GALVANIC CORROSION OF LEAD IN COPPER
PIPEWORK: PHASE II, EFFECTS OF TREATMENT ON GALVANIC CORROSION POTENTIALS

Second Interim Report to the Department of the Environment for the period December 1984 to July 1985

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Report Copy No. II

DOE Contract Reference: PECD 7/7/711-158/83
WRC Reference: 9810 CLD
SUMMARY

OBJECT

The work reported constituted the second phase of a DOE contract concerned with the measurement of galvanic corrosion potentials of lead solder coupled to copper. The objective of this phase, carried out during the period December 1984 to July 1985, was to test the effect of treatments to reduce the galvanic corrosion potential of four waters.

APPROACH

Among the criteria for choosing the four waters was that they should have high galvanic corrosion potentials and the water undertaking concerned would be able to carry out the necessary measurements conveniently. Treatment with silicate, sulphate, zinc and orthophosphate, and the last two in combination, were investigated on some or all of the waters; the work in the first phase had suggested that increasing their concentrations should decrease the galvanic corrosion potential. Corrosion potentials were measured using corrosion cells in a manner similar to that used in the first phase.

RESULTS

All of the treatments investigated produced a reduction in corrosion potential of about a half in the softest water investigated. In the harder waters silicate and sulphate were ineffective and the effectiveness of orthophosphate seemed to increase with time. Zinc, especially in combination with orthophosphate, was the most effective treatment for hard waters.

A commercial zinc orthophosphate corrosion inhibitor was also investigated and was found to be no more or less effective than a mixture at a similar concentration prepared from laboratory reagents. Some differences were observed in the behaviour of cells made at different times. This did not appear to be due to differences in the method of manufacture, but could have been due to differences in composition of the solder.
electrodes. As in the first phase, large differences were often seen in the potentials of the five cells in the same stream. A large increase in corrosion potential of one of the waters tested coincided with the replacement at the water treatment works of activated silica by a polyelectrolyte.

CONCLUSIONS

The soft water was more responsive than the hard waters to all the treatments tested. Zinc, alone or in combination with orthophosphate, was the most effective treatment overall. However, its concentration would need to be chosen carefully to produce the maximum inhibition of galvanic corrosion while avoiding deposition from solution which could lead to "dirty water problems". The optimum concentration is probably about 1 mg Zn/l, with orthophosphate also present at 0.4 mg P/l. The reduction in galvanic corrosion potential by any treatment may not be sufficiently great to eliminate the problem of high lead concentrations, especially if the corrosion potential before treatment is high or the water is relatively unresponsive.

RECOMMENDATIONS

Zinc, possibly in conjunction with orthophosphate, should be the preferred inhibitor of galvanic corrosion of lead-solder in copper pipework. Simple and cheap methods for reliable dosing of zinc need to be established.
To maintain the anonymity of the waters measured, as part of the obligation to undertakings in return for the assistance given, this sheet must be removed before the report is released by either the DOE or WRc to a third party.

**KEY TO WATERS**

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Stevenage (WRc)</td>
</tr>
<tr>
<td>2.</td>
<td>Saltersford, Grantham</td>
</tr>
<tr>
<td>3.</td>
<td>Frankley, Birmingham</td>
</tr>
<tr>
<td>4.</td>
<td>Hanningfield, Chelmsford</td>
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</table>
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BETWEEN CELLS
1. OBJECTIVE

This report presents the work carried out during the period December 1984 to July 1985 as the second part of a contract which was started in December 1983. The objective of the contract is: "to have surveyed selected water supplies in collaboration with authorities to assess the level of galvanic corrosion of lead coupled to copper which might give rise to unacceptable high lead concentrations in water at consumers' taps, and test effects of modifying waters to reduce corrosion".

The first phase, which was concerned with the measurement of galvanic corrosion potentials of 38 different waters using corrosion cells was described in Interim Report No. 392-S. The programme for the second phase with which this report is concerned was:

(i) Select a limited number of waters which cause high corrosion potentials and, following agreement with DOE and authorities, repeat measurements to assess the effect of experimental treatments chosen to reduce corrosion potentials.

(ii) Provide progress and final contract reports to the Department.
Unacceptable concentrations of lead in tap water can be found in some waters drawn from new copper plumbing because of the galvanic corrosion of exposed lead–tin solder. The concentration of lead is dependent on various factors including the rate of corrosion. The rate of corrosion can be measured in terms of corrosion potential using corrosion cells. In the first phase of the work, measurements on 38 different waters confirmed the conclusions of earlier work by WRc on the extent to which various water quality parameters can affect corrosion potential.

Water quality parameters found to influence the rate of galvanic corrosion were:

(i) a high chloride concentration, and in particular a high chloride to sulphate ratio, tends to be associated with a high corrosion cell voltage;

(ii) a high nitrate concentration tends to be associated with high and unstable voltages;

(iii) a high silicate concentration tends to be associated with low voltage.

Knowledge of these water quality parameters alone was not sufficient to predict galvanic corrosion potentials with much confidence. This implies that other water quality parameters and other factors might also strongly influence cell voltage. Earlier work by WRc had suggested that the presence of high zinc concentrations could be associated with low voltage.

The measurements from the 38 different waters and other information also suggested that a substantial proportion of new plumbing systems in the UK might produce water with unacceptable lead concentrations.

Strategies for overcoming the problem of lead contamination from new plumbing could include advice to the consumer on flushing during the early life of the system, but this would be of limited value in institutional buildings. Lead solder could
be replaced by non-lead solders, but the extra cost of the solders, problems of using them and ensuring their use could be a disincentive. Suitable treatment of the water is a possible alternative.

In investigating the extent to which water treatment could be used to reduce galvanic corrosion potential the following treatments were selected for investigation:

(a) addition of sulphate, as magnesium sulphate (in preference to sulphuric acid), to reduce the chloride to sulphate ratio;

(b) addition of silicate, as sodium silicate (accepted for use to control iron concentrations in water distribution);

(c) addition of zinc as zinc sulphate, with or without the addition of sodium orthophosphate (a commercial mixture of zinc and orthophosphate intended for the reduction of corrosion, especially of iron services, is commercially available);

(d) addition of orthophosphate alone, as disodium hydrogen orthophosphate (orthophosphate treatment is gaining acceptance as a method of reducing lead concentrations in plumbosolvent waters, because of the low solubility of lead orthophosphate formed in lead pipe).
3. MEASUREMENTS

3.1. Selection of waters

Four waters were selected for investigation from the 38 waters on which measurements were carried out during the first phase of the contract. The principal requirements were:

(i) high corrosion voltages, suggesting "problem" waters with respect to galvanic corrosion;

(ii) a range of alkalinites and other water quality parameters as representative as possible of the waters studied in the first phase;

(iii) convenience to the undertaking; measurements were therefore restricted to locations in or adjacent to analytical laboratories with the capacity to make frequent measurements of potential and, if possible, to carry out the water quality monitoring required;

(iv) a location in the Midlands or South East of England so as to minimise travel costs in delivering, servicing and collecting the equipment.

