion rate of the metal. The first exponential term in equation 2.2 corresponds to the anodic reaction that occurs on the metal when the potential is raised. The second term corresponds to the reduced cathodic reaction. As the potential is raised, the first term increases exponentially while the second one decreases in the same manner such that at overpotentials $> +0.052V$ the equation simplifies to:

$$i_a = i_o \exp [(1-\beta)\eta_a F/RT] \quad \dots 2.3$$

Similarly for overpotentials more negative than -0.052V

$$i_c = -i_o \exp (-\beta\eta_c F/RT)$$

Taking logarithms of the anodic equation 2.3 gives:

$$\ln i_a = \ln i_o + \frac{(1-\beta)\eta_a F}{RT} \quad \dots 2.4$$

Rearranging this gives:

$$\eta_a = \frac{-RT}{(1-\beta)F} \ln i_o + \frac{RT}{(1-\beta)F} \ln i \quad \dots 2.5$$

and since

$$\frac{RT}{F} \ln x = 0.059 \log x \text{ at } 25^\circ\text{C}$$

$$\text{then } \eta_a = \frac{-0.059}{(1-\beta)} \log i_o + \frac{0.059}{(1-\beta)} \log i \quad \dots 2.6$$

The equation for the cathodic reaction can be shown similarly to be:

$$\eta_c = + \frac{0.059}{\beta} \log i_o - \frac{0.059}{\beta} \log i \quad \dots 2.7$$

These equations are equivalent to the empirical relationship found by Tafel, equation 2.1 above. For values of η outside the range of $\pm 0.052\text{V}$ of the rest potential, a plot of η vs $\log i$ produces a straight line. This can be extrapolated to η_o , the rest potential, to obtain the value of i_o , the exchange current density and the corrosion rate.

For small values of overpotential, $\pm 0.01\text{V}$, where both exponential terms of the equation are significant, the difference between the terms gives a linear portion in the curve. Thus equation 2.2 can be rewritten for this region as:

$$i = i_0 [(1 + (1 - \beta) \eta F/RT) - (1 - \beta) \eta F/RT] \quad \dots 2.8$$

$$\text{or } i = \frac{i_0 F}{RT} \eta \quad \dots 2.9$$

$$\text{or } \frac{i}{\eta} = k \cdot i_0 \quad \dots 2.10$$

where $\frac{i}{\eta}$ is the inverse of the slope of the line around the corrosion potential

k is a constant equal to F/RT

Equation 2.10 is the basic formulae for determining corrosion rates by the linear polarization technique. The term i_0 is an accurate measure of this rate where the dissolution of the metal is the only anodic reaction and activation polarization is the rate controlling step. Other sources of polarization include concentration and resistance polarization. The former (also called diffusion polarization) arises at the anode when a significant concentration of the metal ion builds up at the metal surface, thereby creating a back EMF which retards the reaction. Resistance polarization occurs in electrolytes with low electrical conductivities, this resistance adds to the overpotential by a factor:

$$\eta_{\text{solution}} = i \times R_{\text{solution}} \quad \dots 2.11$$

Descriptions of the apparatus used in linear polarization measurements can be found in the literature⁽⁶¹⁾. In its simplest form the current required to raise or depress the potential of the test metal about its rest potential is determined. The relationship is assumed linear and some expression of the form given in equation 2.10 is used to determine i_0 .

Skold and Larson⁽⁶²⁾ used a linear polarization technique to study the corrosion of cast iron in synthetic and natural waters. They found a relationship between instantaneous corrosion rates, determined from the slope of weight-loss vs time curves, and the reciprocal of the polarization resistance around the rest potential, c.f. equation 2.10. Stum⁽⁶³⁾ has also used the technique in natural waters, to investigate the effectiveness of calcium carbonate precipitation as a corrosion

inhibitor. Stern and Geary⁽⁶⁴⁾, who first used the terms linear polarization and polarization resistance, put the empirical observations on a more quantitative basis with the equation that bears their name:

$$\frac{1}{R_p} = \frac{(\Delta i)}{(\Delta E)E_{\text{corr}}} = 2.303 \left(\frac{b_a + |b_c|}{b_a |b_c|} \right) i_{\text{corr}} \quad \dots 2.12$$

where R_p is the polarization resistance

b_a and b_c are the anodic and cathodic Tafel constants respectively

This can be simplified to the form

$$i_{\text{corr}} = \frac{B}{R_p} \quad \dots 2.13$$

where the constant B , which contains the Tafel constants, can be obtained empirically from weight loss measurements (see Skold and Larson). This 'constant', however, may be time dependent, especially during the early period of the corrosion reaction. Mansfeld⁽⁶⁴⁾ has developed a curve fitting computer program to obtain an instantaneous value of B from the polarization curve at low overpotentials. Such an approach overcomes problems of non-linearity around the rest potential exhibited by some reactions. In the absence of any other forms of polarization, the Tafel constants can be determined from the full polarization curve and directly substituted into equation 2.12. The various sources of errors in the technique have been enumerated in the paper by Moreland and Rowlands⁽⁶¹⁾.

The linear polarization technique was used at the Water Research Centre by Ainsworth, in unpublished work on the corrosion of cast iron by natural waters, using the apparatus described by Neufeld⁽⁶⁵⁾. The present author also used the technique to study the corrosion of lead in synthetic waters. Unfortunately in neither case was satisfactory agreement with weight loss measurements obtained.

2.4.3 A-C Impedence techniques

An electrode in aqueous solution possessing extra charge attracts ions of the opposite sign to achieve electric neutrality. This charged double layer is equivalent to a conventional capacitor and the electrode system, in its simplest form, can be treated as the circuit equivalent of a resistor and capacitor in parallel. In order to obtain information about these different aspects of the electrode processes, A-C impedance techniques have been developed in recent years(66).

An A-C signal of small amplitude is imposed on an electrode which may be polarized from its rest potential by the simultaneous application of a D-C current. The A-C signal is scanned through a range of frequencies and the different impedance values determined. The same electrode arrangement is used as for the linear polarization techniques and the instrumentation required includes a potentiostat (or galvanostat), an A-C generating device and either a phase-sensitive detector (lock-in amplifier), or a digital transfer function analyser, to interpret the output signal. The modern detectors allow low-amplitude signals with frequencies over the range zero to tens of kilohertz to be investigated.

At any frequency, the impedance Z is given by the amplitude ratio

$$\frac{|\Delta V|}{|\Delta I|} = |Z| \quad \dots 2.14$$

where ΔV = change in potential of the AC signal

ΔI = change in current of the same.

The relationship between impedance and frequency is given by:

$$Z(f) = \frac{\Delta V}{\Delta I} = |Z|e^{j\phi} = \frac{|\Delta V|e^{2\pi jft}}{|\Delta I|e^{j(2\pi ft - \phi)}} \quad \dots 2.15$$

where f is the frequency of the A-C signal

j is the imaginary root $\sqrt{-1}$

ϕ is the phase shift i.e. the extent to which the change in current leads the change in voltage

t is time

The function $Z(f)$ can be divided into its real and imaginary parts:

$$Z(f) = \text{Re}(f) + j\text{Im}(f) \quad \dots 2.16$$

and the variation of Z with frequency is usually plotted in the complex plane $j\text{Im}$ vs. Re in what is known as a Nyquist diagram, see Figure 4.

The parameters that can be determined by this technique are:

- (a) electrolyte resistance R_e , at high frequency values,
- (b) polarization resistance R_p , at frequencies approaching zero,
- (c) capacitance of the double layer C_{dl} , at frequencies in the kilohertz range,
- (d) charge transfer resistance R_t , this shows frequency dependence or faradaic impedance which is related to the reaction mechanism.

A-C impedance has been successfully used to determine corrosion rates of iron in sulphuric acid⁽⁶⁶⁾ and aluminium alloys in sodium chloride solution⁽⁶⁷⁾ from the measurement of R_p values. The effectiveness of corrosion inhibitors has been studied by their ability to reduce electrode capacitance, produced by the increased separation of charge following their adsorption onto the metal surface^(66,68). The potential range over which inhibitors are adsorbed, and hence are likely to be effective, can be readily determined with this technique. Capacitance measurements have also been used to determine the thickness of oxide layers on aluminium⁽⁶⁹⁾. A specific impedance test has been developed to assess the acceptability of anodised aluminium and the results successfully correlated with the traditional, but much longer, salt spray test⁽⁷⁰⁾.

2.4.4 Bimetallic corrosion techniques (galvanic couples)

If two dissimilar metals are in electrical contact in an aqueous electrolyte, there is a possibility of enhanced corrosion of the less-noble lower-potential component. The galvanic coupling of the two metals lowers the potential of the more noble component, which stimulates the cathodic reaction, and raises that of the less noble, which stimulates the anodic (corrosion) reaction. The current that flows between the two metals is a measure of the galvanic corrosion generated by the coupling. Measurement of this current allows the galvanic corrosion rate to be determined.

Bimetallic corrosion is best studied in terms of Evans diagrams⁽⁷¹⁾ which allow the cathodic and anodic reactions to be considered separately. In such diagrams the respective potentials of the two metals are plotted against the mod of the galvanic current flowing between them, see Figure 5. It is more usual in polarization curves to plot logarithm of the current density, in accord with the Tafel relationship, see Equation 2.1. However, for the limited current range usually found with galvanic couples, and for a fixed anode and cathode area ratio, a linear plot of the actual galvanic current is usually more convenient.

The galvanic current produced by a bimetallic couple is determined by an Ohms law relationship of the form:

$$I_g = \frac{EMF}{R_a + R_c + R_s} \quad \dots 2.17$$

Where I_g is the galvanic current

EMF is the open circuit potential difference between the two metals

R is the resistance of respectively

anode polarization

cathode polarization

solution (electrolyte) path between the electrodes.

The relationship essentially describes the geometry of the lines on the Evans diagram, See Appendix I. The anode and cathode polarization resistances correspond to the slopes of their respective lines on the

diagram. If one of the resistances is very much larger than the rest, it is rate controlling for the galvanic corrosion. An electrode reaction can be rate determining if the chemical reaction occurring at its surface is slow. This might arise from a protective corrosion product or inhibitor adsorbed on the surface. Alternatively, the reaction is slow when a necessary reactant is present only at a low concentration e.g. dissolved oxygen. A rapid anodic reaction may exhaust the oxygen at cathodic sites, thereby producing a local deficiency, and the reaction becomes controlled by the rate of oxygen diffusion or the rate of flow of the bulk solution. An electrode reaction may be rate controlling because it occurs on a small surface area (high current density). On an Evans diagram, when not plotting current density, this situation is indistinguishable from a high polarization resistance produced from some other cause. The electrolyte can be rate determining if of sufficiently low conductivity and/or when the two metals of the couple are separated by a large distance.

A common method of determining the galvanic current, in a bimetallic test apparatus, is to measure the potential drop across a fixed resistance introduced into the external electrical circuit joining the two metals. This, of course, makes a contribution to the total circuit resistance and has an effect on the galvanic current it is being used to measure, Appendix I. Thus it is obviously important to keep the value of this resistance as low as possible to minimise its distortion of the system under study. The effect can be obviated entirely by use of a zero resistance ammeter that allows a direct measure of the current without introducing any resistance into the circuit.

A bimetallic couple allows only the galvanic corrosion current to be determined i.e. that part of the total corrosion current that passes from one metal to the other. The less noble metal, the anode, also corrodes using cathodic areas on its own surface, internal cathodes. This effect is enhanced when a resistance is present in the external circuit connecting anode to cathode and if the more noble metal, although at a higher potential, does not provide a very efficient cathodic surface. Conversely, if the more noble metal greatly increases the potential of the anode, and/or provides an efficient cathodic surface, and/or the

anode forms a film that decreases its efficiency as a cathodic surface, the measured galvanic current may constitute by far the major part of the total corrosion current. Where it is the anode corrosion rate that is of specific interest, the relationship between the galvanic current and the total corrosion current has to be established by some independent means.

Galvanic corrosion couples have been used by the present author to study the dezincification of brass plumbing fittings in potable water^(72,73). A galvanic cell was devised for the Water Research Association (now Centre) by the British Non-ferrous metals Research Association (now BNF Technology Centre). This was further developed by the author and used to study the effect of silicate and phosphate as corrosion inhibitors, as well as the behaviour of a water that appeared naturally inhibited against dezincification.

Electrochemical measurements were made on copper/solder cells, reported in a Russian paper by Stopchai et al⁽⁷⁴⁾. This work, which was more concerned with the loss of mechanical strength rather than contamination, involved determining potentiokinetic polarization curves for a series of alloys in 0.5 M sodium chloride, and in air at 50°C with 80% relative humidity. The corrosion currents generated by the different alloys were compared at the potential assumed by copper under the same conditions. Corrosion resistance was assessed by eye and by shear strength tests before and after corrosion.

Although some workers have recognised the importance of galvanic couples in the corrosion of lead or soldered joints (47,107), they used solubility measurements alone when investigating the effects of such couples. Only Lyons and Lenihan⁽⁷⁶⁾, below, tried to obtain direct information on the corrosion process by using the galvanic current generated.

Of the different electrochemical techniques outlined above, the galvanic couple method has obvious application to the corrosion of soldered joints. It has the further advantage over the other methods that only simple equipment is needed, such as might be found in any analytical laboratory in the Water Industry. Thus any test method developed using

this technique could conceivably be used by them to examine the corrosivity of their local water sources. It was for these considerations that this technique was used in the present investigation.

2.5 LABORATORY WORK ON CONTAMINATION PROBLEMS FROM SOLDERED JOINTS

Wong and Berrang⁽⁷⁵⁾ reported work on the lead contamination of the water supply to Victoria, British Columbia. Although they did not find any unacceptable levels arising from solder in their survey of domestic systems, they did obtain high results from infrequently used taps in their own laboratory. Their samples were taken 24 hours after flushing out the lines and they obtained a maximum level of 0.41mgPbl^{-1} from an "occasionally used" tap and a maximum level of 3.0mgPbl^{-1} from another, which they believed had not been used for 6 months prior to their experiment. These figures are misleading however, because they are the equivalent concentrations per litre from very small sample volumes. Being very conscious of the change of lead levels with water volume flushed through the system, they started with small volumes (5ml initially, gradually increasing) but quote the concentration as ppb (μgl^{-1}). Thus the 3.0mgPbl^{-1} figure was for a 20ml sample. Allowing for this volume effect, their figures show that the first litre of sample from the second tap contained 0.672mgPb . After the second litre had been drawn the total lead figure was 0.736mg , i.e. equivalent to an average concentration of 0.368mg l^{-1} .

In order to confirm that the lead present was coming from the soldered joints, they fabricated a series of laboratory rigs 15.25 metres long in 15mm copper tube using 20 soldered joints. The joints were made with either 50:50, 60:40 or 95:5 tin-lead alloys. Results were also obtained from a copper-only rig, and another in which silver was possibly used as a solder, perhaps to test the effect of the soldering process itself although no explanation was given in the text. Their results supported the findings of many other authors, namely that high initial lead levels gradually fall as the cumulative volume of water passed through such systems increases. All their figures were for water samples that had been static in the rigs for 1 hour. It was not until a cumulative volume of

12,000 litres had passed through each that a significant difference was observed between the rig constructed using 50:50 solder and the one with the 60:40 alloy. Lead levels of 0.096mgPb l^{-1} and 0.049mgPb l^{-1} respectively were then obtained after the 1 hour static period. Given its effect on the figures quoted in their earlier experiment, it is unfortunate that they give no indication of the sample volume. As the internal volume of their rig can be calculated to have been 2 litres, it is probable they took its whole contents for their sample. The other rigs, including the one with 95:5 soldered joints, all had lead concentrations at background levels of $0.001 - 0.003\text{mgPb l}^{-1}$ from the start.

They reported dissolution rates of $0.4\text{mgPb/soldered joint.hour}$ for the first hour, falling to $0.1\text{mgPb/soldered joint.hour}$ over 24 hours, after a cumulative volume of 150,000 litres had been flushed through each rig. They suggested that this volume of water was equivalent to one year of normal usage, although at 1983 UK domestic usage it is probably closer to a 6 - 9 months' consumption. Tests they did on a real one year old house gave a rate of $0.4\mu\text{gPb/joint.hour}$. They concluded that such systems, with a volume of about 2 litres, would exceed the $50\mu\text{gPb l}^{-1}$ Canadian limit for lead in 4 - 20 hours assuming a rate of $0.1 - 0.5\mu\text{gPb/soldered joint.hour}$. It would appear, although not stated, that the total number of joints in such a system was taken to be between 10 - 50. Their overall conclusions were that the normal tin-lead solder should be replaced by the 95:5 alloy, a new system should be flushed with a year's normal water usage, and that the first 2 litres drawn from a tap should not be used for human consumption if it has been static in the system for more than 24 hours. Unfortunately, nowhere in their paper do they give details of the composition of the water used in their experiments, which would allow an assessment of the general applicability of their conclusions. From the geographical location of British Columbia, it can probably be assumed the water type is similar to that of Seattle (see ref. 45).

In the United Kingdom, people became aware of possible problems with capillary fittings after unacceptable lead levels were obtained in Glasgow from a new building that had no lead pipes. Lyons and Lenihan⁽⁷⁶⁾ investigated the problem and reported that of 216 water samples taken

from the system, 44% contained above 0.1mgPb l^{-1} , with one as high as 4.3mgPb l^{-1} . The pipe work was thin walled, hard drawn copper (Table 2, British Standard 2871(77)), so that the only possible source of lead was the solder used with the capillary fittings.

They also constructed laboratory test rigs, each containing lengths of copper pipe and five capillary fittings, and used these to determine the fall in lead pick up with time. Two series of experiments were run; in the first water was continuously circulated through the rigs for 4.5 hours before being changed whereas the second series was carried out under static conditions with the water being replaced every 12 hours. Both Glasgow tap water and deionised water were tested in these experiments. Initially levels equivalent to 322 and $216\mu\text{g/fitting}$ over 16 hours were recorded for the circulatory and static experiments respectively. The latter figure fell to $20\mu\text{g}$ after 4 - 5 weeks where it remained constant for at least 3 months. There was little difference between the results obtained using deionised water and those for Glasgow tap water, the latter being a soft high purity supply.

Tests were also carried out on systems that had been in service for many years in three large buildings in Glasgow. Because experiments indicated that the samples being taken were highly inhomogeneous (a standard deviation of 58%), the results were presented but no conclusions drawn. Laboratory experiments, on fittings removed from one of the buildings in which they had been in service for 5 years, gave a mean release of $22\mu\text{g/fitting}$ over 16 hours. The details of this calculation are not obvious from the paper, the experimental results used being expressed as a concentration and the final average rate per fitting, presumably, being expressed simply as mass of lead.

The effect on lead pick up of changing the pH of Glasgow tap water was also investigated. They found an exponential decrease with increasing pH. This result suggested to them that the process was unlikely to be under solubility control, because previous authors had found the solubility of the usual lead corrosion products went through a minimum at pH 7.

Their experiments with chemical degreasing, to remove acidic flux residues, usually produced the expected fall in lead pick-up. In those fittings with solder runs in the bore of the tube, however, a large increase was initially produced which rapidly fell to the pre-degreasing levels in a few days. The high metal levels suggested to them that the corrosion must be under galvanic control, rather than simple dissolution of corrosion products. To test this they set up a galvanic cell with 2cm² of solder connected to copper, with Glasgow tap water as electrolyte. They reported the quantity of electricity passed by this cell in the presence and absence of flux, and also when 0.1M potassium chloride was used as the electrolyte. As no details of the conditions under which the experiments were made, e.g. flowing or static, temperature, area of copper, etc., the results can only be considered qualitatively. They showed that the solder was anodic in such a cell, the area around the cathode became alkaline, which suggested the reduction of dissolved oxygen, and that the galvanic corrosion current increased with an increase in the conductivity of the electrolyte.

The presence of flux residues in Glasgow tap water greatly increased its conductivity and this offered an explanation, the authors suggested, of the enhanced metal contamination observed under such circumstances.

The overall conclusions were that Glasgow tap water can pick up large amounts of lead from capillary fittings, sufficient to exceed to 0.1mgPb l⁻¹ on occasions. They also supported the conclusions of Waldron and Stöfen⁽¹⁹⁾ that lead based solders, particularly if used with fluxes insoluble in water, should be prohibited in drinking water supplies.

Laboratory work was undertaken in eastern Belgium by Closset⁽⁷⁸⁾ after high lead levels had been reported from the corrosion of soldered joints. He constructed the usual form of test rig which consisted of ten 50cm lengths of copper tube (internal diameter 1.2cm) with a total of 21 soldered joints. He used this to study the effects of aging of the solder, water flow rates and temperature on the amount of lead pick-up. The joints were made with the normal solder alloy used in Belgium which is low in lead, 23.6% as received rising to about 29% if all the volatile

flux included is driven off during the heating process. The water used in the experiments, an actual supply water, was very soft and acidic (hardness $10 - 30 \text{ mg CaCO}_3 \text{ l}^{-1}$, pH 4.6 - 5.6). From time to time, however, he introduced the much harder Liege supply ($340 - 400 \text{ mg CaCO}_3 \text{ l}^{-1}$ pH 6.8 - 7.5), to speed the aging of the solder. Closset also produced a control rig, with the joints made with a non-leaded brazing alloy, to demonstrate that lead contamination only arose when soft solder was used.