The fourth water originally selected for investigation subsequently became inconvenient to the undertaking concerned because of staff movements. However, the undertaking offered an alternative water nearby. Preliminary measurements, Appendix A, confirmed that this water met the first criterion above so the alternative water was accepted.

To preserve anonymity, these waters are numbered 1 to 4. Waters 1 to 3 were labelled D2, C5 and A4, respectively, in the first interim report; no previous measurements had been made on Water 4.

3.2. Equipment

The equipment used was similar to that in the first phase of the contract. Five cells, constructed as before, constituted each group or stream with six streams being used for each water. Five streams received appropriate treatments to modify water quality while the sixth stream received no treatment. Temperature was regulated to 25°C by water baths, as before. The flow of
test water through the cells, instead of being controlled by stopcock or gravity as before, was regulated by a peristaltic pump. A second peristaltic pump controlled the dosing of reagent solutions. The equipment is described in detail in Appendix B.

During the course of this work it became apparent that corrosion cells manufactured at different times or in slightly different ways might give different corrosion voltages on the same waters. Consequently, an additional test was carried out to compare directly the potentials generated by cells from different batches, as detailed in Appendix C.

3.3. Treatments applied

The treatments investigated for each water, chosen to reflect the quality characteristics of the waters, are listed in Table 1 together with the reagent dose rates and target concentrations. In practice some deviations from the target concentrations occurred, which is discussed in Appendix B7. The flow diagram for Water 4 is shown in Fig. 1. Those for the other waters were similar. The arrangement for each stream of five cells, Fig. 2, was the same as described in the first interim report, except that two test streams were accommodated in one water bath.
Table 1. Treatments investigated

<table>
<thead>
<tr>
<th>Water</th>
<th>Stream</th>
<th>Reagent dose rate (ml/min)</th>
<th>Reagent</th>
<th>Target concentration (mg/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>0.3</td>
<td>SiO₂</td>
<td>15</td>
</tr>
<tr>
<td></td>
<td>C</td>
<td>0.2</td>
<td>SiO₂</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>D</td>
<td>0.2</td>
<td>SO₄</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>E</td>
<td>0.2</td>
<td>Zn</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>SO₄</td>
<td>7.4</td>
</tr>
<tr>
<td></td>
<td>F</td>
<td>0.2</td>
<td>o-PO₄</td>
<td>2*</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>0.3</td>
<td>SiO₂</td>
<td>15</td>
</tr>
<tr>
<td></td>
<td>C</td>
<td>0.2</td>
<td>SiO₂</td>
<td>10</td>
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<tr>
<td></td>
<td>D</td>
<td>0.2</td>
<td>Zn</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>SO₄</td>
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<td>0.2</td>
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<td></td>
<td>E</td>
<td>0.2</td>
<td>Zn</td>
<td>5</td>
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<tr>
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<td></td>
<td>SO₄</td>
<td>7.4</td>
</tr>
<tr>
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<td>F</td>
<td>0.2</td>
<td>o-PO₄</td>
<td>2*</td>
</tr>
<tr>
<td>3</td>
<td>1</td>
<td>-</td>
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<td>0.4</td>
<td>SiO₂</td>
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<td>SiO₂</td>
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<td>D</td>
<td>0.2</td>
<td>SO₄</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>E</td>
<td>0.2</td>
<td>Zn</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>SO₄</td>
<td>7.4</td>
</tr>
<tr>
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<td>F</td>
<td>0.2</td>
<td>o-PO₄</td>
<td>2*</td>
</tr>
<tr>
<td>4</td>
<td>1</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>0.2</td>
<td>SiO₂</td>
<td>15</td>
</tr>
<tr>
<td></td>
<td>C</td>
<td>0.2</td>
<td>Zn</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>SO₄</td>
<td>7.4</td>
</tr>
<tr>
<td></td>
<td>D</td>
<td>0.2</td>
<td>Zn</td>
<td>0.5</td>
</tr>
<tr>
<td></td>
<td>E</td>
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<td>SO₄</td>
<td>0.74</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.5</td>
</tr>
<tr>
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<td>F</td>
<td>0.2</td>
<td>o-PO₄</td>
<td>0.2*</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2*</td>
</tr>
</tbody>
</table>

* as P

+ reduced to 1/10th of this value after 2 weeks
4. RESULTS

4.1. All waters

Despite some problems with the operation of the equipment, described in Appendix B.7, the principal objectives were achieved. The quality of each water tested, Table 2, was considered constant during the period of measurement, except for the pH values of Water 3, which increased from 7.7 to 8.7 during the test. The results of the first interim report suggest that this change should not have had a large effect on the corrosion potential. A change in the flocculant aid from activated silica to Magnafloc LT25 added at the treatment works to Water 4 seemed to produce a considerable change in the corrosion potentials, Appendix C2, but had very little effect on the water quality parameters which were monitored.

The corrosion potentials for Waters 1 to 4 are shown graphically in Figs 3 to 6 respectively. There were occasionally large differences in the voltages given by individual cells in some streams, as discussed in Appendix C1. However, no cells were judged to have failed during the tests and no justification could be found for rejecting results which superficially appeared inconsistent. Consequently the practice in the first phase of averaging the results of all five cells in each stream was followed and the averaged results for Waters 1 to 4 are shown in Tables 3 to 6 respectively.

The waters tested differed considerably in their responses to treatment, Table 7, and the order of effectiveness of the reagents also differed from one water to another. Table 7, from which the principal conclusions of this work are drawn, summarises average results for each stream over the full test period. Differences between individual cells and differences in results from week to week are not discussed in detail in this report because, except for those noted in Appendix C, they appear to be random in nature. Comparison of the results for the final week would not substantially affect the conclusions drawn from Table 7, as found in phase 1, except for streams dosed with orthophosphate.
Table 2. Mean qualities of waters during test periods, before addition of reagents

<table>
<thead>
<tr>
<th>Water</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dates 1985</td>
<td>28/1 to 22/2</td>
<td>20/2 to 20/3</td>
<td>27/2 to 4/4</td>
<td>23/4 to 20/5</td>
</tr>
<tr>
<td>pH</td>
<td>7.4</td>
<td>7.6</td>
<td>8.3</td>
<td>8.5</td>
</tr>
<tr>
<td>Alkalinity mg/l as CaCO₃</td>
<td>264</td>
<td>185</td>
<td>10</td>
<td>116</td>
</tr>
<tr>
<td>Nitrate mg/l as N</td>
<td>6.9</td>
<td>13.0</td>
<td>0.28</td>
<td>5.9</td>
</tr>
<tr>
<td>Chloride mg/l as Cl</td>
<td>19.6</td>
<td>44.7</td>
<td>8.5</td>
<td>69</td>
</tr>
<tr>
<td>Sulphate mg/l as SO₄</td>
<td>26.9</td>
<td>121</td>
<td>6.3</td>
<td>133</td>
</tr>
<tr>
<td>Chloride to sulphate ratio</td>
<td>0.73</td>
<td>0.37</td>
<td>1.35</td>
<td>0.52</td>
</tr>
<tr>
<td>Silicate mg/l as SiO₂</td>
<td>15.3</td>
<td>3.8</td>
<td>2.6</td>
<td>1.5</td>
</tr>
<tr>
<td>Zinc mg/l as Zn</td>
<td>0.04*</td>
<td>0.03</td>
<td>0.02</td>
<td>0.05</td>
</tr>
<tr>
<td>o-Phosphate mg/l as P</td>
<td>0.03</td>
<td>0.02</td>
<td>0.02</td>
<td>0.08</td>
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</tbody>
</table>

General description | Chalk groundwater | Lowland river | Impounded upland water | Stored lowland river water |
<table>
<thead>
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<th></th>
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<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>No chemical treatment</td>
<td>Full chemical treatment</td>
<td>No coagulation pH adjusted</td>
<td>Coagulated and softened</td>
</tr>
</tbody>
</table>

* Excluding one questionable value
<table>
<thead>
<tr>
<th>Stream</th>
<th>Reagent</th>
<th>Mean pH</th>
<th>Mean dose (mg/l)</th>
<th>Control (mg/l)</th>
<th>Dose control</th>
<th>Whole period</th>
<th>Final week</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Mean voltage (mV)</td>
<td>Dosed voltage</td>
</tr>
<tr>
<td>A</td>
<td>None</td>
<td>7.4</td>
<td>-</td>
<td>-</td>
<td>1.00</td>
<td>53.1</td>
<td>1.00</td>
</tr>
<tr>
<td>B</td>
<td>SiO2</td>
<td>7.5</td>
<td>7.75</td>
<td>15.3</td>
<td>0.51</td>
<td>50.8</td>
<td>0.96</td>
</tr>
<tr>
<td>C</td>
<td>SiO2</td>
<td>7.5</td>
<td>6.0</td>
<td>15.3</td>
<td>0.39</td>
<td>53.3</td>
<td>1.0</td>
</tr>
<tr>
<td>D</td>
<td>MgSO4</td>
<td>7.4</td>
<td>11.9(1)</td>
<td>26.9(1)</td>
<td>0.44</td>
<td>71.3</td>
<td>1.34</td>
</tr>
<tr>
<td>E</td>
<td>ZnSO4</td>
<td>7.3</td>
<td>3.63(2)</td>
<td>0.04(2)</td>
<td>91</td>
<td>24.1</td>
<td>0.45</td>
</tr>
<tr>
<td>F</td>
<td>Na2HPO4</td>
<td>7.4</td>
<td>1.97(3)</td>
<td>0.03(3)</td>
<td>75</td>
<td>53.5</td>
<td>1.01</td>
</tr>
</tbody>
</table>

Notes:  
(1) As SO$_4$  
(2) As Zn  
(3) As P

Table 3. Effect of treatment on galvanic corrosion potential, Water 1
Table 4. Effect of treatment on galvanic corrosion potential, Water 2

<table>
<thead>
<tr>
<th>Stream</th>
<th>Reagent</th>
<th>Mean pH</th>
<th>Mean dose (mg/l)</th>
<th>Control (mg/l)</th>
<th>Dose control</th>
<th>Whole period</th>
<th>Final week</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
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<td></td>
<td></td>
<td>Mean voltage (mV)</td>
<td>Dosed voltage</td>
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<td></td>
<td></td>
<td></td>
<td>Control voltage</td>
<td>Control voltage</td>
</tr>
<tr>
<td>A</td>
<td>None</td>
<td>7.6</td>
<td>-</td>
<td>-</td>
<td>1.00</td>
<td>188</td>
<td>1.00</td>
</tr>
<tr>
<td>B</td>
<td>SiO₂</td>
<td>8.0</td>
<td>13.4</td>
<td>3.3</td>
<td>3.5</td>
<td>181</td>
<td>0.96</td>
</tr>
<tr>
<td>C</td>
<td>SiO₂</td>
<td>7.9</td>
<td>10.1</td>
<td>3.3</td>
<td>2.7</td>
<td>212</td>
<td>1.13</td>
</tr>
<tr>
<td></td>
<td>ZnSO₄</td>
<td></td>
<td>5.6(3)</td>
<td>0.03(3)</td>
<td>186</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>D(1)</td>
<td>+</td>
<td>5.2(4)</td>
<td>121(4)</td>
<td>0.04</td>
<td>20.1</td>
<td>0.11</td>
</tr>
<tr>
<td></td>
<td>Na₂HPO₄</td>
<td></td>
<td>0.91(5)</td>
<td>0.02(5)</td>
<td>46</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>ZnSO₄</td>
<td></td>
<td>0.53(3)</td>
<td>0.03(3)</td>
<td>18</td>
<td></td>
<td></td>
</tr>
<tr>
<td>D(2)</td>
<td>+</td>
<td>7.7</td>
<td>0.71(4)</td>
<td>121(4)</td>
<td>0.006</td>
<td>130</td>
<td>0.72</td>
</tr>
<tr>
<td></td>
<td>Na₂HPO₄</td>
<td></td>
<td>0.28(5)</td>
<td>0.02(5)</td>
<td>14</td>
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<td></td>
</tr>
<tr>
<td>E</td>
<td>ZnSO₄</td>
<td>7.6</td>
<td>4.8(3)</td>
<td>0.03(3)</td>
<td>161</td>
<td>162</td>
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<tr>
<td></td>
<td>7.6(4)</td>
<td></td>
<td>121(4)</td>
<td></td>
<td>0.06</td>
<td></td>
<td></td>
</tr>
<tr>
<td>F</td>
<td>Na₂HPO₄</td>
<td>7.7</td>
<td>2.45(5)</td>
<td>0.02(5)</td>
<td>123</td>
<td>158</td>
<td>0.84</td>
</tr>
</tbody>
</table>