While the experiments reported are interesting, even if the results obtained are unsurprising, his explanations of what he observed tend to be involved, difficult to follow and at times appear strange. He reported a series of stagnation trials where samples of water were held in the rig for increasing periods of time, from 2 minutes to 360 hours. The present author's interpretation of his results is that, after an initial period of 5 days during which the rigs came to equilibrium with the test water, the rate of lead contamination followed an exponential law.

In studying the change of lead levels with increasing flow rates, using a rig that had been aged for 1 month, Closset found a negative relationship that fitted an exponential expression. Having found that flow rates in excess of 8 l min^{-1} resulted in no measurable increase in the amount of lead in the water, however, he came to the startling conclusion that at these flow rates the rate of corrosion had become nil!! The contact time between the water and solder surface, he declares, was too short to allow dissolution of the metal.

"On demontre donc que lorsque l'on atteint des debit de l'ordre de 10 l/min., la perte de plomb par doudure devient nulle. Le temps de contact de l'eau avec la surface de la soudure est trop faible pour permettre la dissolution du metal."

Closset also investigated the effects of temperature and flow rate. For flow rates up to 3 l min^{-1} he estimated that a reduction in 10°C reduced the rate of dissolution by 50%. Closset's final conclusion was that his

work had demonstrated the dangers of lead contamination from soldered joints and chemically aggressive water, and that this risk should be drawn to the attention of Public Authorities as a matter of urgency.

2.6 CORROSION INHIBITORS IN AQUEOUS SOLUTIONS

Corrosion inhibitors are reagents which, although present at low concentrations, significantly reduce the corrosivity of an environment to the metal(s) of interest. This very broad topic has been the subject of at least two books^(79,80) as well as various more specific review articles^(81,82). Inhibitors for aqueous environments fall into two main types, those that operate in near neutral solutions (pH5 - 9) and those for aqueous solutions of strong acids. Near neutral solutions include potable water as well as industrial cooling waters and boiler feed supplies. The aqueous acid solutions are mainly those used in acid pickling baths for the cleaning of metals prior to some form of surface treatment or further fabrication. Corrosion prevention specifically in neutral waters is the subject of a book by Butler and Ison⁽⁸³⁾.

The different methods of classifying corrosion inhibitors have been outlined by Mercer⁽⁸⁴⁾. Amongst these is the classification as an anodic or cathodic inhibitor based on the mechanism of the action i.e. whether the reagent increases the polarisation of the anodic (metal corrosion) or cathodic (reduction of dissolved oxygen or hydrogen ion) reactions.

2.6.1 MECHANISMS OF INHIBITOR ACTION

The mechanisms of inhibitor action in aqueous solutions has been reviewed by Thomas⁽⁸¹⁾. He first considers inhibition in acid solutions.

(a) Acid Solutions

In acid solutions the metal has an oxide free surface and the reduction of hydrogen ions is the main cathodic reaction. The inhibitor becomes adsorbed onto this surface, either by simple electrostatic

interactions or donation of electrons from a functional group with either a lone pair or multiple bond, e.g. amines, carboxylic acids and acetylenic compounds.

There are a variety of mechanisms by which an adsorbed species can inhibit the corrosion reaction. Large organic molecules e.g. gelatine and polysaccharides, can form physical barriers that impede the diffusion of molecules and ions. This greatly increases the resistance polarisation and produces concentration polarisation of both anodic and cathodic reactions⁽⁸⁵⁾. An inhibitor may adsorb specifically at reaction sites thereby greatly reducing corrosion while present at very low concentrations, e.g. inhibition of iron in sulphuric acid by 1,6- dimethylquinoline⁽⁸⁶⁾. Polarisation studies often indicate whether at these low levels such inhibitors affect the anodic reaction, while acting more as a mixed inhibitor at higher concentrations, when more of the surface is covered.

Some inhibitors participate in the electrode reactions and, because they remain unaltered, may be considered as negative catalysts, e.g. benzoate-inhibition of iron⁽⁸⁷⁾. Adsorption of certain species onto a metal surface can change the potential of the electrical double layer making certain reactions less favourable, e.g. quaternary ammonium ions makes the potential more positive at the metal solution interface, which discourages the cathodic discharge of hydrogen ions⁽⁸⁸⁾.

Thomas concludes that it is often not possible to assign a single general mechanism of action to an inhibitor. The particular mechanism may vary with such factors as concentration, pH of the acid, nature of the anion of the acid, presence of other species as well as the nature of the metal.

(b) Near-neutral solutions

In solutions of near-neutral pH, Thomas continues, metal surfaces are covered with some kind of film, either an oxide, hydroxide or an

insoluble salt. Also, for solutions in contact with the atmosphere, reduction of dissolved oxygen is the major cathodic reaction. Apart from the high molecular weight organic compounds, e.g. gelatine, agar, etc., inhibitors for acid solutions are not effective at near-neutral pH values. Compounds that are suitable for the latter type of solution can be roughly divided into cathodic and anodic inhibitors.

Salts of various metals that have insoluble hydroxides produce thick films of gelatinous, electrically non-conducting precipitates, in regions of high alkalinity. As such regions occur at cathodic sites, because of the production of hydroxyl ions by the reduction of dissolved oxygen, such compounds act as effective cathodic inhibitors(ref 83 p159). They include the salts of zinc, magnesium, manganese and nickel. In a similar manner the presence of calcium in solution often results in the precipitation of calcium carbonate at cathodic sites, (Section 2.6.2). The mechanism of the action of polyphosphates appears a little more complicated. In the presence of a divalent ion (e.g. Ca^{++} or Zn^{++}) it appears to act as a conventional cathodic inhibitor, but affects the anodic reaction in their absence(89). The various mechanisms proposed for this inhibitor have been reviewed by Butler(90).

The second type of inhibitor in near-neutral solutions acts by stabilising the oxide film on the metal surface and so tends to affect the anodic reaction. They are often oxy-anions e.g. chromate, benzoate, silicate and phosphate. Thomas(81) summarises their important functions as:

- i) Allow the formation and build-up of a passivating oxide film.
- ii) Repair the oxide film by promoting the re-formation of oxide.
- iii) Repair the oxide film by plugging pores with insoluble compounds.

iv) Prevent the adsorption of aggressive anions.

Although more than one of these functions may operate at the same time, the first one listed is often the most important. An earlier explanation of the behaviour of these inhibitors, not specifically mentioned by Thomas, postulates the flocculation of colloidal corrosion products by multiple charged oxyanion species⁽⁹¹⁾. Thus colloidal species of the type $[\text{Fe}_2\text{O}_3 \cdot x \text{H}_2\text{O}]\text{Fe}^{+++}$ have been proposed which are thought to be coagulated by sulphate. The result is a change in the physical form of the corrosion deposit without any alternation in its chemical composition. Analogous colloidal species are known both for tin, $[\text{SnO}_2 \cdot x \text{H}_2\text{O}]\text{Sn}^{+++}$, and lead⁽⁹²⁾, $[\text{Pb}_3(\text{PO}_4)_2]\text{Pb}^{++}$. Production of the latter entity is believed to account for the successful use of anionic adsorption indicators in the titration of phosphate with lead acetate. The well established aggressive action of chloride ions on metal oxide films is explained by its well known peptising properties, i.e. its ability to disperse deposits into colloidal suspensions⁽⁹¹⁾.

The mechanism of oxyanion inhibition mentioned by Thomas involves adsorption onto the metal oxide surface and, if the metal inhibitor complex dissolves at a slower rate than the corresponding metal complex with hydroxyl ion or aggressive anion, a build-up of the oxide layer ensues. Under these conditions, repair of the film at breakdown points is encouraged. This effect may be further enhanced if the inhibitor forms insoluble compounds that can be precipitated in the film. Also, by becoming adsorbed on the metal oxide layer, the inhibitor displaces hydroxyl ions and any aggressive anion that might otherwise encourage breakdown.

Brasher and Mercer⁽⁹³⁾ derived a relationship between the maximum concentration of an aggressive ion, $C(\text{agg})$, whose effect can be nullified by a given concentration of an inhibitive anion, $C(\text{inh})$. This took the form:

$$\log C(\text{inh}) = n \log C(\text{agg}) + \text{const} \quad \dots 2.18$$

where n is approximately equal to the valency ratio of inhibitive ion to aggressive ion. This is believed to be consistent with the competitive adsorption or ion exchange between the anions with the total charge at the metal oxide surface remaining constant. The adsorbed inhibitive anion overcomes the effect of an aggressive anion by reducing the surface concentration of the latter to below a critical value⁽⁸¹⁾.

Brasher found that non-oxidising inhibitive anions e.g. benzoate, phosphate, do not function if the potential of the metal is depressed below a critical value⁽⁹⁴⁾. This is presumably because a negatively charged anion inhibitor is less readily adsorbed onto the metal oxide surface as the latter becomes more negative. Conversely, Kolotyrkin⁽⁹⁵⁾ has suggested there is a potential above which an anion cannot be adsorbed and so act as a corrosion inhibitor. This finds support in the work of Abdul Azin et al⁽⁹⁶⁾ into the corrosion of lead in sea water. They found that chloride was a corrosion inhibitor for freely corroding lead. However, if the potential of the metal was raised, either potentiostatically or by galvanic coupling with steel, chloride became an aggressive ion.

This is more difficult to explain. It might appear that raising the potential of the metal sufficiently polarised the adsorbed chloride for it to become incorporated into the structure of the oxide film, causing disruption and loss of protection. The work by Abdul Azim et al, however, indicated that protection was restored, for lead held at a potential of +0.4VSCE, when the chloride concentration was raised to greater than $10^{-2}M$. This suggests some competitive process under these conditions that simply increases the critical concentration of chloride at which inhibition occurs. Perhaps this process is no more than the increased rate of lead oxidation occurring at the raised potentials which requires a higher concentration of chloride to smother.

2.6.2 CORROSION INHIBITORS USED IN POTABLE WATER SUPPLIES

The problems associated with dosing corrosion inhibitors to the public water supply are:

- i) even for a low concentration of inhibitor, given the millions of gallons of water treated every day, the cost of chemicals is likely to be significant.
- ii) because the water is for human consumption, only compounds with no acute or chronic toxicity can be used.
- iii) the chemicals dosed must not have any side effects that may adversely affect later stages in the water cycle, e.g. sewage treatment.

These considerations have limited the inhibitors used in potable waters to sodium silicate, sodium polyphosphate and sodium orthophosphates as well as pH correction. The subject has been reviewed by Ainsworth⁽⁹⁷⁾ who makes the point that corrosion inhibitors are only dosed in the Water Industry to overcome water quality problems, e.g. red (rusty) water complaints, rather than to prevent mains bursts.

Adjusting the pH of potable waters helps to reduce corrosion in two ways. Not only are metal oxide films more stable in neutral to slightly alkaline conditions but, by adjusting the pH so the solution is saturated with respect to calcium carbonate precipitation, cathodic inhibition can occur, Section 2.6.1(b). This approach minimises chemical dosing by taking full advantage of the constituents naturally present in the source water. The idea of saturating the water with respect to calcium carbonate arose from the work of Langelier⁽⁹⁸⁾ and various "saturation indices" have been developed to quantify the thermodynamic tendency of a water to deposit calcium carbonate scales. The original Langelier saturation index (SI) was of the form:

$$SI = pH - pH_S$$

...2.19

where pH = pH of the supply.

pH_S = pH of the supply when just saturated with respect to calcium carbonate.

A positive index denotes a tendency to deposit calcium carbonate and this was taken to indicate a non-corrosive water. The pH_S of the water is calculated from the formulae:

$$pH_S = p\ Ca + p\ Alk + p(K_2 - K_S)$$

...2.20

where p denotes negative logarithms.

Ca = calcium concentration as ppm $CaCO_3$

Alk = alkalinity, to methyl orange end point, as ppm $CaCO_3$

K_2 = the ionisation constant of the bicarbonate ion

i.e. $HCO_3^- = CO_3^{--} + H^+$

K_S = calcium carbonate solubility product

Criticism has been made recently of common misinterpretations of the index and of its usefulness as a measure of corrosivity of a water, especially in waters of low calcium content⁽⁹⁷⁾. It has also been shown by Campbell and Turner⁽⁹⁹⁾ that the deposit produced has to be in the correct physical form for it to be protective. Similarly, work on the effect of pH adjustment on iron corrosion rates has shown a far from straightforward relationship⁽¹⁰⁰⁾. Raising the pH from 7.5 to 8 has been found to greatly stimulate the corrosion in some waters.

Sodium silicates^(101,102) and sodium polyphosphates^(103,104) have both been dosed to potable water supplies, primarily to alleviate water quality problems. Although quite successful in this regard, their usefulness as corrosion inhibitors has been questioned⁽⁹⁷⁾. Both of these types of reagents, as well as orthophosphate, have been used to combat lead contamination problems, Section 2.7.

2.7 WATER TREATMENTS USED TO OVERCOME LEAD CONTAMINATION PROBLEMS

The majority of work in this field has been to overcome the contamination of water conveyed by lead pipes. The success or failure of a particular treatment has usually been judged by the changes in lead concentration, rather than any attempt at determining the reduction in corrosion rates. Thus the effectiveness of various corrosion inhibitors has been inferred rather than measured directly.

A paper by O'Brien⁽¹⁰⁵⁾ mentions adjusting the pH of a supply to make it over-saturated with respect to its calcium carbonate content, a positive Langelier index, so that it would lay down a protective scale. For the very soft waters of Boston (Massachusetts) with which he was concerned, however, this would have required a pH value greater than 10, which would have increased the solubility of the lead because of its amphoteric nature. He goes on to point out that raising the pH to 8.6, the minimum in the solubility curve of lead carbonate, is futile in the absence of enough carbonate hardness to form the scale in the first place. In his paper, O'Brien presents solubility values for both lead carbonate and lead hydroxide over the pH range.

Karalekas et al⁽¹⁰⁶⁾ reviewed the various water treatments being tried on a number of New England supplies in order to comply with the Environmental Protection Agency (EPA) 0.05mgPb l^{-1} water standard. Among the techniques previously recommended, he mentions the use of phosphates and silicates, as well as adjusting carbonate hardness and pH levels. The commercial phosphate inhibitors being tried in New England included zinc orthophosphate, sodium zinc phosphate glass and sodium hexametaphosphate. The conclusions were that the pH of the supply needed to be above 7 for the inhibitors to be satisfactory. There was some evidence that they might initially increase the lead in solution, and in one case the extra phosphate was particularly detrimental because it produced algae growth problems in the distribution system. Although raising the pH of these waters to between 7 - 8 was not sufficient, in the instance where lime was dosed, such that the pH was raised to above 10 and the hardness increased threefold, no sample exceeded the standard. Both O'Brien and

Karalekas et al emphasise the need for systematic sampling programmes, both before and after a treatment is introduced, to determine its effectiveness.

The paper by Patterson and O'Brien⁽¹⁰⁷⁾ gives a wide ranging review of the medical, corrosion control, and theoretical aspects of the problem of lead in drinking water. The corrosion control section is mostly based on the work of O'Brien in Boston mentioned above⁽¹⁰⁵⁾. Results of laboratory work, involving coupons and short lengths of pipe, are also described. One of these experiments, using zinc orthophosphate as an inhibitor, surprisingly gave a 25% increase in lead over the control. After a further week, although the overall amount of lead corrosion had been reduced, there was still a 60% increase in the amount of soluble lead. No details are given of any cleaning procedures used in order to obtain the total lead figure. Experiments were carried out with galvanically coupled lead-copper coupons, which showed an increase in the rate of lead corrosion. The electrochemical potential of a lead coupon in water was also monitored over 24 hours. The change from corrosion to passivation was inferred when the potential went below the E^0 value for the (unstable) reaction. Because the details were not given, it is difficult to follow this experiment. The theoretical section of the paper deals with the thermodynamics of the various possible reactions that lead and lead compounds can undergo in natural waters. An outline of the construction of the appropriate Pourbaix diagrams is given, together with the predicted change in lead solubility in the absence and presence of carbonate.

This prediction of solubilities from thermodynamic data has been developed further in the **Water Research Centre Technical Report TR152**⁽¹⁰⁸⁾ and in a paper by Schock⁽¹⁰⁹⁾. One of the main conclusions of the WRC work was that associated ion pairs, in particular $PbCO_3^0$, play an important part in controlling the total lead solubility. Low alkalinity waters show a marked decrease in lead solubility with increasing pH, although above a level of $50\text{mg CaCO}_3\text{l}^{-1}$ the rate of decrease is much smaller. Alkalinity itself has little direct effect but provides buffer capacity for pH stability. Chloride, nitrate and sulphate have little effect on total lead solubility at the concentrations found in natural waters. The

presence of orthophosphate favours the formation of highly insoluble lead phosphate solids. This effect is somewhat reduced in waters with high calcium ion, but phosphate dosing ought to provide an alternative treatment to reduce lead concentrations in low alkalinity supplies. The work of Schock supports the conclusions about the importance of ion pairs, and he suggested that there is no reason to increase the alkalinity beyond 30-40mg $\text{CaCO}_3\text{l}^{-1}$, in the pH range 9 - 9.5, as this promotes the formation of complexes that increase the molar solubility of lead.

Richards et al⁽¹¹⁰⁾ reported field experience following the treatment of the Loch Katrine supply to Glasgow by lime addition. Raising the pH of this very soft water from 6.3 to 7.8, as measured at the treatment works, increased compliance to the 0.1mgPbl⁻¹ limit, on random daytime samples, from less than 50 to greater than 80%. Because of the low buffer capacity of the supply, it was not possible to maintain the pH throughout the distribution system. Unsatisfactory samples continued to be obtained from properties with lead lined storage tanks, those with a single occupant or which had been built before 1919, and properties that had copper to lead runs of piping (for discussion of this last point see Section 2.3, page 11). The paper suggests that further reductions in lead levels could be obtained by raising the pH even higher, provided that this could be maintained to the customers' tap. The paper gives details of the careful monitoring scheme that was necessary to demonstrate conclusively the favourable effect of the treatment.

3. EXPERIMENTAL

The experimental method developed in this work was based on the galvanic interaction between copper and tin-lead solder. Fixed areas of copper and solder, physically separated but in electrical contact, constituted a 'galvanic cell'. These cells were exposed to a variety of waters and the galvanic current flowing between the electrodes was determined over time. This current was a measure of the corrosion rate which was dependent upon the composition of the water. By determining the quantity of lead oxidised, the precise relationship between galvanic current and corrosion rate was established. Knowledge of corrosion rates meant that the likelihood of a given set of circumstances producing significant contamination could be assessed.

3.1 DETAILS AND MANUFACTURE OF THE GALVANIC CELL

The galvanic cell consisted of an anode, either solder, lead or tin, with dimensions 1cm x 2cm, connected via an external electrical circuit to a copper cathode with dimensions 1.5cm x 4.5cm, Figure 6, Photographs 1 and 2. The side of the anode facing the cathode was masked with epoxy resin, to stiffen the material and thereby increasing the ease of handling of lead and tin electrodes. This also prevented the cell from shorting if the anode and cathode accidentally touched in the confined conditions in the boiling-tube. The masking was extended along the edges of the electrode to prevent corrosion at these especially reactive regions not found in soldered joints. In this way the effective area of exposed metal at the anode was reduced to 2cm² while the cathode, the copper having both faces exposed, had an area of 13.5cm², which gave a cathode:anode ratio of 6.75:1.

The external circuit connecting the electrodes contained a resistance, nominally 10k Ω , so that the galvanic current could be measured using a millivoltmeter. The electrodes were soldered to this circuit and the junctions masked with epoxy resin. Each electrode was mounted on a thin

perspex plate, using more resin, and the two plates held back to back to produce a galvanic couple. This arrangement allowed the copper cathodes to be reused after treatment with dilute hydrochloric acid; new anodes were obviously required for each run.

The lead, tin and copper electrodes were each made by cutting out material of the appropriate size from AnalaR foil. The electrodes were cut with a short tang, 1cm x 0.3cm projecting from one of the shorter sides, to which the connection with the external circuit was made, Figure 6.