Notes: (1) Days 1 to 13
(2) Days 14 to 29; cells used were probably from Batch I, see Appendix C2
(3) As Zn
(4) As SO₄
(5) As P
Table 5.  
Effect of treatment on galvanic corrosion potential, Water 3

<table>
<thead>
<tr>
<th>Stream</th>
<th>Reagent</th>
<th>Mean pH</th>
<th>Mean dose (mg/l)</th>
<th>Control (mg/l)</th>
<th>Dose control</th>
<th>Whole period</th>
<th>Final week</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Mean voltage (mV)</td>
<td>Dosed voltage</td>
</tr>
<tr>
<td>A</td>
<td>None</td>
<td>8.3</td>
<td>-</td>
<td>-</td>
<td>1.00</td>
<td>93.6</td>
<td>1.00</td>
</tr>
<tr>
<td>B</td>
<td>SiO2</td>
<td>9.5</td>
<td>18.1</td>
<td>2.6</td>
<td>7.0</td>
<td>34.5</td>
<td>0.37</td>
</tr>
<tr>
<td>C(1)</td>
<td>SiO2</td>
<td>9.3</td>
<td>11.7</td>
<td>2.6</td>
<td>4.5</td>
<td>44.9</td>
<td>0.48</td>
</tr>
<tr>
<td>D</td>
<td>MgSO4</td>
<td>8.4</td>
<td>7.8(2)</td>
<td>6.3(2)</td>
<td>1.2</td>
<td>49.6</td>
<td>0.53</td>
</tr>
<tr>
<td>E</td>
<td>ZnSO4</td>
<td>7.5</td>
<td>5.2(3)</td>
<td>7.0(2)</td>
<td>0.02(3)</td>
<td>260</td>
<td>0.35</td>
</tr>
<tr>
<td>F</td>
<td>Na2HPO4</td>
<td>8.0</td>
<td>1.91(4)</td>
<td>0.02(4)</td>
<td>96</td>
<td>40.2</td>
<td>0.43</td>
</tr>
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Notes:  
(1) Not operating Days 20-27 (see Appendix B7)  
(2) As SO4  
(3) As Zn  
(4) As P
<table>
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<tr>
<th>Stream</th>
<th>Reagent</th>
<th>Mean pH</th>
<th>Mean dose (mg/l)</th>
<th>Control (mg/l)</th>
<th>Dose control</th>
<th>Whole period</th>
<th>Final week</th>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Mean voltage (mV)</td>
<td>Dosed voltage Control voltage</td>
</tr>
<tr>
<td>A</td>
<td>None</td>
<td>8.5</td>
<td>-</td>
<td>-</td>
<td>1.00</td>
<td>125.3</td>
<td>1.00</td>
</tr>
<tr>
<td>B</td>
<td>SiO₂</td>
<td>8.8</td>
<td>11.0</td>
<td>1.5</td>
<td>7.3</td>
<td>133.3</td>
<td>1.06</td>
</tr>
<tr>
<td>C</td>
<td>ZnSO₄</td>
<td>8.3</td>
<td>4.4(1)</td>
<td>0.05(1)</td>
<td>88</td>
<td>27.3</td>
<td>0.22</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>133(2)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>D</td>
<td>ZnSO₄</td>
<td>8.5</td>
<td>0.37(1)</td>
<td>0.35(1)</td>
<td>7.4</td>
<td>75.0</td>
<td>0.60</td>
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<tr>
<td></td>
<td></td>
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<td>133(2)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>ZnSO₄</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>E</td>
<td>+</td>
<td>8.5</td>
<td>-</td>
<td>133(2)</td>
<td>-</td>
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<td>0.25</td>
</tr>
<tr>
<td></td>
<td>Na₂HPO₄</td>
<td></td>
<td>0.20(3)</td>
<td>0.08(3)</td>
<td>2.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>F</td>
<td>Na₂HPO₄</td>
<td>8.5</td>
<td>1.99(3)</td>
<td>0.08(3)</td>
<td>27</td>
<td>82.2</td>
<td>0.66</td>
</tr>
</tbody>
</table>

Notes:
(1) As Zr
(2) As SO₄
(3) As P
Table 7. Effect of treatment on galvanic corrosion potential, Waters 1 to 4

Results are for full period of test, except where stated.

<table>
<thead>
<tr>
<th>Reagent</th>
<th>Approximate concentration (mg/l)</th>
<th>Reduction in corrosion potential compared to control (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Water 1</td>
</tr>
<tr>
<td>SiO₂</td>
<td>15 as SiO₂</td>
<td></td>
</tr>
<tr>
<td>SiO₂</td>
<td>10 as SiO₂</td>
<td></td>
</tr>
<tr>
<td>MgSO₄</td>
<td>10 as SO₄</td>
<td></td>
</tr>
<tr>
<td>Na₂HPO₄</td>
<td>2 as P</td>
<td></td>
</tr>
<tr>
<td>ZnSO₄</td>
<td>5 as Zn</td>
<td></td>
</tr>
<tr>
<td>ZnSO₄</td>
<td>0.5 as Zn</td>
<td></td>
</tr>
<tr>
<td>ZnSO₄</td>
<td>0.5 as Zn</td>
<td></td>
</tr>
<tr>
<td>Na₂HPO₄</td>
<td>0.2 as P</td>
<td></td>
</tr>
</tbody>
</table>

* Two-week period only
4.2. Water 3 (soft) Water 3, the only low alkalinity water investigated, was the most responsive to treatment, with all the treatments reducing the corrosion potential by at least 50 per cent for most of the period, Table 3. Over the period as a whole, zinc sulphate (5 mg Zn/l) and silicate (20 mg SiO₂/l) were the most effective. However, the zinc reagent caused deposition of a brown coating on all internal surfaces of the cells and tubing and decreased pH by about 0.8 units. The brown deposit had a 50 per cent loss on ignition indicating a high organic content. The silica reagent raised the pH by about 1.2 units. Sulphate was, though marginally, the least effective. Silicate (10 mg SiO₂/l) and orthophosphate (2 mg P/l) were similar in effectiveness over the period as a whole. However, orthophosphate was the most effective reagent of all in the final week, with the average potential then at only 17 per cent of the value produced by the untreated control stream.