The manufacture of solder anodes was more involved. A template 1cm x 2cm with a tang 1cm x 0.3cm was first cut from the copper foil. A hole was made in the end of the tang so that the template could be mounted on the end of a length of stiff copper wire and, after covering the surfaces with a smear of commercial flux, the whole was dipped into molten solder. Provided the temperature was high, above 230°C, i.e. well above the liquidus point of the solder, a 3 second dip followed by vigorous shaking to remove excess solder produced an electrode with a mirror finish surface. If the temperature of the solder fell, a granular layer was produced. After dipping, the charred flux on the surface of the electrode was removed by immersion in perchlorethylene and polishing with tissue. The electrode was then processed in the usual way, i.e. soldered to one end of the external circuit and the junction, one side of the electrode surface and all edges, masked with epoxy resin.

3.2 THE OPERATIONAL PROCEDURES WITH GALVANIC CELLS - THE CORROSION TRACE

Galvanic cells were operated either under static conditions, when determining the relationship between the quantity of lead corroded and the galvanic current, or flowing conditions, when determining the relationship between aggressivity and solution composition. In both cases the value of the galvanic current was plotted against time to give the corrosion trace. The area under such a graph is related by Faraday's laws of electrolysis to the quantity of metal oxidised and the value of the galvanic current is directly proportional to the corrosion rate, Section 5.3.

3.2.1 CORROSION UNDER STATIC CONDITIONS

One litre samples of the test water were placed in polyethylene bottles in a water-bath held at $20 \pm 1^\circ\text{C}$. All the experiments, both static and flowing, were carried out at this temperature as the highest value that is still representative of real situations for cold water systems, see Section 4.14. A galvanic couple was introduced into each bottle and held in position by trapping the wires of the external circuit with the rubber bung used to seal the mouth of each container. This left the resistance in the external circuit projecting above the top of the bung allowing easy access for measurement, Photograph 4. The galvanic current was calculated, using Ohms law, by measuring the potential fall across the external resistance whose value had been previously determined. This was done twice per day for the duration of the run.

At the end of the experiment each bottle was shaken, to encourage any loose corrosion product on the anode to fall off into the liquid, and the couple removed. The solution in each bottle was acidified with nalar nitric acid to a strength of 0.5% v/v to ensure all the lead entered into solution. The corrosion product still adhering to the anode was removed with boiling 1% acetic acid, Section 3.4, and the two solutions thus obtained for each galvanic couple used, were mixed and analysed by atomic absorption spectroscopy, 3.4, 3.9. In those experiments where only the lead contaminating the water was of immediate interest, 4.1.7, the solution was not shaken at the end of the run and the galvanic couple was carefully removed to avoid loss of adhering corrosion product. The solution in each bottle was then acidified with nitric acid and analysed directly.

3.2.2 CORROSION UNDER FLOWING CONDITIONS

In the experiments carried out under flowing conditions each galvanic couple was placed in a boiling-tube which was sealed with a rubber bung. The latter had inlet and outlet ports, for the water under test, and channels for the wires of the external circuit. The water did not

normally touch the bung, but there was no evidence of any inhibitory action if it did. The boiling-tubes were placed in a water-bath held at $20 \pm 1^{\circ}\text{C}$ and each provided with a water supply delivered by a multi-channel peristaltic pump, Photograph 3. The water was passed only once through the cell at a flow rate of approximately 50ml hr^{-1} , Section 4.1.5. The experiments under flowing conditions were usually run for 28 days, Section 4.1.9. Results were compared by calculating the mean galvanic current over the last week, Section 3.2.4 and Figure 7.

3.2.3 MODIFIED METHOD FOR FLOWING CONDITIONS

The method of operation for cells under flowing conditions was modified when it was found that large differences in results could be obtained between replicates, Sects. 4.1.8, 5.4, and Table 3. Intrinsic differences in the reactivities of galvanic couples meant that results could be biased e.g. by a freak distribution that placed all the cells with high reactivities, high tendency to corrode, at one end of the concentration range of the ion under study and all the low reactivity cells at the other.

To guard against this possibility, all cells in a particular experiment were run for the first seven days on the same water, Figure 7. The galvanic currents produced by the cells at the end of this period were then divided into three ranges of high, middle and low, corresponding to the different intrinsic reactivities of the couples. Each solution in the series being tested was then assigned one couple from each of the three categories. In this way any effect on the final average fourth week result, arising from these differences in intrinsic reactivities between the couples, would tend to balance out. Any consistent trend actually observed across the solution compositions could then more safely be ascribed to the effect of the ion under study.

3.2.4 THE CORROSION TRACE

A 'corrosion trace,' the graph of galvanic current against time, was drawn using the results from each experiment. Although galvanic currents were determined only twice each day, cells run for over 16 hours on a

chart recorder established that this intermittent recording gave an accurate picture of the corrosion behaviour. It also led to the discovery that strong sunlight affected the current produced so that it was necessary to run the cells under shaded conditions, Section 4.1.1.

The results from the experiments under flowing conditions were quoted as 'average galvanic current over the fourth week'. Essentially a straight line was drawn by eye through the corrosion trace over the last week of the run and the value of the galvanic current at the half way point on this line taken as the average figure. Where irregular shaped traces made this process difficult, the area under the curve was calculated using the technique of accurately weighing the graph paper on which it was plotted. This area (units of current x time) was then converted into the equivalent quantity of electricity (coulombs of charge when current is in amps and time is in seconds) and so into the average current for the seven day period, Section 5.3. The latter method was not used as a matter of routine because it was found, where both could be employed, the much quicker visual technique was in agreement to within $\pm 0.1 \mu\text{A}$. This figure equalled the accuracy of measurement of the corrosion current in the first instance and was a significant fraction of the galvanic current only for inhibited solutions where the requirement to discriminate between different aggressivities was lowest. The corrosion trace had to be converted into coulombs of charge, of course, when it was required to relate galvanic current to mass of metal corroded.

3.3 POLARIZATION MEASUREMENT - EVANS DIAGRAMS

Polarization measurements were made in order to study the individual effect of the two electrodes of the galvanic couple separately. The information was used to construct Evans diagrams⁽⁷¹⁾ from which the polarization resistances of the two electrodes were calculated, Figure 5.

The method consisted of changing the resistance in the external circuit through a series of values and at each measuring the potentials of the electrodes against a saturated calomel reference. From the difference between the potentials, and the value of the resistance, the corresponding

galvanic current was calculated using Ohms law. The two potentials and the corresponding current gave two points on the Evans diagram, Figure 5. When sufficient points had been obtained in this way, the anodic and cathodic lines were drawn. In the present work, because of the restricted current range involved (0-20 μ A), a linear plot of the current fitted the data quite satisfactorily, Figures 8 and 9. This has been found to be the case by other workers(71). The slopes of these lines, having units of volts/amps, are the so called 'polarization resistances' for the respective electrode reactions, Section 2.4.4 and Sects. 4.1.6 and 5.3.

In order to make the potential measurements more conveniently, the saturated calomel electrode was fitted with a remote sensing device, consisting of a length of flexible plastic tubing terminating in glass with a sintered glass frit. This was filled with a saturated potassium chloride solution. Because the positioning of the device in relation to the electrode surfaces is likely to affect the value of the potential measured, the values obtained were comparative only. Multi-terminal connectors, see Photograph 3, were used to facilitate a rapid change of the many external resistances and a period of five minutes allowed for the cells to reach equilibrium with each new resistance value. Because of the finite time required for each measurement, this meant that whereas the first cell had five minutes to come to equilibrium, the last in the series (the process was done in batches of twelve cells) had almost fifteen. Although, judging from the behaviour on the 10k Ω resistances, this had little effect, it is another reason why the results from this procedure are comparative only.

3.4 REMOVAL OF CORROSION PRODUCT FROM ANODIC SURFACES

For those experiments in which the total amount of oxidised lead was being determined, electrodes were cleaned by placing them for a measured time period, 5, 10 or 15 minutes, in 1 litre of boiling 1% acetic acid(111). New electrodes were given similar treatment in order to obtain a blank correction figure.

It was necessary to use boiling acetic in order that corrosion products would be removed from the bottom of pits and crevices. The vapour bubbles nucleated at these points lifted the deposits or caused fresh acid to flow into such restricted places. The blank correction figures were not true blanks for the individual electrodes cleaned, but represented the maximum amount of metal that could be oxidised by the procedure. By using extended corrosion periods, this figure was made a small proportion, <1%, of the total amount of material oxidised.

3.5 MEASUREMENT OF THE INTERNAL SOLUTION RESISTANCE IN THE GALVANIC CELL

The internal resistance of the galvanic cells was determined in situ for various solutions, Table 2. An alternating current of approximately 10 μ A and a frequency of 1000Hz was applied across the electrodes only for the minimum time necessary to measure the current and the corresponding potential difference, normally about 5 seconds. The resistance was then calculated using Ohms Law.

3.6 PREPARATION OF TEST SOLUTIONS

The test solutions were prepared in 25 litre heavy-duty polyethylene carboys, by diluting the laboratory tapwater with distilled water to the required hardness levels. Because this supply was a hard borehole water containing mostly carbonate hardness and chloride, the concentrations of the other ions present were usually ignored being very low after dilution. The solutions were aerated for a least 4 hours to ensure 100% saturation with dissolved oxygen and the chloride concentration was adjusted with sodium chloride to the required value. Other ions were adjusted as necessary also using the corresponding sodium salts.

3.7 EXAMINATION OF CORROSION DEPOSITS

In order to elucidate the corrosion mechanisms for soldered joints, various techniques were used to determine the chemical composition of the corrosion products developed on both the anodes and cathodes. The physical form of these deposits was also investigated.

3.7.1 X-RAY EXAMINATION

The corrosion products on anodes were examined in situ by X-rays using a Philips diffractometer. Some material was also removed and examined by the powder method in a Debye-Scherrer powder camera of diameter 114.6mm. Copper $K\alpha$ radiation with a nickel filter was used in both cases. Compounds were identified from their d-spacings by reference to the Powder Index File.

3.7.2 ELECTRON SPECTROSCOPY CHEMICAL ANALYSIS (ESCA)

In this technique the corrosion products on anodes and cathodes were bombarded with soft X-ray irradiation and the energies of the excited photoelectrons determined. The latter characterise the elements present. Because only photoelectrons close to the surface escape from the layer, only the outermost 1-2nm of the material is analysed. The surface of some samples was bombarded with a beam of ionised argon so as to expose deeper layers (argon milling) and allow an analysis through a section of the deposit.

The instrument used was a Vacuum Generator ESCA 3 Mk II machine using aluminium radiation. The X-ray power source was operated at 12kV and 20mA. The vacuum used was better than $0.13\mu\text{Nm}^{-2}$ and the area of analysis was an ellipse of about 10 mm^2 with a depth of analysis of about 20 Å.

3.7.3 SCANNING ELECTRON MICROSCOPY (SEM)

A JXA 50A Micro-probe analyser was used to investigate the physical morphology and composition of the corrosion deposit on some of the electrodes.

3.8 METHODS OF LEAD ANALYSIS

All analyses were carried out by the analytical section of the WRC, using one of four methods depending on the concentration. All the methods were based on atomic absorption spectroscopy (AAS) and over the range 2 - 200 $\mu\text{gPb l}^{-1}$ electrothermal atomisation in a graphite furnace was used.

For the range 2 - 50 $\mu\text{gPb l}^{-1}$ the instrumentation consisted of a Perking Elmer model 460 atomic absorption spectrometer fitted with an HGA-76 electrothermal atomiser and programmer, an AS-1 autosampler and a PRS-10 printer sequencer.

For the range 50 - 200 $\mu\text{gPb l}^{-1}$ samples were diluted into 2 - 50 $\mu\text{g l}^{-1}$ range, by addition of μl quantities of water direct to the sample cup of the AAS instrument. The procedure outlined above was then followed.

Analysis over the range 200 - 400 $\mu\text{gPb l}^{-1}$ was by flame atomic absorption spectrometry at 217nm using direct solution aspiration. Each sample was measured in quadruplicate so that a precision of 5% relative standard deviation could be achieved.

For samples in excess of 400 $\mu\text{gPb l}^{-1}$ the procedure for the 200 - 400 $\mu\text{gPb l}^{-1}$ range was used, except a single analysis only was required to obtain the same precision.

4. RESULTS

INTRODUCTION

The experimental work was divided broadly into two aspects. The first was to establish to what extent the galvanic couple and the test conditions mirrored the corrosion of a soldered joint, and to determine the quantitative significance of the current measured. The second was to measure the aggressivity of the inorganic ions found in potable water over the rather limited ranges at which they are normally present.

4.1 THE PHYSICAL CHEMICAL CHARACTERISTICS OF THE GALVANIC CELL AND THE VALIDITY OF USING THE GALVANIC CURRENT AS A MEASURE OF CORROSION RATE

The design of the galvanic cell, apart from ensuring the surface area of the cathode was significantly larger than that of the anode, ~~Section 5.1~~, was chosen on grounds of pure convenience, namely a size and shape that would fit into a 25cm x 150cm boiling-tube. It was therefore necessary to determine in what ways the design affected the results obtained and hence to what extent the cell truly mirrored the behaviour of a real soldered joint. Also, because a galvanic current usually corresponds to only part of the total corrosion reaction and because the metal of interest in this work was an alloy, it was necessary to determine the precise relationship between the galvanic current produced by the cell and the rate of lead corrosion.

4.1.1 POLARIZATION STUDIES

Polarization measurements were made to establish the individual contributions of the electrodes in determining the galvanic current produced by the couple. Measurements were made for all the water quality parameters investigated. Reference to results of particular significance can be found below, under the individual sections on each of the factors studied. Here only comments that applied to the polarization experiments in general are made.

The polarization results indicated that the cells usually operated under mixed anode and cathode control, Section 2.4.4. For waters with chloride levels around the median for potable supplies i.e. 18 mg Cl l⁻¹(21), the anode polarization resistance was around 20k Ω and that for the cathode around 25k Ω . Ignoring the contribution from the internal solution resistance of the galvanic cell, Section 4.1.2, this meant that the 10k Ω resistance in the external circuit accounted for just under 20 percent of the total circuit resistance. Of course for solutions of greater aggressivity this percentage increases and vice versa, Section 4.1.8.

The effective EMF of the cells, Section 5.2, on the whole remained remarkably constant irrespective of the composition of the solution under test. The values for lead, solder and tin in the solutions used to study the effect of chloride and carbonate hardness Table 1.b, were 449 σ_{n-1} 35mV, 393 σ_{n-1} 30mV, and 388 σ_{n-1} 63mV respectively,

Differences in the galvanic current with water composition usually arose because of changes in the anode polarization resistance, see the results in Table 1.b. The polarization studies revealed that the rapid initial fall in corrosion current, observed with most corrosion runs, also arose from a rapid increase in the anode polarization resistance, Figure 8. The two anions found to inhibit the reactions produced their effect by increasing the anode polarization, Sects. 4.2.4, 4.2.7 and Figure 9. This is to be expected as these inhibitors would, under the circumstances of galvanic corrosion, migrate towards the anode. The other inhibitor discovered, a cation, produced its effect by increasing the cathodic polarization resistance, Figure 28 and Section 4.2.8, Table 1g.

The polarization behaviour of the copper cathode was studied in isolation using an external power source to adjust the potential. Acid cleaning, to remove oxide films, greatly stimulated the cathodic reaction. Certain discontinuities observed in the cathodic curve were tentatively assigned, using the Pourbaix diagram for copper, to the electrochemical reduction of this film. These discontinuities were best observed by arranging that an acid cleaned electrode was at a low potential immediately it was introduced into the solution. The potential was then slowly raised to

more positive values. At a certain point, depending on the pH of the sample, a large spontaneous fluctuation in the potential occurred and lasted several minutes before returning to almost the original value, Figure 10. The change of the value of the potential at which this fluctuation occurred, over the pH range found in potable waters, is shown in Figure 11. This demonstrates that under most of the conditions studied in this work, certainly after the short initial period of high galvanic currents, all cathodes were covered with an oxide film that tended to polarize the electrode. In an attempt to reduce variability between replicates from this source the cathodes, which were reused over several runs, were cleaned with dilute hydrochloric acid before starting each new experiment.

Another interesting feature encountered was the depolarization of the copper cathode by light. The galvanic current was increased by strong sunlight, presumably by a photokinetic effect on the cathode, Figure 12, consequently cells were always shaded from direct sunlight. The fluorescent lighting in the laboratory did not produce this effect.

4.1.2 DETERMINATION OF THE SIGNIFICANCE OF SOLUTION RESISTANCE IN THE GALVANIC CELL

Because of the physical separation of the copper and solder in the galvanic couple, the electrolytic resistance of the test water has a larger controlling effect on the corrosion rate than is the case with a soldered joint. To determine the relative significance of this effect, the conductivities of a range of waters was determined between a pair of clean electrodes in a galvanic couple. The values were used to calculate a 'cell constant' for the given geometry of the couple from the reciprocal of the corresponding specific conductances of the same solutions. It was then only necessary to determine the specific conductance of the solution under test, and multiply its reciprocal by the value of the 'cell constant', Table 2(i), to obtain the solution resistance between the electrodes in a galvanic couple.

A cell constant of 0.35 was found, from which the internal cell resistances occurring in this work were calculated to have been over the range 15 to $0.7k\Omega$, with all but a handful being less than $3k\Omega$, see Table 2. Thus solution resistance has only a minor effect in controlling the galvanic current generated by the corrosion cell, as is the case in soldered joints where there is no physical separation of anode and cathode.

4.1.3 EFFECT OF ANODIC AREA IN DETERMINING GALVANIC CURRENT

Analark lead foil was used as anode in these experiments, because it was easier to fabricate into the large size electrodes than would have been the case with solder. A series of anodes, 1, 2, 4, 8 and $12cm^2$ in area, were each electrically connected to a conventional copper cathode of $13.5cm^2$ in area. The couples were placed in running laboratory tapwater, carbonate hardness $200\text{ mg } CaCO_3l^{-1}$, chloride $15\text{ mg } Cl\ l^{-1}$, pH 7.2. The galvanic corrosion currents of the cells were monitored and polarization curves constructed.

Figure 13 shows the change in galvanic current with surface area of anode, for a $1k\Omega$ resistance in the external circuit, over 19 days of a run. Figure 14 shows the corresponding polarization curves for the 7th day plotted in Figure 13. Essentially the shape of the curve follows a composite of the cathodic polarization curves. As the ratio of anode to fixed cathode area is reduced, the polarization curves meet at successively higher points on the cathodic polarization curve, Figure 14, and the current density on the anode, i.e. slope of the curve in Figure 13, increases. Analogous behaviour can be expected with different areas of solder exposed in the bore of copper tubes provided the system remains under anodic control, Section 5.2

4.1.4 EFFECT OF TEMPERATURE

The contamination of the cold water system by soldered joints was the chief interest in this work; it is tacitly assumed by the Water Industry that nobody draws water for human consumption from the hot system! For that reason, but at the same time in order to maximise the

galvanic currents, most experiments were carried out at 20°C, the highest temperature that could still be claimed as not entirely unrepresentative of real cold water systems.

Examples of higher temperatures in plumbing systems are known, e.g. 30°C where the water supply was in the same ducting system as the heating pipes⁽¹¹²⁾, although such cases are now less common as people become aware of the problems that can arise. With such situations in mind, a limited series of experiments on the effect of temperature was carried out over the range of 14–40°C which produced a corresponding galvanic current range 1.5 – 13 μ A. These indicated a linear increase in current of between 2–3 μ A per 10°C rise in temperature. Of course although a rise in temperature increases the rates of both anodic and cathodic reactions, its effect is complex because it also decreases the equilibrium solubility value of oxygen, while at the same time increasing its rate of diffusion. It is apparent, however, that the effects on the dissolved oxygen do not become rate controlling over the temperatures studied.

4.1.5 EFFECT OF FLOW RATE

Although most soldered joints will experience static water conditions for the majority of each day, the majority of experiments in the present work were carried out under slow flow conditions in order to maximise the value of the galvanic current measured. The general experience with these experiments indicated that the galvanic current was independent of flow rate provided the latter was above 35 ml hr⁻¹. Where the flow rate was interrupted for a few hours, e.g. because of a overnight failure of the tubing on the peristaltic pump, the galvanic current typically fell to 80% of the value previously recorded. This was for galvanic couples in the boiling tubes where the volume of solution was about 50 ml. For galvanic couples under static conditions in 1 litre of solution, after an initial fall when the electrodes came to an equilibrium with the water, it took many weeks before a further significant fall in current was observed, Fig. 15. Experience in using the test cells in the field indicated that above the minimum rate the corrosion current was insensitive to flow up to values as high as 700 ml.min⁻¹ i.e. 42 l.hr⁻¹(113)

4.1.6 RELATIONSHIP BETWEEN THE QUANTITY OF LEAD CORRODED AND THE GALVANIC CURRENT

Although the galvanic current can be directly related to a quantity of metal corroded, Appendix II, this may only represent a fraction of the total corrosion that is occurring, Section 5.3.

In early experiments, in which lead/copper galvanic couples were corroded in 0.5% v/v nitric acid, the quantity of lead found in solution was five times that calculated by applying Faraday's laws to the measured galvanic current, i.e. the latter constituted only 20% of the total corrosion current.

To determine what occurred in potable waters, where the higher pH would allow some form of corrosion film to be produced on the anode, galvanic couples were corroded under static conditions. The total amount of lead oxidised was determined and related to the quantity of electricity (coulombs) in the galvanic current generated, Sects. 3.2.1, 3.2.4 and Appendix II.

This experiment was performed using lead anodes and a range of solders, 40:60, 60:40, 95:5 tin-lead. The 40:60 and 60:40 samples were both commercial alloys but the 95:5 was made in the laboratory, by adding the appropriate amount of Analar tin to a sample of the 60:40 alloy. The results for lead and the 40:60 alloy are given in Figure 16, and for the 60:40 and 95:5 alloys in Figure 17. Theoretical lines, calculated by Faraday's laws, see Appendix II, are included indicating the maximum amount of lead to be expected according to whether the alloy composition is calculated as percentage lead by weight or percentage lead by volume, Section 5.3.

All the results show an excellent correlation between the amount of lead oxidised and the quantity of electricity passed in the external circuit. Some of the results for the pure lead were higher than the maximum theoretical by weight because the corrosion had started to disintegrate the electrodes.

4.1.7 RELATIONSHIP BETWEEN THE QUANTITY OF LEAD CONTAMINATING THE SOLUTION AND THE GALVANIC CURRENT

Only a proportion of the lead corroded contaminates the water phase, (and the majority of this will be as a fine precipitate of corrosion product), the rest adheres to the electrode surface as a corrosion product layer. Because it is the contamination of the water that is the primary concern, experiments were carried out under static conditions in which only the lead in the water phase was determined, Section 3.2.1.

High galvanic currents were produced by using an aggressive water, hardness $55\text{mg CaCO}_3 \text{ l}^{-1}$, chloride 60mg Cl^{-1} , pH 8, and low values for the resistance in the external circuit, 1 or $3\text{k}\Omega$. Different corrosion periods were then used to ensure an even distribution of charge values over the range, see Figure 15. The solder normally used in joints, 40:60 tin-lead, was the only one used in this work. The results, Figure 18, indicated that as the cumulative charge passed in the external circuit increased, an ever increasing proportion of the lead oxidised appeared in the liquid phase, almost certainly as a precipitated lead salt at the high concentrations of the metal observed.

A more general confirmation of the relationship between coulombic charge equivalent of the galvanic current and the level of contamination of the water can be seen in Figure 19 where a series of results for nitrate solutions are summarised. With these, because of the much narrower range of charge equivalent, and because the electrodes had already corroded for over a month and hence had acquired a corrosion product layer, the relationship appears linear rather than a curve.

The general conclusion of these experiments was that the galvanic current did accurately measure the corrosion rate of the lead and solder tested and was an indicator of the contamination of the water to be expected from this attack.

4.1.8 VARIABILITY IN THE RESULTS

A significant feature of this work was the large scatter in the galvanic currents obtained from replicates, Table 3. Although every effort was made to reduce this, by controlling the conditions of manufacture of the anodes and scrupulously cleaning the surfaces of the electrodes, none of this proved successful.

The polarization studies showed the cathode was an equal source of the scatter between replicates, despite the acid cleaning procedure before each experiment. In an attempt to obtain more reproducible cathodic behaviour, nickel foil was used in the hope that a more consistent oxide would be produced on this metal. These experiments were soon abandoned, however, because of the very high polarization resistances developed by such electrodes, about $550\text{k}\Omega$. In comparison, the cuprous oxide produced on copper electrodes proved a far more effective cathodic surface with polarization resistances of the order of only $20\text{k}\Omega$, Table 1. Again this result finds support in the literature⁽¹¹⁴⁾.

Results in Table 3a) indicate the effect of changing the value of the resistance in the external circuit on the variability between replicates. Increasing this resistance dampens the scatter, reducing the standard deviation as a percentage of the mean galvanic current, as it moves towards becoming the largest component in the total circuit resistance; 3, 10 and $30\text{k}\Omega$, for a solution of low aggressivity, representing approximately 6, 18 and 40% respectively of the total circuit resistance. This reduction in scatter is of course achieved at the expense of a loss in sensitivity, as the higher resistances also reduce the galvanic current. Because of this $10\text{k}\Omega$ was chosen as the normal value for the external resistance, a compromise between extreme variability and low sensitivity. For more aggressive solutions, Table 3b, this effect is not observed because of the low anode and cathode polarization resistances produced. Even at moderate values the external resistance represents a significant proportion of the total circuit resistance in such solutions. For one

cell in 3b), with anode and cathode polarization resistances of 5.0 and 14.1k Ω respectively, external resistances of 3, 10 and 30k Ω represented 14, 33 and 61% respectively of the total circuit resistance.

Similarly increasing the concentration of an aggressive ion that affects only one of the electrodes, e.g. chloride which lowers the anode polarization resistance, reduces the contribution of that electrode to the scatter, while leaving the contribution of the unaffected electrode unchanged, Table 1.b).i) and ii). Conversely, ions that act as corrosion inhibitors reduce the variability in the results, not by reducing the variation in electrode polarization resistance, but by creating such large circuit resistances that the small galvanic current generated becomes quite insensitive to all variations, Table 1.c). Thus, in general, the scatter in the results was found to be greatest with solutions of moderate to low aggressivity where the galvanic couples are under mixed anode and cathode control. Aggressive ions allowed the external resistance to dampen the effect of variability between similar electrodes, at the expense of reducing sensitivity, and inhibitors made the cells totally insensitive to all but the largest variability in polarization resistances.

4.1.9 THE LONG TERM CORROSION RATES OF GALVANIC COUPLES

A 28 day test period was chosen in this work because this was about the minimum time required for the establishment of a quasi-equilibrium between the galvanic couple and the water. Typically the corrosion current fell rapidly over the first 24-72 hours of a run and then much more slowly over the following 4-10 days, Figure 7. Although a third week was allowed to pass before determining the average galvanic current over the fourth, this did not ensure the elimination of all erratic behaviour. Similarly, although rapid changes in corrosion current had ceased, it did not rule out the possibility of further slow decreases that might produce significant effects over much longer periods.

Lead and 40:60 solder galvanic couples were corroded under the normal test flow conditions of 50ml hr⁻¹ in the laboratory tapwater (chloride

15mgCl l⁻¹) and a high chloride water (60mgCl l⁻¹) for at least 5 months, Table 4i). Despite some erratic behaviour, produced by the extensive corrosion damage that had occurred during this period, the results from the less aggressive, low chloride, water indicated the galvanic currents had fallen to about 10% of their respective 4th week values. In the higher chloride solution the reduction had been less pronounced at 25-50%. The former figure for low chloride waters is supported in the literature⁽⁷⁶⁾.

4.1.10 COMPARISON OF GALVANIC CORROSION RATES WITH THOSE FOR UNCOUPLED LEAD

Uncoupled lead coupons were also corroded over 5 months in the same high and low chloride waters used in 4.1.9. A third test with coupons was run with the laboratory tap water and high flow conditions, ~ 20l hr⁻¹. All coupons were fabricated from AnalaR lead foil and were 0.6dm² in area. At intervals samples were removed, cleaned in boiling 1% acetic acid, and weight losses, and hence corrosion rates, determined, Table 4ii).

Somewhat surprisingly the results indicated that whereas the corrosion of galvanically coupled lead was stimulated by an increase in chloride, means after 5 months of 2.5mdd and 50mdd for the 15mgCl l⁻¹ and 60mgCl l⁻¹ solutions respectively, for uncoupled lead in the same solutions the situation was reversed, a decrease from 0.43mdd to 0.06mdd respectively. This latter result finds support in the literature⁽⁹⁶⁾. The comparison between lead coupon corrosion at the two flow rates indicated the reaction decreased significantly with flow, which is in contrast with the galvanically stimulated corrosion. The latter has significant consequences for the contamination problem from soldered joints, Section 5.4.

4.2 EFFECT OF WATER QUALITY PARAMETERS ON GALVANIC CORROSION

INTRODUCTION

Only a limited number of inorganic entities are found of any significance in potable waters, and even these are present at quite low concentrations

and over limited ranges. Amongst these are the anions bicarbonate, (usually present in potable waters as carbonate hardness), chloride, sulphate and nitrate. The major cation is usually calcium with small amounts of magnesium and sodium, although the latter can be high in borehole supplies from zeolite rock formations where the water is naturally softened.

Similarly, only a limited number of water treatment options are available, because of health and/or cost considerations, to combat corrosion problems. These are adjusting the pH, changing the carbonate hardness concentration, and addition of silicate or phosphates as corrosion inhibitors. The above considerations quite naturally defined the area most relevant to a study of the effect of water quality parameters on the corrosion of soldered joints.

4.2.1 EFFECT OF pH

In potable waters 80% of all supplies have a pH within the range of 7.0 to 8.3 with a median value of 7.5⁽²¹⁾. Some waters of low carbonate hardness, however, can achieve pH values as low as 5 and in others, which are treated by lime softening, values in excess of 9 can occur.

Experiments were carried out to study the effect of pH on solder. Solutions were made up frequently, to minimise the drift from the desired pH value by loss or absorption of carbon dioxide, and stored in enclosed containers open to the air via capillary tubing only, Photograph 5. (The solution at pH 9 was open to the atmosphere via a soda-lime trap.)

The solutions were based on a water containing 50 mg $\text{CaCO}_3 \text{ l}^{-1}$ carbonate hardness and 15 mg Cl l^{-1} chloride and the pH was adjusted using either 10% nitric acid or a 1M sodium hydroxide solution. This resulted in solutions of pH 5, 6 and 7 having nitrate levels of 10.3, 7.8 and 2.7 mg N l^{-1} respectively.

In these experiments all the galvanic couples were run for the first week on the same solution at pH 5 in order to gauge any differences in the intrinsic reactivities of the test cells. They were then grouped into high, middle, and low categories to ensure the different pH solutions had

a representative from each, thereby avoiding introducing bias into the results arising from innate differences between the cells. The results are given in Table 5(iii) and Figure 20, where the mean galvanic current over the fourth week is plotted against the mean pH values for the solutions. The significant effect of pH on the corrosion rate is obvious.

4.2.2 EFFECT OF CARBONATE HARDNESS

In potable waters 80% of all supplies have carbonate hardness levels in the range 16 - 255mg $\text{CaCO}_3 \text{ l}^{-1}$ with a median value of 134mg $\text{CaCO}_3 \text{ l}^{-1}$ (21). The concentrations studied in this work were at the lower end of this range where any effect would be expected to be both more pronounced and most significant from the point of view of control of contamination.

The results, Table 5iv) and Figure 21, indicated there is either no significant or, surprisingly, a slight positive correlation between corrosion rates and carbonate hardness levels, cf Section 4.3.1.1.

4.2.3 EFFECT OF CHLORIDE

The median concentration of chloride in potable waters is 18.0 mg Cl l^{-1} with 10 and 90 percentile values of 9 and 44.5 mg Cl l^{-1} respectively(21).

As with carbonate hardness, a great deal of information was collected on the behaviour of chloride with respect to solder corrosion, often in the course of studying the effect of other ions, Figure 22. Despite the scatter, a strong positive correlation between corrosion rate and logarithm of the chloride concentration is still obvious.

4.2.4 EFFECT OF SULPHATE

The median value for sulphate in potable waters is 29 mg $\text{SO}_4 \text{ l}^{-1}$ with 10 and 90 percentile values of 5.8 and 86.0 mg $\text{SO}_4 \text{ l}^{-1}$ respectively(21).

The effect of a range of sulphate concentrations on the mean galvanic current for a water of pH 8, carbonate hardness $55\text{mg CaCO}_3\text{l}^{-1}$ and chloride levels of 15 and 120mgCl l^{-1} respectively was examined. The results show that sulphate reduces the corrosion rate, although the magnitude of the effect was highly dependant on the corresponding chloride level, Figure 23.

Expressing the results in terms of sulphate:chloride ratio, Figure 24, indicates that with sulphate concentration more than double that of the chloride, on a weight for weight basis, the corrosion is largely inhibited.

4.2.5 EFFECT OF NITRATE

The median value for nitrate in potable waters is 1.8mgNl^{-1} with 10 and 90 percentile values of 0.1mgNl^{-1} and 12mgNl^{-1} respectively(21).

The effect of nitrate on solder couples was studied over a wide range, $0\text{--}50\text{mg Nl}^{-1}$, so as to make any trend in the results more obvious. In point of fact this range exceeded the maximum permissible concentration allowed for potable waters, 11.3mgNl^{-1} (20). The base solution used had $55\text{mg CaCO}_3\text{l}^{-1}$ carbonate hardness, 15mg Cl l^{-1} chloride and pH8. Although the results, Table 5(vii), Figure 25, show little correlation between galvanic current and the logarithm of nitrate concentration, some of the corrosion rates obtained were amongst the highest in the whole study. Furthermore the corrosion product developed on the anode had a very distinctive physical form, Photograph 6. See Section 5.7 page 97 for further discussion.

4.2.6 EFFECT OF SODIUM ION

No specific experiments were performed to study the effect of sodium ions on the corrosion of soldered joints, because high sodium contents are relatively rare in potable waters; median value 10mg Na l^{-1} 10 and 90 percentile values of 4.6 and 46.0mg Na l^{-1} respectively(21). Most of the waters tested contained at least 10mgNa as counter ion to the

chloride present. The few experiments with high sodium ion concentrations, replacing the calcium normally present, indicated a tendency to increase corrosion. This effect, however, was only pronounced at concentrations outside the normal range for potable waters.

4.2.7 EFFECT OF CORROSION INHIBITORS

a) Effect of silicate

Although silicates occur naturally in potable waters, median $6.5 \text{ mg SiO}_2 \text{ l}^{-1}$, 10 and 90 percentile 1.7 and $15.4 \text{ mg SiO}_2 \text{ l}^{-1}$ respectively (21), (all results obtained using the molybdate method of analysis), none of this material appears to have any inhibitory effect on the corrosion of metals. This is usually ascribed to it being present as unreactive long chained polymers⁽¹¹⁵⁾; in order to obtain inhibition silicate ions SiO_3^- are necessary.

A commercial sodium silicate liquor was used to produce a range of silicate concentrations in a base solution of $60 \text{ mg CaCO}_3 \text{ l}^{-1}$ carbonate hardness, 15 mg Cl l^{-1} chloride, and pH 8. The results for solder couples, Figure 26, showed a pronounced decrease in the corrosion rate with increasing silicate. Many of the solder electrodes, particularly those that had been in high silicate solutions, retained a bright metallic appearance over large parts of their surface at the end of the 4 week test.

In other work⁽⁷³⁾ the effectiveness of silicate was found to be very dependent on the length of time it had been dissolved in the test water. This was ascribed to the silicate ion rapidly hydrolysing to silicic acid, H_2SiO_3 , which then formed polymeric sols⁽¹¹⁶⁾ which had no inhibitory action on the metal system being studied. It was obvious from the results that this was not a major effect in the corrosion of solder. However, to determine if silicate was a still more effective inhibitor when freshly dissolved, a second series of tests was performed.

In these experiments the undosed base solution was trickled down a column containing pieces of sparingly soluble sodium silicate glass, with the result that freshly dissolved material was continuously fed into the cells. Corrosion rates similar to those previously found with solutions containing $40\text{mg SiO}_2\text{l}^{-1}$ silicate were obtained with concentrations of only $10\text{mg SiO}_2\text{l}^{-1}$ of silicate dissolved from the column, Table 5 viii).

b) Effect of orthophosphate

The maximum level of phosphate allowed in potable water is 2.2mgPl^{-1} , because of its tendency to promote excessive growths of zooplankton in the lakes and rivers to which it is eventually discharged. For this reason orthophosphate was tested as a potential corrosion inhibitor over a very limited range, Figure 27. No inhibitory effect was observed; cf Section 4.3.2.1.a.

4.2.8 EFFECT OF FLUX

One of the problems with soldered fittings, that arises solely from the method of making a joint, is the use of corrosive fluxes which may remain in the system if used in excessive amounts. Only one of the variety⁽³⁹⁾ of fluxes commercially available was tested for its effect on the corrosion of soldered joints. It was based on mineral grease.

Approximately 20g of the material was refluxed in 300ml distilled water for 7 hours. After cooling, the flux became solid and was separated from the water by filtration. The filtrate was then made up to 1 litre and half of it analysed for chloride, nitrate, sulphate and silicate. The remaining 500ml, to which 0.5% v/v nitric acid had been added as preservative, was analysed by inductively coupled plasma atomic emission spectroscopy. Although trace amounts of sulphate, nitrate, magnesium, calcium and silicon were detected, the overwhelming chemical entities present were zinc and chloride, indicating the flux contained 4% by weight of zinc chloride.

In another extraction experiment 2.2g of flux was melted, using a water bath, and run around the walls of a boiling-tube until solid, thereby giving an exposed surface area of 55cm^2 . Sufficient water (23ml), with carbonate hardness $30\text{mg CaCO}_3\text{l}^{-1}$, chloride 15mg Cl l^{-1} and pH 7.5, was added to just cover the area of flux. Over an initial 3 day extraction period, a pH of 6.8 and chloride level of 90mg Cl l^{-1} were obtained. After three successive extractions over a further 10 days, a 7 day extraction produced a pH of 6.1 and chloride at 47mg Cl l^{-1} .

In experiments with galvanic couples a variety of arrangements was tried. Thus 2g of flux, exposing 55cm^2 , was introduced into the solution flow prior to the boiling-tube containing the actual couple, or around the walls of the tube containing the couple. Alternatively the flux was daubed directly above the anode, on the plastic mounting sheet, so that any material going into solution would stream down the face of the electrode. An intermittent flow regime was also introduced, leaving the cells static overnight, so as to increase the concentration of the leachate in the water.

In these experiments, far from an increase in corrosion rate being observed, unusually low galvanic currents were obtained. This was in part due to the flux residues producing only small changes in solution composition. The initial water had a pH of 8, carbonate hardness $55\text{mg CaCO}_3\text{l}^{-1}$ and chloride of 5mg Cl l^{-1} . The chloride level in eight test cells only increased on average to 22mg Cl l^{-1} with a maximum figure of 31.4mg Cl l^{-1} . In all these cells the buffer capacity of the carbonate hardness was sufficient to prevent the pH from falling below 7. Even so, the average galvanic current of $3.5\mu\text{A}$ observed for the cells was significantly lower than $7.5\mu\text{A}$ to be expected Figure 22, with the mean level of chloride obtained.

Of course, concomittant with the leaching of chloride from the flux, zinc was also added to the solution. To determine the effect of this cation, zinc nitrate was added to the test solution at a concentration of

20mgZn l⁻¹, this level being proportional to the increase in chloride observed with the ZnCl₂ based flux. This resulted in a sharp fall in the observed galvanic current.

The test was repeated using a zinc salt with a counter ion that had no effect on solder corrosion. A high chloride solution, 60mg Cl l⁻¹, was used to ensure a high corrosion rate (there being no flux present in these experiments to increase the concentration). Initially sodium acetate was added at a concentration of 60mg Acetate l⁻¹. After establishing that the acetate was not inhibiting the corrosion, the sodium salt was replaced by zinc acetate in sufficient amount to maintain the acetate ion at the same concentration. This gave a zinc level of 30mgZn l⁻¹. An immediate fall in the corrosion currents was observed, see Figure 28. Polarization studies showed this arose mainly from the increased polarization of the cathode. The cathodic polarization resistance increased by 16.6kΩ over the first three days following the change whereas that for the anode rose by only 6.3kΩ over the same period, Table 1g. Thus the surprising action of flux observed in this work is explained in part by the test water, which although of quite low carbonate hardness had sufficient buffer capacity to resist large changes in pH, and in part by the zinc flux, which inhibited the cathodic reaction and so stifled the galvanic effect of the couple.

4.3 MECHANISM OF SOLDER CORROSION INHIBITION IN POTABLE WATERS

Two possible mechanisms for explaining the observed corrosion behaviour of solder in potable water readily spring to mind. They are:

- i) the presence of an ion in the water that produces an insoluble corrosion product which stifles the reaction.
- ii) the presence of an ion in the water that, while not changing the chemical nature of the corrosion product, favourably affects the physical form so that a protective layer is produced.

In both situations the films would be subject to penetration and breakdown by aggressive ions in the solution and the observed corrosion rate would be the resultant of these competing processes. With a galvanically stimulated process a third controlling mechanism is possible namely:

iii) changes in the efficiency of the cathodic reaction at the second electrode.

Various experiments were performed to test the applicability of these mechanisms to the corrosion of soldered joints, it being recognized that no one mechanism need necessarily explain the observed behaviour under all circumstances.