4.3. Waters 1, 2 and 4 (hard) Of the three "hard" waters examined, Water 4 was the most responsive to treatment, perhaps because of its lower alkalinity and higher pH, Table 2, but other unmeasured water quality factors might have been partially responsible.

(i) Silicate caused either no change in corrosion potential or a slight increase or decrease, and was therefore considered ineffective for hard waters.

(ii) Sulphate was investigated only with Water 1 because the sulphate concentrations of the other two waters were too great to be worth manipulating. Interpretation of the results is complicated by the intrinsically unstable potential obtained with Water 1, Fig. 3, and the apparent change in dose from about 23 mg/l to about 6 mg/l on about Day 10, if the analytical results prior to Day 10 are correct. However, the average potentials given by this test stream exceeded those of the control stream, though less so during the first week than later. Consequently the treatment was considered to be of little value.
(iii) **Orthophosphate** caused mixed results. With Water 1 there was no discernible improvement compared to the control although lower potentials were produced in Waters 2 and 4, especially by the fourth week of the test, see Tables 4 and 6. The tendency for this reagent to become more effective with time was also observed with Water 3.

(iv) **Zinc**, when dosed at 5 mg/l, also had variable effects. Lower corrosion potentials were obtained with each of the waters investigated, being very pronounced with Water 4, Table 6, but only marginal with Water 2, Table 4, except in the final week. This reagent caused some deposition from all the waters examined when dosed at 5 mg/l and some of the large effect observed with Water 4 in particular may have been due to the formation of a coating on the electrodes. The compositions of the precipitates and coatings were not determined. The dosing of Water 4 at 0.5 mg/l produced progressively lower potentials compared to the control, resulting in approximately 50 per cent reduction by Week 4, without any obvious deposition from solution.

(v) **Zinc and orthophosphate** in combination, when first investigated at high concentration (5 mg Zn/l and 2 mg P/l), with Water 2 produced a white floc causing heavy coating of all cell surfaces. This coating probably contributed to the pronounced reduction in corrosion potential compared to the control, Table 4, because when one of the coated cells was returned on Day 20 to Stream D at the reduced reagent concentration (0.5 mg Zn/l and 0.2 mg P/l), the potential increased significantly after about a week, see Fig. 4. The effect on the new cells introduced at Day 14 of dosing at the lower concentration was first a marginal reduction in potential compared to the control for about 10 days which was followed by a more substantial reduction. Water 4 was treated with the lower concentration from the beginning and an immediate and substantial reduction in potential was obtained, Table 6.
This reduction was not as pronounced as that produced by zinc at 5 mg/l (which in practice would have led to "dirty water" problems) but was more than either zinc at 0.5 mg/l or phosphate at 2 mg P/l.

Measurements on Water 1 to compare the effects of treating with a commercial zinc orthophosphate corrosion inhibitor and a laboratory reagent mixture of the same substances, see Appendix C3, found no significant difference between the effectiveness of the commercial product and the laboratory reagent mixture. For Water 1 a zinc concentration of 0.8 mg Zn/l and orthophosphate of 0.32 mg P/l was necessary to give a substantial reduction in corrosion potential.

Comparisons of the results from cells made at different times, Appendices C2 and C3, showed that the later batches of cells tended to give potentials which were higher, by up to a factor of two, than those given by the earlier cells. It is concluded from this that greater standardisation of cell manufacture is needed.
The results showed that suitable treatments can be effective in reducing the galvanic corrosion potential of lead solder coupled to copper. With the softest water tested, Water 3, all of the treatments had a considerable effect. If this water is typical, the choice of treatment for further investigation in soft waters would depend on such factors as cost, convenience and effect on other water quality problems such as plumbosolvency. Orthophosphate dosing, which was particularly effective during the final week of the test, might be the preferred choice.

The only treatments which significantly reduced the corrosion potentials of the two hardest waters, Waters 1 and 2, were zinc alone and in combination with orthophosphate. Addition of zinc is limited by the EC Directive Guide Level (there is no Maximum Admissible Concentration) for drinking water to 5 mg/l after 12 hours standing at consumers taps and to 0.1 mg/l at entry to distribution. The WHO Guideline value is also 5 mg/l. Zinc hydroxide, carbonates and orthophosphate have low solubilities and simple solubility predictions and measurements of turbidity for all four waters showed that precipitation starts at concentrations of zinc which depend on water quality but for all waters was less than 2 mg/l. Consequently concentrations of zinc which exceed its solubility in a given water can be expected to be a potential cause of discoloured water. This was noticed in at least two cases. Treatment with zinc alone at 0.5 mg/l was investigated only with Water 4, in which an overall reduction in the corrosion of 40 per cent compared to the control was obtained, without any apparent deposition from solution. However, the relatively small effect of zinc even at 5 mg/l in Water 2 suggests that smaller concentrations of zinc would not produce a significant reduction in corrosion potential in some hard waters.

Zinc in combination with orthophosphate, about 0.5 mg Zn/l and 0.2 mg P/l, appears to offer the most favourable option for
treating the hardest waters, though orthophosphate alone at 2 mg P/l could be as effective for waters of intermediate hardness after a few weeks (compare the results for Water 4 in the final week, Table 6).

The corrosion potentials serve only as a guide to levels of lead which might occur in newly plumbed buildings. If it is postulated that galvanic corrosion potentials below 30 mV normally give rise to acceptable lead concentrations (first interim report), then for treatment to be considered effective a reduction of at least 70 per cent must be achieved for waters with galvanic corrosion potentials above 100 mV. The results in Table 7 suggest that a reduction of this scale might be difficult to achieve and that for hard waters, and waters with particularly high corrosion potentials, treatment might provide only a partial answer to the problem.

The effects of treatments has been shown only for corrosion cells and needs to be demonstrated for lead-soldered copper pipework. If the dosing of zinc is to be an acceptable strategy for reducing contamination of lead in tapwater by solder then simple and cheap methods for reliable dosing need to be established.
6. CONCLUSIONS

* The effects of dosing four waters with silicate, sulphate, orthophosphate and zinc to reduce the galvanic corrosion of lead solder coupled to copper have been measured.

* All the treatments were more effective at reducing corrosion potentials in the soft water than in the three hard waters.

* For the soft water all the treatments were effective at reducing the corrosion potential by about 50 per cent for most of the test period. Choice of treatment would therefore depend on cost, convenience and the effect on other water quality problems (such as discoloration and lead solubility).

* In hard waters silicate and sulphate appear to be ineffective whilst the effectiveness of orthophosphate increased during the test period.