4.3.1 PRODUCTION OF AN INSOLUBLE CORROSION PRODUCT LAYER AS A CONTROLLING MECHANISM

4.3.1.1 Effect of carbonate hardness at pH6.

Computer calculations⁽¹⁰⁸⁾ of equilibrium solubility values for lead carbonate salts (basic and normal) indicate very little change with increasing carbonate concentration at pH 8, Table 6. To determine if this accounted for the lack of inhibitory effect on the corrosion current previously observed for carbonate ion, the experiment was repeated at pH 6 where the change in solubility is pronounced. The pH of the solutions was adjusted with nitric acid and the previously described precautions to minimise drift from the desired value were taken, Section 4.2.1.

A parallel series of experiment was carried out at pH8. In this second series sufficient nitrate was added, as the sodium salt, to make the solutions in the two experiments equal in this respect, because of the slight aggressive effect of nitrate on solder corrosion found previously, Section 4.2.5. Both experiments were carried out in the revised manner, starting all solutions on the same water. The results

indicated that even at a pH where significant changes in the solubility of lead carbonates occurs, no effect on the galvanic current is produced by changes in carbonate concentration, Table 5x), Figure 29.

4.3.1.2 Analysis of the corrosion product on solder electrodes

Two techniques were initially used to analyse corrosion products, X-ray powder diffraction and Electron Spectroscopy Chemical Analysis (ESCA).

(a) X-ray analysis

Corroded solder electrodes from the different experiments carried out in this investigation were directly irradiated with nickel filtered copper $K\alpha$ X-rays in a Phillip powder diffractometer. Apart from tin and lead, the only chemical species found, identified by d-spacings, was a hydrated lead oxide of the formulae $PbO \cdot 0.33H_2O$. This was the case irrespective of the solution composition to which the electrode had been exposed, even when some inhibitory effect had been observed e.g. in the presence of high sulphate.

By scraping off the loose corrosion deposit on several electrodes that had been exposed to similar solutions e.g. different concentrations of chloride or sulphate, it was possible to obtain enough material for X-ray powder photographs. This avoided the scattering from the uncorroded solder that reduced the sensitivity of the first series of analyses. The pattern from the powder photographs was identified as that for normal lead carbonate, $PbCO_3$. Again this was the case irrespective of which solution had produced the corrosion film.

(b) ESCA examinations

The results from ESCA supported those obtained by X-ray in that little difference was observed between deposits on the electrodes from the various solutions tested. There was a tendency for sur-

face enrichment of tin on electrodes that had been exposed to especially aggressive solutions e.g. high chloride. There was little tendency, however, for the electrode surfaces to pick-up ions present in the solutions to which they had been exposed, even where these had significantly reduced the corrosion. That this was not due to a superficial layer masking the presence of these ions was established by argon milling through the deposit to the metal beneath.

The one exception to this general picture was the electrodes exposed in solutions containing silicate. These electrodes produced very little corrosion product and maintained a bright metallic appearance over large areas even after a four week exposure. ESCA detected the presence of silicon on the surfaces of these electrodes, Figure 30. ESCA was also used to examine the deposits developed on the cathodes, the results are given in 4.3.3.

Thus, apart from the effect of silicate, the observed corrosion behaviour of solder galvanic couples cannot be explained in terms of the presence or absence of ions that produce an insoluble corrosion product on the anode. The layer actually formed is substantially the same in all solutions. Also, one of the most effective ions for reducing the corrosion, sulphate, does not have a particularly insoluble lead salt. On the other hand, phosphate, which has a very insoluble lead salt, has no effect on the corrosion rate, Table 6. It is debatable whether the inhibiting effect of silicate can be ascribed to the production of a lead silicate precipitate that stifles corrosion, the layer that is formed being so thin as to allow the electrode to retain its bright metallic appearance over most of its surface.

4.3.2 CHANGING THE PHYSICAL FORM OF THE CORROSION PRODUCT AS A CONTROLLING MECHANISM

Having established that the chemical composition of the corrosion product layer produced was the same from all but one of the solutions, this

suggested that the observed differences in corrosion rates may have arisen from differences in the physical form of that layer. The literature mentions at least two ways in which ions in solution can affect the physical form of a layer without directly changing its chemical composition, Section 2.6.1.b. These are:

- a) the coagulation of a normally colloidal corrosion product
- b) adsorption of an ion onto the metal surface which reduces the rate of dissolution of the corrosion product layer and thereby changes its physical form.

4.3.2.1 Precipitation of colloidal material

At first sight the colloidal mechanism could explain the observed behaviour. Positively charged colloidal lead species have been reported in the literature⁽⁹²⁾ and the two most effective inhibitors found in this work are both divalent negative species, i.e. SiO_3^- and SO_4^{2-} , which theory suggests would be far more effective in precipitating colloidal material than monovalent negative ions, Section 2.6.1.b. Chloride is an effective peptising agent, i.e. it is antagonistic to colloidal precipitation and encourages the formation of colloidal species, which would account for its observed stimulation of the corrosion reaction. The lack of effect from phosphate, the only other double negative ion tested, could arise from the low concentration used, 2.2mg l^{-1} being the maximum admissible concentration in potable waters. Even sulphate had to be present at high enough concentration to overcome the aggressive action of any chloride present.

(a) Effect on corrosion of high phosphate concentrations

Using a solution containing 30mg Cl l⁻¹ chloride, a range of phosphate concentrations were tested up to a maximum of 60mg PO₄ l⁻¹ (i.e. =19.6 mg P l⁻¹). At this last concentration the phosphate to chloride ratio* was 2:1 PO₄:Cl, a ratio at which sulphate had been found to have a major effect.

The results (Table 5xi), Figure 31, indicated phosphate was without effect even at these higher concentrations. This further demonstrates the inadequacy of any insoluble lead salt mechanism to explain the observed corrosion behaviour of solders, considering that at under the solution conditions lead phosphate would be even more readily precipitated. It also throws doubt on a colloidal precipitation mechanism where the charge on an ion is of greater importance than its chemical identity and, as such, HPO₄⁼ ought to show the same behaviour as SO₄⁼ at the same concentration.

(b) Detection of colloidal species in an aggressive solution by the Tyndall effect

Attempts were made to detect colloidal material in an aggressive solution by the light scattering produced by such species, the well established Tyndall effect⁽⁹²⁾. In order to directly observe the corrosion layer produced, two anodes were fabricated with a surface area of 36cm². These anodes could only conveniently be made of lead because of the large size involved. Each was coupled to a copper cathode with an area of 240cm², giving an electrode ratio approximately the same as that used in the normal galvanic couples employed in this work.

* No correction is required to this weight for weight ratio calculations for differences in molecular weights between PO₄ and SO₄ given their near equivalence i.e. 95 and 96 respectively.

The two solutions used in these experiments both contained chloride at a concentration of 1000mg Cl l^{-1} , in order to encourage the formation of colloidal material.

One of the solutions, however, also contained sulphate at a sufficiently high concentration, $2000\text{mg SO}_4 \text{ l}^{-1}$, to produce inhibition of the corrosion.

The large galvanic couples were placed in 2 litres of their respective solutions in covered beakers. The solutions were stirred very rapidly to encourage the removal of corrosion product from the anodes by an hydraulic scouring effect. A resistance of only $1\text{k}\Omega$ was used in the external circuit to ensure a high corrosion rate that might also favour the transfer of colloidal material into the solution.

After 3 weeks the couple in the sulphate/chloride solution was corroding at 18% of the rate of that in the chloride only solution, 41 versus $224\mu\text{A}$ respectively. The physical forms of the corrosion product layers were quite obviously very different, Photographs 7 and 8.

Samples of the solutions were taken and, after centrifuging for 5 minutes to remove precipitates and other extraneous matter, examined as to their ability to scatter light. Neither solution scattered light, both gave similar low readings (as measured against a 0.01M platinum standard) to a control solution exposed for 3 weeks under similar conditions but without electrodes. The control was used to allow for the effect of dust particles from the air that inevitably contaminate solutions when exposed under the conditions of the experiment. These experiments established that while the effect of sulphate was on the physical form of the corrosion product, no colloidal species were involved.

4.3.2.2 Change in the physical form of the corrosion deposit

(a) Examination of the corrosion products by SEM

The corrosion deposits produced in the high chloride only and the high chloride plus sulphate solutions, used in the colloid experiment, were examined in a JXA 50A micro-probe analyser. The deposit from the chloride only solution contained two distinct crystal types, Photograph 9. The cubes were analysed and found to contain both lead and chloride, whereas in the needle shaped crystals only lead was detected. In the solution containing sulphate and chloride, crystalline plates were formed which were found to contain lead, but virtually no (<4%) chloride, Photograph 10. No trace of sulphate was detected despite its high concentration in the solution. The pronounced difference in the physical form of the two deposits can easily be seen in the photographs.

Solder electrodes, of the more usual size of 2cm^2 , exposed to the same high sulphate solution produced a similar deposit, although the picture is a little more complicated because of the presence of tin corrosion deposits, Photograph 11.

(b) The corrosion of lead when not galvanically coupled

It had been found that the corrosion of lead when not coupled to copper is inhibited by chloride, Section 4.1.10. Bearing in mind the relatively high solubility of lead chloride, Table 6, this led to the conclusion that the controlling mechanism must be the same as that for sulphate i.e. the production of a corrosion deposit with a favourable physical form for the protection of the metal. This prediction was tested by exposing an uncoupled lead electrode in a solution containing a 1000mg Cl l^{-1} of chloride. An SEM picture of the corrosion deposit developed after 3 weeks, Photograph 12, shows the corrosion deposit is similar to that produced in the high sulphate solution, Photograph 10, thus

vindicating the prediction. Further, the chemical analysis of the deposit showed the virtual absence of chloride which is in contrast with the situation of galvanically coupled lead in the same solution, but parallels the situation for the same couple in the high sulphate solution.

4.3.3 INHIBITION OF THE CATHODIC REACTION AS A CONTROLLING MECHANISM

The galvanic stimulation of the corrosion of soldered joints raises the possibility of corrosion control by inhibiting the cathodic reaction, the reduction of dissolved oxygen at the copper. The occurrence of such inhibition would be indicated by a high value for the polarization resistance of the cathode concerned. Obviously only the positively charged ions in solution, which migrate towards the cathode, are candidates for possible cathodic inhibitors.

In this work only zinc was found to act as a cathodic inhibitor. This was established by polarization measurements, Table 1g, and the presence of zinc on the cathode confirmed by the ESCA studies. The ESCA work also indicated the presence of lead, presumably from the migration of ions from the nearby anode, so that this process, acting in an analogous manner to zinc, might provide an intrinsic inhibitor for the corrosion of soldered joints.

The effect of stimulating the corrosion reaction by replacing all calcium ions with sodium has already been mentioned, Section 4.2.6. This may be indicative of cathodic inhibition by calcium, from the precipitation of calcium carbonate, that would be present as a background effect in most of the solutions tested in this work.

5. DISCUSSION

5.1 CHOICE OF EXPERIMENTAL METHOD

The most obvious approach, to study the contamination arising from tin-lead soldered joints, would be to take a large number of water samples from different real plumbing systems, covering as wide a variety of water types as possible. This method was not pursued for the following reasons:

- a) The difficulty in obtaining the agreement of the general public to sample their own domestic plumbing systems, a necessary step where first-draw samples are arguably the most informative. A first-draw sample is the first sample of water to be taken from the kitchen tap after the system has been static overnight. Even where willing cooperation is obtained, the competence of the people to carry out the prescribed procedure reliably on each occasion, over what could be a prolonged period, may be in doubt.

In sampling larger non-domestic systems, where problems may be more acute because a larger number of soldered joints are involved and longer static periods may occur, the necessary detailed knowledge of the system prior to the individual sampling points may be difficult to obtain. Furthermore the state of the system at the time of sampling, i.e. precisely how long the water has been static, may be more uncertain given the large number of outlets.

- b) Because a wide variety of water types would need to be studied, it would entail an exercise spread over the whole country. Accepting that the organisational difficulties would not be insurmountable, the waters actually studied would not cover the full range possible in potable waters for each individual ion or combination of ions. Inevitably, the actual waters studied would be determined to some extent by the willingness of the different regions to cooperate, and some overlap in type or composition would probably be unavoidable.

Additionally, as a public supply would be involved, it would not of course be possible to experiment with potential inhibitors, or to adjust a particular ion concentration, without at least having some laboratory evidence beforehand as to the likely effect of such action.

- c) Although ultimately the most significant parameter, simply measuring the lead concentration in a sample of water withdrawn from the system gives no information as to the mechanism that determines the level observed. No direct information is obtained about the corrosion reaction that causes the metal to be oxidised in the first instance. It remains an open question whether the rate of corrosion, or the solubility of the corrosion product layer, determines the level of contamination observed in the supply. Sampling from real systems does not allow a distinction to be drawn between high lead levels arising from the action of the specific water composition with the soldered joint, over which the water supplier has some direct control and hence responsibility, and those arising from poor plumbing practice, e.g. in design of the system, start up procedure and skill in making the joints, concerning which the water supplier can only advise.

Given the above drawbacks to a study of tin-lead soldered joints based primarily on field sampling, the second choice would appear to be the use of simple laboratory test rigs. With this approach the various parameters involved, e.g. static and flow periods, rates of flow, etc. can be quite precisely defined. The range of waters that are studied can be readily controlled, as well as the use of various inhibitors. This approach shares some of the disadvantages of the field study method, discussed in b) and c) above.

Other difficulties arise from the virtual impossibility of repeatedly producing a standard soldered joint, i.e. with the same area of solder exposed in the bore of the tube in the same state of oxidation. Because each rig will have several joints, a large variation in lead levels can be expected between rigs on the same water. This would necessitate a large amount of replication for each variation in water composition studied. Similarly, because ideally each rig should only be used once (the behaviour

of a rig on a new water would be affected by its previous history and any cleaning process is likely to introduce artifacts not encountered in real systems), this would further increase the number required. This is likely to be awkward even with the simplest design, and the volumes of water required are likely to be inconveniently large.

In the light of the above considerations the technique adopted was the galvanic corrosion cell. The extreme simplicity of the design eased the necessary replication of the system, something in excess of 400 cells were manufactured in this work, and in each test the area of exposed solder was standardised. The compactness of the system, and the relatively small volumes of solution required, allowed as many as thirty cells to be run at one time. This enabled around 200,000 corrosion hours to be completed in this work for a cumulative volume of test solutions approaching 6,500 litres. Measurement of the electrical current in the external circuit (the galvanic current) allowed information on the corrosion reaction to be obtained, and determination of the lead in the water allowed this to be related to the level of contamination being produced.

This approach specifically studies the effect of water composition on the corrosion of tin-lead soldered copper joints and the level of contamination arising therefrom. It is the aggressiveness of the supply that is of major interest, being the responsibility of Water Utilities. The technique does not directly assess the effect of factors associated with the plumbing itself, such as the design of the system, water usage patterns, area of solder exposed at each joint etc., that also have a significant effect on the final level of lead at the customer's tap. The importance of these factors can be gauged, however, once the galvanic corrosion cell technique has allowed the effect of water composition to be quantified.

5.2 THE COMPARABILITY, REVEALED BY THE POLARIZATION STUDIES, BETWEEN THE CORROSION BEHAVIOUR OF THE GALVANIC TEST CELL AND THAT OF A SOLDERED JOINT

The behaviour of a galvanic couple can be expressed by a mathematical formulae that describes the polarization (Evans) diagram, Appendix I and Figure 5. As noted previously, Section 2.4.4, when the current axis of the

latter is plotted in a linear fashion, this formulae is based on Ohms law and takes the form:

$$I_g = \frac{EMF}{R_a + R_c + R_s} \quad \dots 2.17$$

where I_g is the galvanic current

EMF is the electromotive force.

R is the resistance of respectively:

anode polarization

cathode polarization

solution (electrolyte) between the electrodes

When the lines on the Evans diagram, that best describe the anode and cathode behaviours at high current values ($I > 1 \mu A$), are extrapolated to the potential axis, the difference between the two points of intersection with that axis equals the "effective" EMF for the cell, see Figure 5. It is this value strictly speaking, that should be substituted in equation 2.17. In actual fact, for the vast majority of cells, there was negligible difference between the effective EMF and the actual EMF, the latter obtained by simply subtracting the open circuit potentials of the two electrodes. The average values calculated from all the solder galvanic cells, Table 1, were $370 \sigma \pm 63$ versus $381 \sigma \pm 42$ mV for effective EMF and actual EMF respectively.

It is feasible to average the EMF results for all the solder galvanic cells because the values were in close agreement, showing variation but no consistent change with the composition of the solution under test. In other words all the differences in the corrosion rates observed in the tests arose from changes in the total circuit resistance. The fact that the EMF, the thermodynamic driving force of the cell, remained essentially the same is indicative that the actual chemical reactions occurring were the same in all the different solutions tested i.e. presumably:

where M is either Pb or Sn.

Obviously these reactions will occur in the corrosion of a soldered joint and no differences in behaviour between the galvanic test cell and such joints will arise from this source.

As far as the circuit resistance is concerned, the polarization diagram allows the anodic and cathodic polarisation resistances to be individually determined, Figure 5. The resistance of the solution between the electrodes being measurable by other means, Section 4.1.2, and the resistance of the external circuit being known, it is possible to determine the effect of each individual source of the circuit resistance in controlling the galvanic current produced.

A major difference between the galvanic test cell and a soldered joint is that the latter has nothing equivalent to the external circuit resistance, the solder and copper being in direct physical contact. A resistance was used in the external circuit of the former, in the first instance, so that the galvanic current could be determined by simply applying Ohms law to the measured potential fall it produces in the circuit. Such measurements are readily made using the high impedance pH meters with which most laboratories in the Water Industry are equipped. Also, this method allows many test cells to be run simultaneously. The alternative of using a zero resistance ammeter is not so convenient in this regard. The value of $10k\Omega$ for the external resistance was chosen as a compromise between the even larger variation in results between replicates produced by lower values and the loss in sensitivity that arises when using higher values, Section 4.1.8 and Table 3.

The only situation where this external resistance produces major differences in behaviour from that of a soldered joint, is in highly aggressive solutions or in the early stages of the corrosion in other solutions.

Under these circumstances the term $R(\text{anode}) + R(\text{cathode})$ is very small and the external resistance is the major contributor to the total circuit resistance, $R(\text{solution})$ being small in most cases. A simple calculation then shows that, with an effective EMF of 370mV for most solutions, the maximum galvanic current obtainable from the test cell with $10\text{k}\Omega$ in the external circuit is 37 μA . Obviously there is no such restriction on a soldered joint. However, because with most potable waters some kind of film is produced on each of the electrodes, the term $R(\text{anode}) + R(\text{cathode})$ is not usually negligible.

The highest galvanic current measured in this work, for water of potable quality, was <20 μA . It can be calculated, using an effective EMF of 370mV and ignoring the small contribution from the solution resistance, that for a galvanic current of 20 μA the combined effect of the electrode polarization resistance must be contributing $8.5\text{k}\Omega$ to the circuit resistance. Under these circumstances, the external circuit resistance of $10\text{k}\Omega$ contributes 54% of the total resistance and is the main controlling influence on the galvanic current. This is the extreme case however, for most of the solutions tested the combined contribution from the electrodes was >40 $\text{k}\Omega$ (Table 1) hence they, and not the external resistance, were the controlling factor for the galvanic current. This would be the case with a soldered joint.

By extrapolating the anodic and cathodic curves of the polarization diagram until they cross, it is possible to estimate the value of galvanic current when the external resistance and solution resistance are zero. For actual soldered joints, where R_{ext} is virtually zero because the two metals are in physical contact, the significance of the solution resistance is to determine the effective cathodic area. This is the length of copper pipe with which the anode is in sufficient electrolytic contact, i.e. by ionic migration through the solution, for it to act as a cathode for the anodic reaction on the solder. In a soldered joint the effective cathodic area is likely to be very much greater than the anode for all but the largest areas of exposed solder. This situation counters the tendency for the cathode to polarize, arising from the slow rate of oxygen diffusion to the electrode surface. Thus the corrosion of soldered joints will be controlled more by the reactions at the anode than cathode.

This may be the case even where quite large areas of solder are exposed in the bore. Such areas usually occur as runs of metal along the tube which brings them into contact with a correspondingly larger area of copper. Along the length of the run the maximum separation of anode and cathode is the diameter of the pipe. It is the area of cathodic surface beyond the ends of such runs that is determined by the solution resistance.

For corrosion reactions under anodic control, i.e. $R(\text{anode}) \gg R(\text{cathode})$, any difference in extent of cathodic polarization between the test cell and a soldered joint has only a minor effect on the galvanic current produced. When operating under cathodic control, however, the galvanic cell is likely to give a lower galvanic current than an actual joint, because with the former the smaller cathodic area would be more polarised for a given current flow. Thus, overall, the galvanic current produced by the corrosion cell, with zero resistance in the external circuit, agrees approximately to a similarly exposed area of solder in a real joint, perhaps slightly underestimating the value where the reaction is under cathodic control.