* Zinc, alone or in combination with orthophosphate, was the most effective treatment overall, but if dosed close to the limit of 5 mg/l imposed by the EC Directive and WHO Guidelines would probably give rise to "dirty water" problems in many waters. At a concentration of 0.5 mg/l, when "dirty water" problems would probably be avoided, a greater reduction in corrosion potential was obtained when orthophosphate was dosed simultaneously at 0.2 mg P/l.

* The reduction in corrosion potential achieved by treatment, especially for hard waters and those with corrosion potentials above 100 mV before treatment, may not be sufficient to reduce concentrations of lead resulting from galvanic corrosion to acceptable levels.

* Further standardisation of the materials and manufacture of the corrosion cells, and perhaps a reconsideration of their design, is required. The cause of the very low corrosion potentials given by a minority of cells should be investigated.
* The effectiveness of zinc dosing on actual lead-soldered copper pipework needs to be demonstrated and cheap and simple methods for reliable dosing of zinc to plumbing systems need to be established.
ACKNOWLEDGEMENTS

The work reported was carried out with the assistance of the following:

* Water undertakings:
  Anglian Water Authority
  Essex Water Company
  Lee Valley Water Company
  Severn-Trent Water Authority

* Colleagues throughout WRc
It was originally intended that Water E9 (first interim report) would be the fourth water to be investigated in this series of tests, but because of staff changes it became inconvenient to the water undertaking to carry out the measurements. A different water, but with similar water quality characteristics, was offered instead. Before testing the effect of treatment, it was necessary to establish that the first criterion listed in Section 3.1 applied, namely the galvanic corrosion potential before treatment was sufficiently high.

At that time only three cells were available (five would have been preferred). These were probably from the batch of cells used for the work described in the first interim report and the measurements on Water 1 (referred to as Batch I in Appendix C2) but one or more may have been from a later batch. Measurements of corrosion potential were carried out for 26 days. Water quality during this period was similar to that shown for Water 4 in Table 2 for most parameters but differed in respect of high values of pH, silicate and orthophosphate; pH was in the range 8.8 to 9.1, silicate fell from 4.5 mg SiO₂/l at the beginning of the period to 0.9 mg/l by about Day 21 and then rose to 1.9 mg/l by Day 26, whilst orthophosphate was in the range 0.18 to 0.25 mg P/l.

The galvanic corrosion potentials are shown graphically in Fig. 7 and are summarised in Table 8 below.

<table>
<thead>
<tr>
<th></th>
<th>Cell 1</th>
<th>Cell 2</th>
<th>Cell 3</th>
<th>Cells 1-3</th>
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</thead>
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<tr>
<td>Mean potential (mV)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Days 0-26</td>
<td>34.0</td>
<td>153.8</td>
<td>117.7</td>
<td>101.8</td>
</tr>
<tr>
<td>Mean potential (mV)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Days 21-26</td>
<td>20.9</td>
<td>152.3</td>
<td>105.6</td>
<td>92.9</td>
</tr>
</tbody>
</table>
Although Cell 1 gave consistently lower potentials than the other two, only once rising for two to three days around Day 19 to approximately 100 mV, the average potential for all three cells was about 100 mV, which satisfied the first criterion in Section 3.1. The other criteria were also satisfied.
APPENDIX B
EQUIPMENT AND OPERATION

B1. Corrosion cells
The design of the corrosion cells used in this work was the same as in an earlier contract to DOE and was also described and discussed in the first interim report (Appendix A1) on this contract. Following experience during the first phase, the soldered electrodes were "reinforced" round the edges with epoxy resin to prevent separation of the solder electrode from the epoxy resin masking.

The cells used for the measurements on Water 1 had remained unused from the first phase of the contract, and a second batch of cells was prepared for measurements on Waters 2 to 4 (Batches I and II respectively, see Appendix C2).

B2. Water baths
The water baths used were from the twelve purchased for the first phase of the contract (first interim report, Appendix A2). The lids were redesigned to allow two groups of five cells, each with their own pre-heating coils and thermometer tubes, to be accommodated in each bath. Consequently three baths were required for each set of equipment, so economising on space and power requirements. Two complete sets of equipment were assembled, allowing measurements on two waters to be made simultaneously.

The thermostat of one of the baths failed during testing of Water 4 and the bath was quickly replaced.

B3. Peristaltic pumps
The flow of test water to each stream was controlled by a Cole-Parmer peristaltic pump which was used to deliver nominally 100 ml/min to each test stream. There were two drive shafts on each pump, each shaft driving a maximum of five roller heads. The pumps were usually operated with three roller heads to each drive shaft, except when equipment failure prevented it. The rollers caused distortion and weakening of the pump tubing so that from time to time, depending on the extent of wear, it was

* Walker, R. and Oliphant, R.J. "A cell to study corrosion of materials in the water supply industry". Jour. Instn Water Engrs and Scientists 1983, 32(2), 143-150
necessary to pull the pump tubing through the roller head so that the rollers were operating on a fresh section of tubing. The tubing was prevented from being pulled through the pump heads by the pumping action by wrapping it with adhesive tape. A pump speed setting of approximately 4.7 was required to produce a flow of 100 ml/min. The flows were initially set slightly higher than 100 ml/min on average, because the flow tended to decrease slowly with time. Although the roller heads were nominally the same and they were all operating at the same speed, the flows delivered varied by up to ±10 per cent (i.e. from 90 to 110 ml/min). This was probably attributable to uneven wear of the roller heads and did not seriously affect the test. The pumps were generally noisy and hot when operating.

Reagent solution was pumped to each stream as required by a single Watson-Marlow peristaltic pump operating on five or six channels. The size of pump tubing was chosen to deliver 0.2 or 0.3 ml/min. The target flows were achieved more consistently than with the Cole-Parmer pump but again there were slight variations from the average between individual channels, even though they shared the same roller head. This was probably due to slight differences in the diameters of the pump tubing and their tensions. Because the flows were low it was difficult to measure them accurately. Flows tended to reduce slightly with time, so they were set initially or reset after the periodic checks about 5 per cent above target. The pumps operated quietly and the tubing showed no obvious signs of wear during the four-week operating period.

B4. Digital voltmeters

Voltages were measured using the digital multimeters described in Section A3 of the first interim report.

B5. Reagents

Reagent solutions five to seventy times more concentrated than required were prepared at WRc Stevenage using laboratory grade reagents and were diluted with distilled water on site appropriately for the dose rate and target concentration of the dosed water. No problems were experienced with this except that some crystallisation from the concentrate of the orthophosphate solution had been found to occur under the cold storage temperatures at the site where Water 2 was being measured, so the reagent solution would have been slightly less concentrated than it should have been.