The polarization results in Table 1 indicate that for solutions of low aggressivity, i.e. chloride 15mg Cl l^{-1} , pH 8, the test cell operated under mixed anodic and cathodic control, both electrodes having polarization resistances of about $20\text{k}\Omega$. Changes in aggressivity were usually reflected in differences in the anode resistance. This was particularly noticeable in the presence of inhibitors or in aggressive waters. Thus in the presence of inhibitors, anode polarization resistances could rise to above $500\text{k}\Omega$ and, in the presence of an aggressive ions, fall as low as $5\text{k}\Omega$. The cathodic polarization showed much smaller variation ie $\pm 15\text{k}\Omega$. The exception to this was in the presence of a cathodic inhibitor when values in excess of $100\text{k}\Omega$ were obtained, Table 1.g.

5.3 RELATIONSHIP BETWEEN THE GALVANIC CURRENT AND THE LEVEL OF LEAD CONTAMINATION

The relationship between the corrosion current and the quantity of metal oxidised is derived from Faraday's laws of electrolysis. The formulae is:

$$m = \frac{A (It)}{ZF} \quad \dots 5.1$$

where m = mass of metal oxidised (grams)

A = atomic weight of metal

Z = number electrons involved in oxidation (= 2 for lead and tin)

I = current generated by the oxidation (amps)

t = time for which current flows (seconds)

(It) = quantity of electricity (coulombs)

F = Faraday constant

= 96,500 coulombs, the quantity of electricity generated by the oxidation of 1 gram equivalent of metal.

The equation can be simplified into the form:

$$m = k(It) \text{ where } k \text{ is a constant} = \frac{A}{ZF}$$

Thus the quantity of metal oxidised is proportional to the corrosion current and the time for which it flows. Alternatively the equation can be expressed as:

$$\frac{m}{t} = k.I$$

which indicates that the corrosion current is directly proportional to the corrosion rate.

In applying the Faraday equation, a distinction must be made between corrosion current and galvanic current. The former is that generated by the total corrosion reaction and is the one to which Faraday's laws can be applied to determine the amount of metal oxidised. The galvanic current is that proportion of the corrosion current that flows between the two dis-

similar metals in a galvanic couple. In the test cell this is obviously the current that flows in the external circuit and is the only current measured.

A potential problem with any galvanic method of determining corrosion rates is that the galvanic current measured may only represent a fraction of the total corrosion current, Section 4.1.6. The material may corrode using internal cathodes, such as impurities or precipitates, because their proximity results in a much lower electrical resistance in the corrosion path. This produces no contribution to the galvanic current flowing in the external circuit. The chances of this occurring were increased with the cell used in this work, because the external copper cathode was 'hidden' behind the $10k\Omega$ resistance in the external circuit.

Another difficulty is that with the tin-lead alloy only the corrosion of the lead has any medical significance. It was thus necessary to determine what proportion of the galvanic current was generated by the corrosion of lead rather than tin and if there was any preferential corrosion of one metal over the other. Even if there was no preferential attack, it was still possible that the proportion of the galvanic current to be accredited to lead corrosion might be dependent more upon relative area of the lead rich phase exposed to attack, composition by volume, rather than the composition of the alloy calculated on a weight basis.

Although corrosion in acid solutions produced wide discrepancies between the galvanic current and the amount of metal oxidised, Section 4.1.6, the experiments carried out using waters more akin to potable supplies, i.e. with near neutral pH values, showed a remarkably close relationship between galvanic current and total corrosion rate, Figures 16 and 17. With the lead electrodes, greater than maximum theoretical amounts of lead were oxidised at high charge values. In both of these cases corrosion had progressed to such an extent that disintegration of the electrodes had occurred. Presumably this resulted in pieces of metal becoming detached, adding ultimately to the lead concentration but without contributing to the galvanic current.

For all the other electrodes, although strong linear relationships were obtained between galvanic current and total lead oxidised, the amount of lead was less than might have been expected by Faraday's laws. For the 40:60 and 95:5 alloys, the relationship did lie between the maximum theoretical lines (assuming no preferential corrosion of one of the phases), calculated as composition by weight or composition by volume Figures 16 and 17. The phases present in these alloys are lead rich and eutectic in the former and tin rich and eutectic in the latter. The line for the 60:40 alloy, however, Figure 17, fell below the percentage by volume theoretical line. This composition is virtually all eutectic with a small amount of lead rich phase, see Figure 1.

A separate experiment was performed on a 60:40 alloy to determine the total amount of tin oxidised. Unfortunately the determination of the two metals on the same sample is not possible, because the 0.5% nitric added at the end of the experiment to keep the lead in solution causes the precipitation of tin as stannic oxide. Similarly, the 10% sulphuric acid, recommended to preserve solutions for tin analysis, precipitates the lead and the 15% solution of trisodium phosphate (111), used to remove the tin corrosion products, is not suitable for lead salts. Difficulties were encountered with the analytical method and, as there was not sufficient time to overcome these, the results cannot be considered very accurate and so are not presented. They did show, however, that more tin than the 60% maximum theoretical by weight was being oxidised i.e. the tin experimental line ran above both theoretical lines, the mirror image of the corresponding line for lead, Figure 17.

The simplest explanation of the results for the 60:40 near eutectic alloy is that the tin phase corrodes in preference to the lead. At first sight this appears unlikely although the free corroding potential of lead is not much lower than that of tin, mean 446, σ_{n-1} 29.5 versus mean 400, σ_{n-1} 36.6 mV respectively, Table 1bi) and biii). The potentials of the lead-rich and tin-rich phases in the eutectic metal need not necessarily reflect the potentials of the pure metals of course. It is conceivable that a reversal of potentials occurs in the near eutectic alloy such that the tin-rich phase is preferentially attacked. Alternatively the very fine grain

structure of the near eutectic alloy may have an effect. Perhaps the lead rich phase of the eutectic grain becomes rapidly etched, leaving a metal surface effectively enriched in tin. If this were the case, however, there would be an initial period during which more lead would corrode than the 40% by weight maximum theoretical, and this has not been observed. There is thus no satisfactory explanation of this very interesting result and a more detailed study is required.

All the results however, even for the 60:40 near eutectic alloy, do show a strong linear correlation between the quantity of lead corroded and the galvanic current, even if this relationship does not vary on a simple pro rata basis with alloy composition.

Although the galvanic current measures the rate of metal oxidised, not all this material necessarily appears in the water. A proportion stays on the metal surface as a corrosion product layer. The experimental results, however, Figure 18, indicate that with time a progressively larger proportion of the oxidised metal appears in the solution. Presumably the corrosion product eventually covers the entire metal surface and reaches an equilibrium thickness after which, with continued corrosion, the deposit starts to break off and enter the water. If the curve in Figure 18 were continued, it can be expected to become parallel with the 60% maximum theoretical by weight line, after which all further metal oxidised would enter the water.

All these results were obtained under completely static conditions however, whereas in actual plumbing systems the scouring action produced by the stopping and starting of the water flow is likely to readily remove loosely adhering deposits. Thus, after an initial period in which the corrosion product reaches equilibrium, all the metal subsequently oxidised appears in the water, in one form or another, so that the galvanic current is a direct measure of the average rate of contamination of the supply.

5.4 VARIABILITY BETWEEN REPLICATES

The dilemma of the scatter in results obtained between replicates was that, although it would be pointless to treat electrodes in such an esoteric manner that their behaviour became unrepresentative of the corrosion of real soldered joints, variation between replicates was entirely unwelcome when studying the individual effect of ions in solution. Chemical treatment of the electrodes, to make their initial surface films more comparable, is likely to affect the two phases of the solder differently, leading to the enrichment at the surface of one or the other. Mechanical cleaning, e.g. polishing, destroys the natural grain structure by smearing the top layer of the soft metal. From previous work on the galvanic corrosion of lead, it is known this is likely to reduce the rate of corrosion. Of course, any chemical treatment subsequent to polishing, to clean back to the grain surface, has the objections outlined above.

An obvious cause of variation between electrodes is the presence of charred flux embedded in the metal surface. This was minimised by using as little flux as possible on the copper template of the electrode and, after dipping in the molten solder, cleaning the surface with perchlorethylene and rubbing with tissue to remove obvious contamination, Section 3.1.

Rigorous control of the temperature of the solder in the dipping bath did not significantly improve reproducibility in the results. Dipping out of contact with air was not considered practicable and in any case would be unrealistic. Sufficient skill was developed in dipping to consistently produce electrodes with a mirror-like finish i.e. non-granular surfaces that were without gross dissimilarities obvious to the naked eye. Of course, if the causes of the variations occur at the grain or atomic level, there is little that can be done about these and the situation does no more than reflect the behaviour to be expected of real soldered joints.

The main problem of variability between replicates is the possibility of bias being introduced into the results. This danger is of course greatest for ions that have little effect on the corrosion rate, illustrated by the earlier experiments on carbonate hardness some of which suggested an

increase in corrosion with concentration, Figure 21. This result was not supported when the experiment was repeated in the revised manner, introduced to minimise the effect of bias, Section 3.2.3 and Figure 29. Other methods of improving confidence in the results, given the problem of variability, include increasing the number of replicates and extending the range of concentrations studied, rather than limiting this simply to that found in potable waters.

5.5 THE VALUE OF SHORT TERM CORROSION TESTS TO PREDICT LONG TERM CORROSION BEHAVIOUR

It is well established that the majority of metals corroding in aerated waters at near neutral pH values produce an oxide as the initial corrosion deposit, because of its high thermodynamic stability⁽¹¹⁷⁾. If the film is non-protective and the corrosion continues, whereas the dissolved oxygen is prevented from reaching the metal surface, because of the physical barrier of the corrosion product, the passage of charged species can still occur because of the potential gradient across this film⁽¹¹⁸⁾. This results in secondary corrosion deposits being formed, very often of metal carbonates. With lead the basic carbonate, hydrocerussite, would be expected from thermodynamic considerations. However, in this work, as in many cases of lead pipe deposits examined at the WRC, the normal carbonate was in fact found.

One of the unavoidable problems of using short term tests to predict long term corrosion behaviour is that the corrosion layer produced over the four week laboratory test is the initial oxide layer. This would in practice convert with time to a carbonate deposit, which could have a substantially different effect on the corrosion process and be more protective. This possible difficulty does not seem to arise, however, because if a protective layer is formed it is almost invariably the initial one. Failure of this film to protect the metal leads to further corrosion and the laying down of a thicker deposit in solutions where the salt formed is insoluble. This slows reaction rates further by its sheer bulk, but rarely goes on to form a protective layer. This is in accord with the well known observation that the initial film formed on a metal surface is very

influential on the subsequent corrosion. Corrosion inhibitors are more effective if applied from the moment a metal is brought into service, when the surface has only a thin air-formed film, than if it is applied to a system that has a well established corrosion product layer(119). Similarly, if copper tubes are left standing full of water, as can happen after trials to prove a plumbing system, they may develop non-protective oxide layers that remain unsatisfactory, even after the system has been brought into operation and conditions established which, if the pipe experiences them from the first, allows satisfactory films to be developed(112). Considerations such as these make it feasible to use a short term test to predict long term corrosion behaviour.

5.6 COMPARISON OF GALVANICALLY MEDIATED CORROSION OF LEAD AND SOLDER WITH FREELY CORRODING LEAD PIPE

The present work has established important differences between the galvanic mediated corrosion of lead and that of the freely corroding pipe. Work at the WRC and elsewhere has shown that the concentration of lead contaminating the supply from lead pipes is ultimately determined by the solubility of the corrosion product layer(108,109). Little work has been done to measure corrosion rates of lead directly and it is still an open question as to how they are affected by a change of solubility of the corrosion product that is formed. The present work on galvanic couples, however, has produced water samples with lead levels several orders of magnitude higher than the calculated equilibrium solubility levels, e.g. $> 20\text{mg l}^{-1}$ compared with a calculated equilibrium solubility for basic lead carbonate of 0.093mg l^{-1} for a water with $40\text{mg CaCO}_3\text{l}^{-1}$ carbonate hardness and pH 8(108). Presumably most of the excess material was present in the water as a fine precipitate.

Thus, whereas a water treatment can be devised to overcome a contamination problem from lead pipes by calculating the respective equilibrium solubility values of the possible lead salts, for galvanically stimulated corrosion, whether of lead pipe or solders, this approach is unsatisfactory. Increases in carbonate hardness and phosphate, both of which have been successfully used to overcome problems from lead pipe, have little or no

effect on the galvanic corrosion rate. Sulphate, one of the most effective ions in reducing galvanic corrosion, does not have a very insoluble lead salt, Table 6, and is not used as a treatment for lead. Finally chloride, which stimulates galvanic corrosion, surprisingly acts as a corrosion inhibitor with uncoupled lead pipes. For these reasons, the galvanically stimulated corrosion of both lead and solder has to be treated as a completely separate phenomenon from the corrosion of the uncoupled metals. Galvanic coupling does not simply increase the rate of attack on these metals, it can also introduce qualitative differences as well, Section 5.8.

Another important difference between the two situations is that whereas the corrosion of uncoupled lead is sensitive to flow-rate, Table 4ii) with galvanic couples, even under completely static conditions, the corrosion rate decreases only slowly with time, Figure 15. Indeed if the flow rate is above 35 ml hr^{-1} (a slowly dripping tap) the galvanic current was found to be independent of flow conditions up to rates of at least 700 ml.min^{-1} ($42 \text{ litres hr}^{-1}$ or 9.2 gal hr^{-1}) (113). Thus, whereas the slow rate of corrosion of lead pipe can be expected to fall even further during the overnight static period, the corrosion rate of soldered joints, higher in the first instance, will hardly be affected.

From the above considerations it would appear that, for galvanically mediated corrosion, the only ultimate limit on the possible level of lead contamination is the total exhaustion of the dissolved oxygen in the water. If this is the case, it can be calculated from the overall corrosion reaction:

that a water containing $8.8 \text{ mg O}_2 \text{ l}^{-1}$, the saturation value at 20°C , would oxidise 68.4 mg of lead (assuming 60% utilisation of the oxygen to corrode lead)!

5.7 EFFECT OF WATER QUALITY PARAMETERS ON GALVANIC CORROSION RATES

The main water quality parameters that determine galvanic corrosion rates were found to be pH, chloride and sulphate. The effectiveness of the sulphate, which inhibited the attack, was determined by its ratio to the chloride content. Although the additions of silicate as sodium silicate was also found to inhibit the galvanic attack, the silicates present naturally in potable waters are unlikely to be of the right form to affect the corrosion. This has been found to be the case for the corrosion of iron⁽⁹⁷⁾ and the dezincification of brass⁽⁷²⁾ in potable supplies.

Although solutions containing nitrate produced some of the highest corrosion rates observed in this work, Table 5 vii), and the corrosion product produced had a very distinctive physical form, Photograph 6, no significant correlation was found between the corrosion current observed and nitrate concentration, Figure 25. The presence of nitrate effectively increased the range of scatter in the results without apparently imposing any trend. The limit on nitrates in potable waters of 11.3mgNl^{-1} , because of medical considerations, effectively restricts the significance of this factor in determining corrosion rates at soldered joints. Sodium ion, which was found to stimulate the corrosion, is also likely to be of only limited importance because waters with high sodium contents are not common.

A regression analysis was performed on a selection of the results to relate the mean galvanic current over the fourth week to the water composition, see Table 7. Only the results for solder were considered and solutions containing ions not normally found in potable water, or not normally found at such high concentrations, were specifically excluded. The results excluded were those from the tests on the effect of silicate, phosphate, nitrate and zinc. Essentially the figures in Table 5 sections iii) to vi) inclusive were used, in all a total of 121 results.

The analysis confirmed that the most significant water composition factors were chloride concentration, sulphate to chloride ratio, and pH. The linear regression equation was:

$$I = 2.90 \log Cl - 2.69 \log \text{Ratio} - 1.17 \cdot \text{pH} + 9.75$$

where I = mean galvanic current over fourth week

Cl = Chloride concentration, $\text{mgCl} \cdot \text{l}^{-1}$

Ratio = ratio of $\text{SO}_4:Cl$ concentrations

This indicated that at least for the specific set of results analysed, the pH was the major factor in determining the corrosion rate. Given the limited pH range found with potable waters, however, the chloride concentration is the chief source of variation between different supplies. The effect of the chloride is reduced by sulphate. The equation, however, accounts for only 42.7% of the variance in the results, thus suggesting that the major factor in determining the corrosion rate is the intrinsic reactivities of the individual electrodes, rather than the composition of the water to which they are exposed.

The basic mechanism for the corrosion of metals in aqueous solutions involves the production of an oxide film by a reaction such as⁽¹²⁰⁾:

This produces the stifling of the high corrosion rates initially observed when the metal is first immersed, Figure 8. When the oxide has covered the entire surface, the rate of the continuing corrosion is determined by the thickness and coherence of the film formed. The coherence is controlled by the atomic discontinuities at the surface of the individual metal specimens. These include such things as grain boundaries, vacancies (molecules missing in surface layers), kink sites (molecules missing at edge of layers), emergence of dislocations and impurity inclusions in the metal surface.

In the absence in the aqueous phase of any active ion that has an effect on the film, the observed corrosion rates will be under the sole influence of these discontinuities. Thus there will be little correlation between corrosion rate and solution composition, and the variation in the results

will be large, dependent as it is on the differences in the atomic disarray of the metal samples under test. In the presence of aggressive or inhibitory ions in solution, however, which encourage either film breakdown or repair, the intrinsic differences between the metal samples becomes less significant, the variation in results decreases and the corrosion rates obtained show a far higher correlation with water composition.

With the above considerations in mind, the results previously analysed were subdivided into two categories, those with solution compositions that could be expected to be fairly inactive, containing neither aggressive ions nor inhibitors, and those with compositions that were active in one of the these ways. The criteria used to define an active composition was $\text{pH} < 7$ or chloride $> 60 \text{mgCl l}^{-1}$ or sulphate:chloride ratio > 1 . This divided the original sample into 64 inactive solutions and 56 active ones. Repeating the regression analysis on these two data sets gave an accounted for variance with the inactive solutions of only 13%, but for the active solutions the figure rose to 63.8%, Table 7. This demonstrates that for corrosion in inactive, or mildly aggressive, solutions it is the surface condition of the metal that is of overwhelming importance. It is only in aggressive or inhibited waters that the solution composition becomes the major factor determining corrosion rates.

The aggressive behaviour of pH and chloride to solder galvanic couples can be fairly readily understood in terms of current theories. At low pH values, the solubility of the protective metal oxide film increases, and the thinning of the layer which results produces high corrosion rates. The aggressive action of chloride, derived from its tendency to penetrate and disrupt protective films, is also well established. This effect arises from the high potential gradient across such films⁽¹¹⁸⁾ and the high polarizability of the chloride ion⁽¹²¹⁾. The behaviour of the corrosion inhibitors discovered in this work also exemplify various mechanisms found with other metals corroding in aqueous environments, Section 5.8.

The one ion that does not readily fit into any current category is nitrate. This ion produced very high corrosion rates, Table 5 vii), a very distinctive and loosely adhering corrosion product, Photograph 6, and a

very large scatter in the results such that little correlation between corrosion current and nitrate concentration was observed, Figure 25. The results appear to fall into two distinct groups. The first series, at the highest corrosion rates, show an increase in corrosion rate with nitrate concentration. The large second group suggest no correlation between corrosion rate and nitrate concentration. These results can be explained if the nitrate is assumed to exacerbate the corrosion while not having the ability to penetrate the surface oxide film to initiate it. The nitrate might thus be described as an "aggressive ion of opportunity". The number of discontinuities in the corrosion film is not changed by the nitrate; the number is determined as in an inactive, mildly aggressive, solution by the atomic irregularities of the individual metal sample. Thus the spread of results is that found with mildly aggressive solutions. At the higher corrosion rate values, however, where more discontinuities in the surface film are present, nitrate exacerbates the attack and the corrosion rates observed do show some correlation with nitrate concentration.

5.8 MECHANISMS OF SOLDER CORROSION INHIBITION IN POTABLE WATERS

The three corrosion inhibitors discovered in this work, silicate, sulphate and zinc, each exemplified a different control mechanism for the galvanically stimulated corrosion of metal in potable water.

These mechanisms were:

- (a) changing the chemical nature of the corrosion product to form a protective layer (silicate).
- (b) changing the physical form of the normal corrosion product to form a protective layer (sulphate)
- (c) formation of a precipitate on the cathodic electrode inhibiting the reaction and hence reducing the effect of the galvanic stimulation (zinc).

(a) Effect of the silicate

The effect of silicate was quite distinctive from that of the other parameters studied. The relationship between silicate concentration and galvanic current showed a better fit when the former was expressed in a linear fashion, rather than the logarithmic relationship found for the other variables, Figure 26. At the concentrations of silicate which gave very low corrosion rates i.e. $>20\text{mg SiO}_2\text{l}^{-1}$ the surface of the solder retained its bright metallic appearance even after 4 weeks in the solution. This was in contrast with sulphate, the other anodic inhibitor, which gave the electrodes an olive drab non-metallic appearance, Photograph 8. The third distinctive feature of silicate was its adsorption onto the metal surface. Although solder electrodes were exposed to a wide range of solutions, only in two cases did the corrosion product layer show any deviation from the usual lead oxide/lead carbonate mixture. One of these was with silicate, where ESCA analysis of the anode surface indicated the presence of silicon, Figure 30.

It is debatable whether the action of silicate can be described as protection by the formation of an insoluble corrosion product layer, very little in the way of corrosion product being formed in completely inhibited solutions. Rather the action appears to be one of forming a silicon-rich layer over the surface that is either itself more effective at preventing corrosion than the normal oxide layer or which reinforces the oxide making it more protective. The effectiveness of the inhibition seems to depend on the rate at which the silicate layers forms versus the rate at which the normal oxide layer is produced, for it has been noted with other metals that silicate is very much less effective on metal surfaces that already have substantial corrosion deposits(119). Silicate does not appear to stifle the reaction of a corroded surface by the precipitation of lead silicate into the pores of the corrosion film, thereby making it a more effective barrier to the various ion migrations necessary for corrosion. For these reasons it seems somewhat misleading to describe the action of silicate as arising from the production of an insoluble corrosion product layer.

(b) Effect of sulphate

Sulphate differed in its action from silicate in showing no tendency to become absorbed into the corrosion product, the latter not changing its composition even in the presence of very high sulphate levels, Section 4.3.2.2(a). This obviously suggested some effect on the physical form of the deposit.

The possibility that coagulation of colloidal corrosion deposits might explain the observed behaviour was suggested by the fact that both the inhibiting anions, sulphate and silica, represented two of the three bivalent ions in the investigation, Section 2.6.1(b). The lack of effect of the phosphate, HPO_4^{2-} , might be explained by the low concentration used in the initial experiments.

The lack of effect of phosphate when tested at high concentrations, Section 4.3.2.1.(a), and the total failure to detect colloidal species under the most favourable circumstances, Section 4.3.2.1.(b), however, clearly demonstrated that the colloidal mechanism could not be used to explain the behaviour of sulphate. The examination of the deposits by SEM, Section 4.3.2.2(a), clearly established that sulphate was indeed having a profound effect on the physical form of the corrosion product. The mechanisms whereby such effects are produced have been discussed previously, Section 2.6.1(b).

Brasher and Mercer derived a relationship between the maximum concentration of an aggressive ion, $C(\text{agg.})$, whose effect could be nullified by a given concentration of an inhibitive anion, $C(\text{inh.})$, 2.6.1(b). It took the form:

$$\log C(\text{inh}) = n \log C(\text{agg}) + \text{const} \quad \dots 2.18$$

where n is approximately equal to the ratio of valencies of the inhibitive ion to aggressive ion. The log/log relationship was taken as indicative of some competitive action between the anions, either of

adsorption or film repair versus breakdown. The apparent agreement between the exponent n of the formulae and the ratio of 2:1 $\text{SO}_4 : \text{Cl}$, observed in the present work to be necessary for successful inhibition, is deceptive because the concentrations in the formulae are in moles while all those in this work are on a weight/volume basis.

The behaviour of chloride observed in this work is difficult to explain in terms of competitive adsorption. Kolotyркин's⁽⁹⁵⁾ suggestion, that a critical potential exists above which an anion can not become adsorbed and thereby act as an inhibitor, is in accord with the observations in the present work. Thus whereas chloride inhibits the corrosion of freely corroding lead, it does not do so when its potential is raised by galvanic coupling with copper. This result is also supported by the work of Abdul Azim⁽⁹⁶⁾ et al on the corrosion of lead in seawater, Section 2.6.1(b). However, these workers also found that chloride would inhibit the corrosion of galvanically coupled lead when present at high enough concentrations i.e. $>10^{-2}\text{M}$.

This suggests that the ratio of sulphate to chloride, necessary for the inhibition of galvanically stimulated corrosion of lead and solder at the concentrations of chloride found in potable waters, cannot be explained in terms of a simple process of competitive adsorption. It is difficult to see, if competitive adsorption is occurring, how an aggressive ion can be converted into an inhibitive one by raising its concentration! If the chloride was being adsorbed in preference to the sulphate then, naively, it would be expected to inhibit the reaction at all concentrations. Either the chloride at low concentrations, while not being adsorbed itself, crowds out the sulphate from the metal surface, or it penetrates and disrupts the oxide film formed. Thus the favourable ratio of sulphate to chloride, required for inhibition, may arise more from the necessity of film repair than competitive adsorption. Increasing the concentration of chloride compensates for its low adsorption energy at the raised potentials so that eventually it starts to be adsorbed and turns from an aggressive ion into an inhibitor.

(c) Effect of Zinc

Zinc acts as a cathodic inhibitor, Figure 28, and was detected on the cathodic surface using ESCA. Presumably it reacts with the cathodically produced hydroxyl ions thereby precipitating as a layer of zinc hydroxide on the electrode surface.

This layer, by limiting the access of oxygen to the metal surface or by increasing the work function for the transfer of electrons to the dissolved oxygen⁽¹²¹⁾, polarizes the cathode and so reduces the rate of the corrosion reaction at the anode. The presence of lead on the cathode, also detected by ESCA, can be explained in a similar manner.

The precipitated lead hydroxide could have a similar inhibitory effect as zinc, thus providing an intrinsic cathodic inhibitor in the corroding soldered joint system. With potable waters, however, the extreme insolubility of the lead carbonates probably prevents significant migration of lead ions from anode to cathode.

The possible effect of carbonate hardness, which was only revealed when all calcium ions were replaced by sodium, can also be explained in terms of precipitation by cathodically produced hydroxide.

An analogous reaction cannot occur in the presence of only sodium ion because sodium carbonate is soluble.

5.9 ASSESSING THE LIKELIHOOD OF CONTAMINATION FROM SOLDERED JOINTS

It has been established, Section 5.6, that no mechanism operates to stifle the galvanic corrosion of solder before an unacceptable level of lead is obtained. That being the case, the amount of lead contaminating the water phase will be controlled by the following factors:

- (a) the area of solder exposed in the bore of the copper tube
- (b) the galvanic corrosion rate
- (c) the residence time of the water in the pipe
- (d) the temperature, e.g. if the water becomes warm when static for long periods in the plumbing systems

From this present work it is possible to estimate the range of lead contamination likely to arise from the corrosion of soldered joints.

Although any calculation of lead levels has to use arbitrarily chosen values for the factors (a), (c) and (d) above, they are to a large extent determined by the choice of a criterion of "acceptable" contamination. In the following calculations the old WHO limit of not more than 0.1 mg Pb l^{-1} after 16 hours standing was used, however it is a straightforward matter to repeat the calculations if some other criteria is considered more appropriate. The calculations involved determining the maximum area of solder that could be exposed in the bore of tube and still meet the chosen standard. The figure obtained effectively quantifies the quality of joint necessary for it to be acceptable from the point of view of health.

The calculations require:

- i) conversion of the galvanic current, measured under the conditions of the test cell, into a long term corrosion rate under the conditions prevailing at a soldered joint.

- ii) a realistic estimate of the volume of water available in the pipework to dilute the lead entering the aqueous phase around a joint, and hence calculate what the average lead concentration will be once all this material has been taken into solution by the acid in the consumer's stomach.
- iii) the residence time of the water in contact with the corroding joint having been decided by choosing to use the WHO standard (16 hours being reckoned as an overnight standing period), it is only necessary to decide some appropriate water temperature and allow for this in the corrosion rate.

5.9.1 CORROSION RATE

The corrosion current measured by the galvanic cell is a direct measure of the corrosion rate and can be converted to mass of lead oxidised in unit time by a Faraday calculation (see Appendix II). These galvanic currents were determined after only 4 weeks corrosion, for 2cm^2 of solder, at 20°C , with a flow rate of $50\text{ml}\cdot\text{hr}^{-1}$ and a $10\text{k}\Omega$ resistance in the external circuit. It is necessary to adjust all these factors so they mirror the long term situation at soldered joints in plumbing systems. This has been done as follows:

(a) Effect on corrosion rate of area of solder exposed

With a fixed cathodic area, the changes in galvanic current with area of anode follow an exponential curve, Section 4.1.3 and Figure 13. However, for the much more limited area of solder likely to be exposed in the bore of the tube at joints, $<2\text{cm}^2$, a linear relationship is a good approximation. The errors introduced into the calculation in this way may be even smaller for a soldered joint, where the cathodic area is larger than in the test cell and may actually increase with increases in the area of solder exposed, Section 5.2

(b) Long term corrosion rates

The experimental results indicated that, after 5 months corrosion, rates had fallen to between 10 and 50% of their fourth week mean value measured in the laboratory test, Section 4.1.9. The evidence in the literature⁽⁷⁶⁾, and some of the longer term experiments in this work, suggest that the corrosion is stable at these lower rates for many years. These figures were used in the calculations as the limits of the range of reduction of the fourth week corrosion rate to be expected in the long term.

(c) Effect of flow rate

The majority of the galvanic currents measured in the tests were for flowing conditions, 35-50ml hr⁻¹. In the calculations, however, a 16 hour static period is involved. Because galvanic currents decrease only slowly when the water flow stops, Figure 15, little error is introduced by using figures obtained under flowing conditions in the calculations. It is assumed that the rate measured under these conditions would be maintained with little diminution throughout a 16 hour static period.

(d) Effect of the external resistance

Nearly all the results from this work were obtained with a 10k Ω resistance in the external circuit. Of course in a soldered joint, because the copper and solder are in physical contact, this resistance is absent and the corrosion current is correspondingly higher. The different values of corrosion current are affected to different extents by this external resistance and it can be shown, Appendix I, that the corrosion current in the absence of this resistance is given by:

$$\frac{1}{I} = \frac{1}{I^1} - 0.027 \quad \text{where } I^1 = \begin{array}{l} \text{galvanic current} \\ \text{measured by cell}(\mu\text{A}) \end{array} \quad \dots 5.2$$

$I = \text{galvanic current in the absence of the external resistance } (\mu\text{A})$

5.9.2 VOLUME OF WATER PER JOINT

The significance to health of a contaminant is dependent, amongst other things, on its concentration. Thus with soldered joints, not only is the corrosion rate important, the volume of water available per joint also has to be estimated. There are two different types of copper tubing used in plumbing systems, unannealed material, so called Table Z of the British Standard 2871, and half-hard tube or Table Y of the same standard. Because the former cannot be bent, a much higher frequency of joints occurs than with the latter. One of the major British manufacturers has estimated, from their sales patterns, that on average there is one fitting per metre of Table Z material decreasing to one per 2m with Table Y⁽¹²⁾. This agrees well with the paper by Lyons and Lenihan⁽⁷⁶⁾ where they report the results of various surveys of authentic plumbing systems in Glasgow, detailing the lengths of copper pipe used and the number of fittings.

Using these figures, the volumes of water per soldered joint can be calculated. This has to be done not only for the two types of copper tube used, the different tempered materials having slightly different internal diameters, but also for 15 and 22mm diameter tubing which are the two sizes most commonly used in plumbing systems.

5.9.3 CHOICE OF TEMPERATURE

The galvanic corrosion tests were all carried out at 20°C as the highest temperature that could be used without being completely unrepresentative of real cold water systems, Section 4.1.1. For the purposes of these calculations that argument is still valid and so no temperature correction was applied to the galvanic currents measured.

5.9.4 THE CALCULATIONS

- (a) The majority of galvanic corrosion currents measured in this work was in the range 0.5 - 15 μA .

- (b) From Equation 5.2 the corresponding range when the resistance in the external circuit of the test cell is absent can be calculated i.e. 0.51 - 25 μ A.
- (c) Applying the factors for the long term reduction in corrosion rate of between 10 - 50% of the mean of the fourth week value to these figures gives the results 0.05 - 0.25 and 2.5 - 12.5 μ A, i.e. a range of 0.05 - 12.5 μ A.
- (d) Applying Faraday's law, Appendix II and footnotes to Table 4(i), and assuming that for a 40:60 solder 60% of the corrosion current is produced by the oxidation of lead, Section 4.1.6 and Figure 16, converts this current range to a corrosion rate range of 0.003 - 0.75 mg Pb/cm²/24 hours static period at 20°C.
- (e) Reducing the corrosion rate pro rata to unit area of solder gives the corrosion rate range of 0.0015 - 0.375 mg Pb/cm²/24 hours static period.
- (f) Calculating the concentrations of lead produced when dispersed in the volume of water available per joint obviously depends upon the pipe size and type. For 15mm tubing of Table Y material, probably the most commonly used pipe, this means 1 joint per 2 metres of tube which corresponds to an internal volume of 265 cm³. The range of lead concentrations to be expected in the long term in this instance, given the corrosion rates above, is thus:

0.006 - 1.42 mg Pb/litre/cm²/24 hours static period at 20°C.

- (g) For a 16 hour static period this concentration range is reduced to:

0.004 - 0.95 mg Pb/litre/cm² at 20°C

- (h) The reciprocal of these figures gives the area of solder that produces a concentration of 1mg Pb l^{-1} after 16 hours standing i.e.

$$250 - 1.05 \text{ cm}^2/\text{mgPb/litre at } 20^\circ\text{C}$$

- (i) If the sample is required to comply with the WHO European Standard for lead in drinking water, i.e. $\leq 0.1 \text{ mg Pb l}^{-1}$ after a 16 hour static period, the area of exposed solder has to be limited (again assuming a pro rata reduction in corrosion rate) to:

$$25 - 0.11 \text{ cm}^2 \text{ (depending on the galvanic corrosion rate).}$$

- (j) This area limit can be expressed in terms of the permissible length of a circumferential solder run exposed in the bore of the tube, where a circumferential solder run is defined as one that forms a complete ring around the internal circumference of the tube.

A 15mm Table Y tube has an internal diameter of 13mm which corresponds to a circumference of 4.1cm. The limit to the length of a circumferential solder run is thus in the case under consideration:

$$6.1 - 0.026\text{cm}$$

This procedure can be followed for the other possible pipe sizes and fittings frequencies. The formulae used in these calculations are summarised below, equation 5.3, and the range of results and other information given below, Table 8.

$$i) \quad q = I \times 0.1 \times y \times \frac{1}{2} \times \frac{16}{24} \times \frac{1}{v} \times 10^3 \quad \dots 5.3$$

where I = galvanic current (μA) with zero resistance in the external circuit

y = percentage lead by weight in alloy (only strictly applies to non-eutectic alloys)

v = volume pipe per fitting (cm^3)

ii) $a = \frac{0.1}{q}$ $q =$ concentration of lead mgPb/litre/cm²/16 hours static period

iii) $l = \frac{a}{c}$

a = area of exposed metal that complies with the 0.1mg Pb/litre/16 hrs. standard (cm²)

c = circumference of pipe (cm)

l = length of circumferential metal run that allows compliance with the standard (cm).

The results have been summarised graphically, Figures 32 and 33, where the average 4th week galvanic current, measured by the laboratory test procedure, is related to different areas of solder run exposed in the bore of the copper tube. It has been assumed that in the long term, > 5 months, the galvanic current falls to between 50 - 10% of its 4th week value and stabilises. The zone in which a particular combination of galvanic current with solder area falls indicates if it is likely to give acceptable contamination levels in the long term. The values plotted in these graphs are given in Table 9.

Obviously there is always some area of solder exposed and in an attempt to quantify this minimum value vertical lines representing circumferential solder runs of lengths 0.5, 1.0 and 3mm are shown, Figures 32 and 33. The latter could represent the situation where the ends of the copper tubing have not been pushed hard against the tube stops in the fitting and the gap left fills with solder.

5.9.5 CONSEQUENCES

The curves in Figures 32 and 33 arise from the mathematics describing the phenomenon under study and the values assigned to the many variables involved. This work has developed an experimental method of measuring the corrosion rate and has provided information that allows realistic values to be assigned to the other variables. The rest is a consequence of the mathematical logic. Three main difficulties arise when attempting to apply the results to reality.

- i) The first is the problem of assigning a precise corrosivity to a particular water composition. It is clear from this work that, as with many other corrosion processes, a major factor in determining the rate of attack is the intrinsic propensity to corrode of individual samples of solder, Section 5.7. Thus for the same water a range of corrosion rates is obtained.
- ii) The second difficulty arises with a consideration of the duration of the problem. The area of solder exposed affects the amount of corrosion and hence the level of contamination, but it is the mass of solder exposed with the corrosion rate that determines the duration of the problem. The maximum capillary gap between fitting and tube that still allows a successful joint to be made has been estimated to be 0.16mm (36). It can be calculated, using this figure, that for a 15mm fitting, with the solder flush with the end of the capillary space, an area of metal 0.05cm^2 per solder ring will be exposed i.e. 0.1cm^2 in total for a straight or right angled bend. This area of solder falls in the pass zone of Figure 32 for all but the most aggressive solutions, and even here it is only just over the line in the intermediate zone for the Table Z case. Thus, assuming corrosion of the solder in the capillary space occurs at the same rate as freely exposed solder, it will not be a source of long term contamination. A problem only arises, and only continues, as long as solder remains actually exposed in the bore of the tube.

The contamination from a small area of solder exposed in an aggressive water may be intense, but it is of short duration. The contamination from the same area of solder exposed in a less aggressive water, although it may be less, may still be unacceptable and lasts longer. The conundrum is whether it is preferable to have an intense but brief problem, or a less intense longer one. The significant point, however, is that the very small areas, that seem necessary in aggressive waters for the joint to be acceptable in the long term, are not so critical. They represent in all probability only small amounts of solder that will be completely removed by the corrosion process itself during the more active first few months of

the joint's service life. Long term problems are only likely to arise from large areas of exposed solder that also corresponds to large quantities of solder. It is difficult to estimate precisely what area of exposed solder may be ignored, as far as long term contamination is concerned, but it is not likely to be less than the equivalent area of a 1mm circumferential solder run.

- iii) The third difficulty is the uncertainty in the exact long term reduction in the corrosion rate. Although insufficient results are available to be precise on this point, they suggest that the higher corrosion rates measured in the laboratory may suffer the least reduction in the long term (to < 50% after 5 months). Other workers⁽⁷⁶⁾ have obtained results which indicate that the rate reached after a few months is maintained for several years. They also suggest a ten-fold reduction in rates for a low chloride water, which agrees with the findings of this work, Section 4.1.9.

As an illustration of the use of Figures 32 and 33 consider a water of low aggressivity that in the test cell produces an average galvanic current of 5 μ A over the fourth week, e.g. a water of pH8, chloride 5mg Cl l⁻¹ and zero sulphate. For a 15mm, Table Z, tube the left hand diagram of Figure 32 indicates that, if the long term corrosion rate fell to 10% of its fourth week value, the joint would only significantly contaminate the supply if the area of solder exposed in the bore of the tube exceeded 1.4cm². If corrosion rate only fell to 50% of its fourth week value, however, the acceptable area of exposed solder would only be 0.3cm²

The figure of 5 μ A is of course an average value and at least half the joints exposed to this water would corrode at higher rates. The work on the variability between replicates, Section 4.1.8 and Table 3, has indicated that the standard deviation (σ) is about 40% of the mean value for waters of low aggressivity, falling to about 20% of the mean at higher current values. If the distribution of corrosion currents around a particular mean value is taken as approximately normal, it is possible to calculate the limits on the area of exposed solder for a larger proportion of the joints to be satisfactory.

For the water presently under consideration, by taking a standard deviation between replicates of 40% of the mean it follows that 68% of the joints ($\pm 1 \sigma$) corrode in the range of 3 - 7 μ A, 95.5% ($\pm 2 \sigma$) in the range 1 - 9 μ A and 99.5% ($\pm 3 \sigma$) 0 -11 μ A. These values can be used with Figure 32 and the results show that to ensure all joints are satisfactory, even in a water of low aggressivity, the maximum area of exposed solder allowable becomes very small indeed, Table 10.

6. CONCLUSIONS

This is the first comprehensive investigation of the contamination of water by lead arising from the corrosion of tin-lead solder used to join copper pipe in plumbing systems. It is the first study that has investigated the corrosion mechanisms in detail and to determine actual reaction rates. The scientific results of this work are as follows:-

1. A technique for quantifying the corrosion of solder has been developed, based on the galvanic interaction between the solder and copper. It has been demonstrated that in potable waters the galvanic current generated by the device can be used to calculate the rate of lead corrosion, Section 4.1.6. It has been further demonstrated that the cell design used, i.e. electrode areas, their physical separation, the external circuit resistance, etc., is unlikely to make the corrosion behaviour of the device significantly different from that of an authentic soldered joint, Sections 4.1.1 to 4.1.5.
2. Evidence has been presented which suggests that the galvanic current also gives the "average rate" at which the lead contaminates the water, a figure that is important when calculating the exposure of the consumer to the lead, Sections 4.1.7, 5.3 and Figure 18. Initially, only a proportion of the lead corroded enters the water phase, the majority staying on the metal surface as a corrosion product layer. Eventually, however, this layer reaches a critical thickness after which all subsequent growth is unstable and will break off intermittently and enter the water as particulate material. Thus after the attainment of this equilibrium thickness by the corrosion product, the galvanic current becomes a direct measure of the average rate of contamination by the lead.
3. The investigation of the effect of water composition indicated that for mildly aggressive solutions the surface characteristics of the individual solder electrode under test was the most important factor in determining corrosion rates. This produced a large scatter in the results for such solutions. Only when the solution contained a

strongly aggressive ion, or conversely contained an effective corrosion inhibitor, did the observed corrosion rate correlate with solution composition. Sections 4.1.8, 5.4 and 5.7.