B6. Assembly and operation

In general the equipment was assembled at Stevenage and was colour-coded so that it
could be split into components for ease of transportation. The sub-contractor reassembled the equipment on site, connected the water supply to start the test, overcame any initial problems such as leaks, took the first set of potential readings and instructed staff on site on the operation of the equipment. Staff of the water undertaking took most of the subsequent voltage readings, collected samples and analysed them; the samples for Water 2 were taken to WRc Stevenage for analysis because the water undertaking did not have sufficient manpower available. The sub-contractor visited the site weekly to check the equipment, deal with any breakdowns or other problems, replenish reagent solutions, check the pumps and adjust them as necessary.

The measurement programme over the four weeks of the test on each water was as follows:

(i) the voltage of each cell to be measured twice per day from Monday to Friday, with measurements to be carried out at weekends and public holidays if possible;

(ii) the temperature of each stream to be measured twice per day;

(iii) the water flow through each stream to be measured daily (the volumes delivered by the dosing pump to be measured weekly by the sub-contractor) and adjustments made if necessary;

(iv) samples to be collected for water quality analysis on each Monday, Wednesday and Friday with analyses as follows:

dosed streams - pH value, together with the substance being dosed, i.e. sulphate, silicate, orthophosphate, zinc plus sulphate or on streams receiving zinc and orthophosphate in combination, zinc, sulphate and orthophosphate

control - each of the substances being dosed together with pH value, alkalinity, chloride and nitrate.

The measurement programme, particularly for water quality parameters, was subject to variation as a consequence of equipment breakdown, manpower availability and assessment of results. The period of measurement of Water 3 was extended to five
weeks because of interruptions due to equipment breakdowns. The measurements were carried out from January to May 1985.

B7. Performance

In general the equipment functioned adequately although some problems common to each test were experienced in addition to specific breakdowns and difficulties. As described in Appendix B3, the flows delivered by the two pumps could be as much as 10 per cent above or below target. Consequently the concentrations in the dosed water could be as much as 20 per cent above or below target due to the performance of the pumps although most reagent concentrations were within 10 per cent of the target (compare Table 1 with Tables 3 to 6). Some precipitation occurred where the silicate reagent entered the main water stream and this might have led to blockages if allowed to accumulate. Deposition occurred on the internal surfaces of tubing and cells, especially when the water was being treated with zinc at around 5 mg/l (see Section 4.3), and in the case of Water 4 white particles in suspension, presumably of zinc carbonate or zinc hydroxide, were visible. Although contributing to the analytical result because the sample was acidified before analysis, this fraction of the added zinc could not have been effective at reducing galvanic corrosion.

Problems unique to each of the tests were as follows:

Water 1 There were no equipment failures but difficulties were experienced with dosing, causing the achieved concentrations of silicate and sulphate to be significantly below target (compare Tables 1 and 3) although the silicate concentrations were relatively constant during the four weeks. The sulphate concentration appeared to be approximately twice what it should have been until about Day 10 and then fell to about two-thirds of its target level, but it is believed that the results of sulphate analyses before Day 10 are wrong.

Water 2 Because of the loss of a retaining stud in the required position, the Cole-Parmer pump was operated throughout with Streams A and B on the left-hand drive shaft and Streams C to F on the right. The initial concentrations of zinc and orthophosphate chosen for Stream D, Table 2, caused substantial floc formation and deposition in the cells and tubing, leading eventually to a blockage after two weeks of operation. The contaminated cells were then replaced with four unused cells which were
probably from the same batch as those used for Water 1, Appendix C2, and the reagent 
concentrations were reduced to one-tenth of 
their former level. One of the contaminated 
cells, after rinsing out loose deposit, was 
replaced in Stream D for the last nine days 
of the test, receiving the same reagent dose 
as the other four cells during this period.

Water 3 The test was interrupted on Days 4 
and 5 (a weekend) because of leaks, but this 
does not appear to have had a marked effect 
on the corrosion potentials. No silicate 
was dosed for the first six days of 
operation because the reagent container was 
moved soon after the equipment was set up 
causing the end of the suction tube to be 
above the level of the liquid. A brief 
interruption in the dosing of orthophosphate 
seems also to have occurred towards the end 
of this period. On Days 18 and 19 (also a 
weekend) the Cole-Parmer pump broke down and 
from Day 20 until Day 27, when it was 
repaired, no water or reagent was pumped 
through Stream C (low silicate treatment, 
considered the least important) because only 
five streams could be operated. The water 
undertaking agreed to continue the test for 
an extra week because of these problems.

Water 4 The dosing pump malfunctioned at 
the beginning of the test, giving low or 
zero doses of some reagents, but began to 
operate effectively within the first 24 
hours. The thermostat of the water bath 
serving Streams C and D malfunctioned 
intermittently during the first nine days, 
giving a varying temperature averaging about 
3°C above the intended 25°C, at least from 
about Days 6 to 9. No correction has been 
made for this difference in temperature 
because its duration and magnitude are 
uncertain and the effect was comparatively 
small, although the corrosion potentials in 
Streams C and D may be slightly higher 
during that time because of it than they 
would otherwise have been. The water bath 
was replaced on Day 10. At some time 
between Days 19 and 21 (a weekend period) 
the dosing pump broke down so that no 
reagent was delivered. It was repaired 
temporarily on Day 21 but continued to 
malfunction intermittently until repaired on 
Day 23. This may account for the unstable 
potentials of many cells in Streams D to F 
during this period. The tubing of the 
Cole-Parmer pump leaked slightly on two 
occasions during the test, but this did not 
adversely affect performance.

Very few voltage readings were missed. The 
number of samples collected and analysed
from Waters 2 and 4 were somewhat fewer than planned, because of staffing problems, but this caused no difficulties in evaluating the results.

**B8. Data handling**

The results were entered on the WRC computer for ease of handling and generation of graphs.
APPENDIX C
DIFFERENCES IN PERFORMANCE BETWEEN CELLS

C1. Intra-stream differences

Throughout this work large differences have been observed frequently between the results given by the five cells used together in series in each test stream. These differences are amply illustrated in Figs 3 to 6. One cause of this phenomenon in the earlier work described in the first interim report (Appendix A1), was the failure of the epoxy-resin coating used on the "back" face of the solder electrode which led to increased potentials. This problem has been almost completely overcome by "reinforcing" the epoxy-resin coating round the edges of the electrode although an occasional small gap in the edge coating may sometimes lead to elevated potentials.