4. The water quality parameters that were found to stimulate the galvanic corrosion were pH, chloride, nitrate, and sodium ion.

Low pH values increased the corrosion presumably by stimulating the dissolution of the semi-protective corrosion product layer. Sections 4.2.1, 5.7 and Figure 20. This would have a major effect at points of weakness in the film e.g. where it has greater discontinuity or is unusually thin.

Increases in chloride stimulated the galvanic corrosion of both lead and solder, presumably because of its high polarizability that allows it to penetrate surface films, Section 4.2.3 and Figure 22. What was more surprising, however, was that chloride behaved as a corrosion inhibitor to the free (i.e. non-galvanic) corrosion of lead. Under these circumstances it changed the physical form, but not the chemical composition, of the corrosion product layer produced. Sections 4.1.9, 4.3.2.1.4 and 5.8(b). This result finds support in the literature⁽⁹⁶⁾.

Although the presence of nitrate appeared to stimulate the corrosion rate, there was little correlation with nitrate concentration, Sections 4.2.5, Figure 25. It appears that while the ion stimulates the corrosion, it cannot penetrate the corrosion film to initiate attack. Thus although the corrosion rates are in general increased, they bear little correlation with nitrate concentration, being determined instead by the individual characteristics of the solder electrodes under test, Section 5.6.

Evidence for sodium ion increasing corrosion rates was obtained where the calcium content of a solution was completely replaced by sodium, Section 4.2.6. This might be explicable in terms of absence of

calcium, preventing the precipitation of calcium carbonate on the cathode surface, which could reduce corrosion rates in those cells operating under mixed control, Sections 2.4.4, 4.1.1 and 5.8(c).

5. The ions found to inhibit the galvanic corrosion of solder were sulphate, silicate and zinc. The sulphate was found to change the physical form of the corrosion product layer without altering its chemical composition, (compare the behaviour of chloride on uncoupled lead, 4. above). It was necessary for the sulphate to be present at a high enough concentration to overcome the effect of any chloride also present; a ratio in excess of 2:1 $\text{SO}_4:\text{Cl}$, calculated on a weight basis, being necessary for the inhibitory effect to predominate, Sections 4.2.4 and 5.8(b) and Figures 23 and 24.

Silicate was shown by ESCA analysis to produce a silicon rich layer on the solder. If the silicate was present in the solution at a high enough concentration, $>20\text{mgSiO}_2\text{l}^{-1}$, this effect was sufficient to maintain the bright metallic appearance of the solder even after 4 weeks exposure. Dosing silicate is a possible if expensive water treatment to overcome contamination problems from soldered joints. Sections 4.2.7(a), 5.8(a) and Figure 26.

The inhibitory action of zinc was initially discovered from work on the effect of flux residues. The latter was based on zinc chloride and, despite producing a decrease in pH and raised chloride levels, gave lower corrosion rates than would have been expected, Section 4.2.8. On further investigation this was found to be due to the zinc which also leached into the solution and acted as a very effective cathodic inhibitor, Sections 4.2.8, 5.8(b) and Figure 28.

6. Increases in carbonate hardness and high levels of orthophosphate were found to be without effect on the corrosion rate. This is at first sight surprising, as both have highly insoluble lead salts and might be expected to affect the corrosion product layer that develops on the solder.

At pH8, the usual value at which the corrosion experiments were carried out, there is little change in the solubility of the lead carbonate with carbonate concentration. Experiments were therefore carried out at pH6, at which value large changes do occur, Table 6. In none of these experiments was any effect of carbonate concentration on corrosion rates observed, Sections 4.2.2, 4.3.1.1 and Figure 30.

Orthophosphate was tested at levels far in excess of those allowed in potable water by the EC Directive i.e. 19.6mgPl⁻¹ vs 2.2mgPl⁻¹, but it was totally without effect on the corrosion rate, Sections 4.2.7b), 4.3.2.1a) and Figure 31. Furthermore, analysis of the corrosion product on the solder indicated no change in chemical composition from that produced in the total absence of phosphate. It was found that in general the composition of the corrosion product layer developed on the solder was the same irrespective of the solution under test, Sections 4.3.1.2a) and 4.3.1.2b).

The conclusions from this work that are significant for public health and from the point of view of the Water Supply Industry are as follows:-

- (1) It is not the case that soldered joints can be dismissed as an insignificant potential source of lead in the environment.
- (2) Soldered joints cannot be considered as the same as freely corroding lead pipe. The galvanic stimulation that occurs at a soldered joint, and around a copper-lead pipe junction, not only produces a quantitative change in the corrosion rate, it can produce qualitative changes also, Section 5.6. Thus chloride, which acts as a corrosion inhibitor for freely corroding lead, becomes an aggressive ion when the lead is coupled to copper. Also, the dosing of orthophosphate, which is an effective water treatment for preventing contamination from lead pipes, is without effect on the galvanically mediated corrosion. Conver-

sely, silicate, which is only moderately effective at reducing plumbosolvency⁽¹²²⁾, is an effective inhibitor for the galvanic corrosion. Increasing pH is the only water treatment that is effective for both types of problem.

(3) This work also revealed that changing the equilibrium solubility of the corrosion product in the water has no restraining effect on the corrosion rate. This has the consequence that no matter how small the area of solder exposed in the bore of the tube, the maximum acceptable concentration for lead in potable water will always be exceeded provided the residence time of the water is long enough, Section 5.6. The reaction continues unabated after the solution has become saturated with lead, resulting in either a thickening of the corrosion product on the metal surface and/or the appearance of insoluble material in the water phase. The exhaustion of the dissolved oxygen in the water is the ultimate brake on the corrosion reaction, but by the time this occurs the maximum admissible lead concentration has been exceeded by several orders of magnitude. Thus, even with a slow corrosion rate and only a small area of exposed solder, prolonged residence time in the pipe eventually results in unacceptable contamination.

(4) From the corrosion rates measured in this work, and by making assumptions about:

(a) residence time of water in the pipe,

(b) volume of water available per joint to dilute the lead,

(c) water temperature,

it has been possible to calculate the area of solder that can be exposed in the bore of the tube without producing unacceptable contamination, Section 5.9. These calculations indicate that,

even for mildly aggressive supplies, for all joints to be satisfactory the maximum area of solder that can be exposed is very small indeed, Figures 32 and 33.

The most effective way of limiting the contamination from soldered joints is minimising the area of solder exposed in the bore of the tube. Unfortunately this is entirely in the hands of the person who makes the individual joint, being dependent on both his skill and conscientiousness. Bearing in mind that in the future solders will be the main source of lead still allowed in plumbing systems, the only certain way of avoiding contamination problems is to use only lead-free solder or compression fittings. It is therefore the final conclusion of this work that the appropriate steps should be taken to ban the use of leaded solders in potable water systems.

REFERENCES

(1)	Bouton, G M	Encyclopaedia of Science and Technology, Vol XII
McGraw-Hill 1960, p471
(2)	BS 219:1977	
(3)	Forbes, R J	Studies in Ancient Technology
Volume VIII
Edited E J Brill
Leiden
Netherlands 1964, p137
(4)	Allen, B M	Metall. and Mat. Tech.
Oct 1978, p537
(5)	T Lucreti Cari	De rerum natura 1.1079
2nd ed. repr.
Clarendon
Oxford 1962
(Quoted in (4) above).
(6)	Smith, C S and Hawthorne, J G
(translators)	Mappae Clavicula, Sélestat
17 V.20 and 34 v.12
Trans. Am. Phil. Soc.
<u>64</u> , 4, 1974, pp 82 & 88
(7)	Dodwell, T R
(translator)	Theophilus, De diversis artibus
Thomas Nelson
London 1961
(cited in (4) above).
(8)	Akers, C J and Fellows, R	Envir. Health, <u>87</u> , 7, 1979, p148.
(9)	Foster, J	Unit M 15
Course on Corrosion and Metal
Finishing
Polytechnic of the South Bank
London 1976, p5.
(10)	Skeat, W O
(editor)	Manual of British Water Engineering
Practice
Vol. 1 4th Ed.
W Heffer and Sons Ltd
Cambridge 1969, p20.
(11)	BS 864:Part 2:1971	
(12)	Firth, W (Yorkshire
Imperial Fittings Ltd.)	Personal communication, March 1981

(13)	Browning, E	Toxicity of Industrial metals
Butterworths
London 1961, p149
(14)	Thackrah, C T	The effects of Arts, Professions and
of Civic States and Habits of Living
on Health and Longevity
Longmans, Green
London 1831
(cited in (13) above)
(15)	Legge, T M and Goadby, K W	Lead Poisoning and Adsorption
Longmans, Green and Co
London 1912
(cited in (13) above)
(16)	Ingelson, H	DSIR Wat. Pollution Res.
Technical Paper No. 4
HMSO 1934
(17)	Carter, J M	Water, September 1979, p2
(18)	World Health Organisation	European Standards for Drinking
Water
2nd Ed.
Geneva
The Organisation 1970.
(19)	Waldron, H A and Stöfen, D	Sub-clinical Lead Poisoning
Academic Press
London 1974
(20)	Commission of European
Communities	Off. Journ. Eur. Communities
No. L 229/11, July 1980
(21)	Ainsworth, R G, Bailey, R J
et al	Water Research Centre Technical
Report
TR 43, 1977
(22)	Department of the Environment	Pollution Paper No. 12
HMSO 1977
(23)	Pocock, S J	Arch. Environ. Health
<u>35</u> , 1, 1980, p45
(24)	Beattie, A D, Moore, M R,
Devenay, W T, Miller, A R and
Goldberg, A.	Brit. Med. J. <u>ii</u> , 1972, p491
(25)	Moore, M R, Meredith, P A,
Campbell, B C, Goldberg, A
and Pocock, S J	Lancet <u>ii</u> , 1972, p661

- (26) Thomas, H F, Elwood, P C Nature, 282, 1979, p712
Welsby, E and St Leger, A S
- (27) David, O, Clerk, J and Lancet ii, 1972, p900
Noeller, K
- (28) Landrigan, P J, Whitworth, R M, Lancet i, 1975, p708
Baloh, R W, Staehling, N W,
Barthel, W F and Rosenblum, B F
- (29) Needleman, H L, Gunnoe, C, New Eng. J. Med. 300, 1979, p689
Leviton, A, Reed C, Peresie, C,
Maher, C and Barret, P
- (30) Beevers, D G, Erskine, E, Lancet ii, 1976, p1
Robertson, M, Beattie, A D,
Goldberg, A, Campbell, B C,
Moore, M R and Hawthorne, V A
- (31) David, O, Hoffman, S, McGaun, B, Lancet ii, 1976, p1376
Sverd, J and Clerk, J
- (32) Campbell, B C, Beattie, A D, Brit. Med. J. 1, 1977, p482
Moore, M R, Goldberg, A and
Reid, A G
- (33) Shaper, A G Jour. Am. Med. Assoc. 230, 1, 1974,
p130.
- (34) Crawford, M D, Gardner, M J Lancet i, 1972, p988
and Sedwick, P A
- (35) Department of the Environment Model Water Byelaws
1966 ed.
Department of the Environment
(formerly Department of Housing and
Local Government).
HMSO 1966
- (36) Ainsworth, P A Metals Mat. 5, 1971, p374
- (37) Smith, J F Mat. Eng. 80, 3, 1974, p76
- (38) Davies, R L Weld. J. 55, 1976, p838
- (39) BS 5625:1980
- (40) Delahay, P, Pourbaix, M J. Electrochem. Soc. 98, 57, 1951
and van Rysselberghe, P
- (41) Shreir, L L Corrosion
(editor) Vol. 1, 2nd ed., Table 4.14
Newnes-Butterworth
London 1979.

- (42) Deltombe, E, de Zoubov, N and Pourbaix, M. Tech. Report No. 25
Centre Belge d'Etude de la Corrosion
1955
- (43) Shreir op. cit. Vol.1, Ch. 4.6
- (44) Nielsen, K International Water Supply Assoc.
10th Congress, Brighton, England
1974
Subject 3.
- (45) Dangel, R A Environmental Protection Agency
Report
EPA-670/2-75-036 1975
- (46) Karalekas, P A, Craun, G F, Hammonds, A F, Ryan, C R and Worth, D J J. New Engl. Wat. Wks. Assoc.
90, 2, 1976, p150.
- (47) Britton, A and Richards, W N Inst. Wat. Eng. & Sci. 35, 4, 1981,
p349
- (48) Richards, W N Personal communication March 1981.
- (49) Edkins, A Personal communication December 1980
(North West Water Authority)
- (50) Shreir op. cit. Vol. 1 Table 3.18
- (51) Hoar, T P and West, J M Proc. Roy. Soc. A268, 304, 1962
- (52) Cornwell, F J, Wildsmith, G and Gilbert, P T Br. Corros. J. 8, 1973, p202
- (53) Lucey, V F Br. Corros. J. 2, 1967, p175
- (54) Wranglen, G Introduction to Corrosion and
Protection of Metals
Butler and Tanner
London 1972.
- (55) May, R J. Inst. Metals 40, 1928, p141
- (56) Pourbaix, M UK Pat. 1 261 544 January 1969.
- (57) Pourbaix, M Atlas of Potential/pH Diagrams
Pergammon
Oxford 1962
- (58) Pourbaix, M Lectures on Electrochemical
Corrosion
Plenum Press
New York, London 1973

- (59) Tafel, J Z. Physik. Chem. 50A, 1905, p641
- (60) Shreir op. cit. Vol. 1, Ch. 9.1.
- (61) Moreland, P J and Rowlands, J C Brit. Corr. J. 12, 1977, p72
- (62) Skold, R V and Larson, T E Corrosion 13, 1957, p139
- (63) Stum, W Indust. Eng. Chem. 51, 1959, p1487
- (64) Mansfeld, F J. Electrochem. Soc. 120, 1973, p515
- (65) Neufeld, P Corr. Sci. 4, 1961, p245
- (66) Epelboin, I, Gabrielli, C, Keddam, M and Takenouti, H. Electrochemical Corrosion Testing American Society for Testing and Materials 1916 Race Street, Philadelphia Pa. 19103, USA ASTM STP 727 1981 p150
- (67) Anthony, W H J. Electrochem. Soc. 115, 1968, p610
- (68) Farquhar, G B and Mosier, B Mat. Protection & Performance 10, 1971, p38
- (69) Heine, M A, Keir, D S and Pryor, M J J. Electrochem. Soc. 112, 1965, p24
- (70) B457-67 Annual Book of ASTMS Standards, Part 9, 1974. ASTMS Philadelphia (Pa)
- (71) Evans, U R Metallic Corrosion Passivity and Protection Arnold & Co. London 1937, p219
- (72) Oliphant, R J Water Research Centre Technical Memorandum TM112, 1975
- (73) Oliphant, R J Water Research Centre Technical Report, TR88, 1978
- (74) Stopchai, E I, Shein, F, Lantushenko, N and Timashova, G I Chem. Pet. Eng. 8, 2, 1972, p138
- (75) Wong, C S and Berrang, P Bull. Envir. Contamination Toxicol 15, 5, 1976, p530

- (76) Lyon, T D B and Lenihan, J M A Br. Corros. J. 12, 1, 1977, p41
- (77) BS 2871:Part 1:1971
Part 2:1972
- (78) Closset, J La Tribune du Cebedeau 31, 413,
1978, p159
- (79) Putilova, I N, Balezin, S A and Metallic Corrosion Inhibitors
Barannik, V P Pergamon
Oxford 1960
- (80) Bregman, J J Corrosion inhibitors
Macmillan
New York - London 1963
- (81) Shreir op. cit. Vol. 2, Ch. 18.3
- (82) Walker, R Anti-corrosion Methods and Materials
17, 9, 1970, p9
- (83) Butler, G and Ison, H C K Corrosion and its Prevention in
Waters
Leonard Hill
London 1966
- (84) Shreir op. cit. Vol. 2, Ch. 18.2
- (85) Machu, W First European Symposium on
Corrosion Inhibitors (1st ESCI)
Ferrara 1960
University of Ferrara (UF), 1961,
p183
- (86) Hoar, T P and Holliday, R D J. Applied Chem. 3, 1953, p502
- (87) Kelly, E J J. Electrochem. Soc. 115, 1, 1968,
p111
- (88) Iofa, Z A 2nd ESCI
Ferrara 1965
UF, 1966, p93
- (89) Wormwell, F Br. Corros. J. 2, 1967, p6
- (90) Butler, G 3rd ESCI
Ferrara 1970
UF, 1971, p753
- (91) Gatty, O and Spooner, E C R The Electrode Potential Behaviour of
Corroding Metals in Aqueous
Solutions
Clarendon Press
Oxford 1938, p291

- (92) Glasstone, S Textbook of Physical Chemistry
2nd Ed.
Maxmillan
London 1948, p1231
- (93) Brasher, D M and Mercer, A D Br. Corros. J. 3, 1968, p120
- (94) Brasher, D M Proc. 1st International Congress on
Metallic Corrosion 1961
Butterworths
London 1962, p156
- (95) Kolotyrkin, Y M Usp. Khim. 131, 322, 1962
- (96) Abdul Azim, A A, Gouda, V K,
Shalaby, L A and Afifi, S E Br. Corrs. J. 8, 3, 1973, Papers I
and II, p76 et seq
- (97) Ainsworth, R G Water Services 84, 1009, 1980, p145
- (98) Langelier, W F J. Amer. Wat. Wks. Assoc. 28, 1936,
p1500
- (99) Campbell, H S and Turner, M E D Jour. Inst. Wat. Eng. & Sci. 37, 1,
1983, p55
- (100) Larson, T E and Skold, R V Corros. 14, 6, 1958, p43
- (101) Dart, F J and Foley, P D J. Amer. Wat. Wks. Assoc. 62, 1970,
p663
- (102) Dart, F J and Foley, P D J. Amer. Wat. Wks. Assoc. 64, 1972,
p244
- (103) Large, J M and Lackington, D W WRC Conference : Water Distribution
- Maintenance of Water Quality and
Pipeline Integrity
Oxford September 1978. Paper 17
- (104) Prothero, H and Shaw, B E Brit. Wat. Supply August 1971
- (105) O'Brien, J E J. New Engl. Wat. Wks. Assoc. 90, 2,
1976, p173
- (106) Karalekas, P C, Ryan, C R,
Larson, C D and Taylor, F B J. New Engl. Wat. Wks. Assoc. 92,
1978, p159
- (107) Patterson, J W and O'Brien, J E J. Amer. Wat. Wks. Assoc. 71, 1979,
p264
- (108) Jackson, P J and Sheiham, I Water Research Centre Technical
Report TR152, 1980.

- (109) Schock, M R J. Amer. Wat. Wks. Assoc. 72, 1980, p695
- (110) Richards, W N, Britton, A and J. Inst. Wat. Eng. and Sci. 34, 4, 1980, p315
Cochrane, A
- (111) Shreir op. cit. Vol. 2, p20.106
- (112) Felsted, R K Hospital Engineering
October 1974, p20
- (113) Carruthers, F B Personal communication February 1979
- (114) Scully, J C The Fundamentals of Corrosion
2nd Ed.
International Series on Materials
and Technology, Volume 17
Pergamon Press
Oxford 1975, p18
- (115) Steriker, W Industrial and Engineering Chem. 30,
1938, p348
- (116) Walker, J G Wat. and Wat. Engng. 54, 1955, p534
- (117) Camp, T R and Meserve, R L Water and its Impurities
2nd ed.
Dowden, Hutchinson, Ross, Inc.
Stroudsburg, Pennsylvania, 1974,
p165
- (118) Shreir op. cit. Vol. 1, p1.235
- (119) Evans, U R Corrosion and Oxidation of Metals
Arnold
London 1961, p163
- (120) Shreir op. cit. Vol. 1, p1.28
- (121) West, J M Electrodeposition and Corrosion
Processes
2nd ed.
Van Nostrand Reinhold Company
London 1970, p123
- (122) Forest, R D and Clarke, K B WRC Symposium on Lead in Drinking
Water
Lorch Foundation, High Wycombe 1981,
Water Research Centre 1982
Paper 16