In extreme cases, for example in Fig. 6 Streams A and B on Days 19-28, voltages can differ by a factor of up to 100 although much smaller differences are more common. The extent to which cells diverge in their performance seems to be related to water quality factors: for example Water 3, perhaps because of its low nitrate content, showed considerable agreement between the cells in each stream, as it had done previously as Water A4 in the measurements described in the first interim report.

Most of the differences between the performance of cells in the same stream seem to be due to differences in the properties of the individual solder electrodes. Examination of the cells at the end of each test usually, though not invariably, showed differences in the extent of corrosion which related to the average corrosion potentials during the test. Cells which gave lower corrosion potentials than the others frequently had an area of corrosion covering a smaller fraction of the electrode face or the corrosion layer was thinner. The cause of these differences is probably related to the nature of the electrode surface which can be affected by flux, the temperature of the melted solder, the manner of cooling, presence of an impurity or contamination with a thin layer of grease. This indicates that more attention to the design, preparation and storage of the electrodes is
required. An investigation of the cause or causes of the very low corrosion potentials given by a minority of cells might prove beneficial as it could suggest a means by which the galvanic corrosion of lead from solder could be minimised. Some differences in performance between electrodes is probably inevitable, however, and averaging of the results from five cells provides a means of partially overcoming this problem.

**C2. Inter-stream differences**

The success of the tests on the effects of treatment obviously depends on the assumption that, in the absence of dosing, the six streams in each test would have given substantially similar results. This assumption is vindicated by the results from Water 1, Table 3 and Fig. 3. These show that, despite considerable differences in voltages between cells and from day to day, the four-week and fourth-week averages of Stream A (control) and Streams B, C and F (with apparently ineffective treatment) were remarkably similar. The higher potentials given by Stream D are probably due to the presence in this stream of a more than average number of cells tending to give a high corrosion potential rather than to the effects of treatment; the reverse tendency may have been present in some streams in this and other waters which apparently showed a good response to treatment.

The results obtained from the control streams in the current series of measurements are compared in Table 9 with those from the same water when measured in 1984 during the course of the work described in the first interim report.

There were no significant changes in the measured water quality parameters between the 1984 and 1985 measurement periods, except that the silica content of Water 3 increased from 1.2 mg/l in 1984 to 2.5 in 1985, a change expected to lead to a negligible to slight decrease in corrosion potential. Changes in water quality parameters not measured may, of course, have occurred.

The cells used for all the measurements in 1984, and the measurements in 1985 on Water 1, were air-cooled after manufacture. These cells had a dull surface to the solder electrode and are designated Batch I. The cells used for the treatment tests on Waters 2 to 4 were cooled in water. These cells had a shiny surface and are designated Batch II. Table 9 suggests there is a systematic difference between the results given by Batch I and Batch II cells.
Table 9. Comparison of results from control streams in 1985 with results from the same waters in 1984

<table>
<thead>
<tr>
<th>Water</th>
<th>Cell batch*</th>
<th>1985 results</th>
<th>1984 results</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mean potential (mV)+</td>
<td></td>
<td>Mean potential (mV)+</td>
</tr>
<tr>
<td>1</td>
<td>I</td>
<td>53.1</td>
<td>D2</td>
</tr>
<tr>
<td>2</td>
<td>II</td>
<td>188</td>
<td>C5</td>
</tr>
<tr>
<td>3</td>
<td>II</td>
<td>93.6</td>
<td>A4</td>
</tr>
<tr>
<td>4</td>
<td>II</td>
<td>125</td>
<td>-</td>
</tr>
</tbody>
</table>

* See text

Average from good cells (i.e. no failure of resin backing) over whole period of test (approximately four weeks)

No measurements on Water 4 were made in 1984 but the preliminary set of measurements described in Appendix A gave an average potential of about 100 mV over four weeks. The three cells used for these measurements and the four cells substituted into Stream D of Water 2 on Day 14 were almost certainly from Batch I, but one or more of the cells could have been from Batch II. The potentials of the four cells used for Stream D of Water 2 averaged 169 mV after at least an hour of exposure to the test water, compared to the average potential of the control stream on that day of 180 mV. The slightly lower potential in Stream D might have been caused by the zinc orthophosphate treatment. Consequently these seven cells behaved similarly to Batch II cells.

In this context some of the results from the treatment tests on Water 4 are interesting. The potentials of the many cells in Streams A, B, D and F which were between 70 and 100 mV at the beginning of Day 7 had increased by about 70 mV by the end of Day 8, Fig. 6. This increase might have been the result of a change in water quality because at about this time the use of activated silica as a coagulant aid was suspended, resulting in a reduction in silica concentration of no more than 2 mg/l, and treatment with a polyelectrolyte (Magnafloc LT25 at 0.1 mg/l) was begun. The change in potential is difficult to associate with the reduction in silica concentration, because the much higher concentration of silica added to Stream B had little effect. The cause might have been the polyelectrolyte itself, or a consequent change in a water quality parameter which was not monitored, unless activated silica is much more effective at
moderating corrosion than sodium silicate. (The reduction in potential in Streams C and D around Day 10 was the result of replacing a defective water bath and the unstable potentials in several streams between Days 19 and 23 were probably due to failure of the dosing pump, see Appendix B7.)

C3. Effect of method of manufacture on cell performance

In view of the differences between the results given by the Batch I and Batch II cells, Table 9, possibly due to the differences in manufacture, it was decided to carry out a further trial. This also provided the opportunity to test a commercial zinc orthophosphate anti-corrosion product known as Virchem V931, manufactured by Virginia Chemicals Inc., compared to a mixture of zinc and orthophosphate made up from laboratory reagents.

For the purposes of this trial, which was carried out using Water 1 during April and May 1985, a further batch of cells were manufactured. Half of these (Batch IIIA) were air-cooled like Batch I and half (Batch IIIB) were water-cooled, as Batch II. Five of each of the cells from Batches IIIA and IIIB were placed alternately in Streams A and B. The control stream (Stream C) contained cells from Batch I, and received no treatment throughout. Streams A and B received no treatment until Day 21, when after an initial brief high dose to saturate the system, both received zinc at 0.4 mg/l (orthophosphate at 0.16 mg P/l). Stream A was treated with Virchem V931, Stream B with the laboratory reagent mixture. On Day 32 the concentration of zinc in both streams was raised to 0.8 mg/l (orthophosphate at 0.32 mg P/l).

The results of the trial, shown graphically in Fig. 8, revealed no significant difference between treatment with Virchem V931 and the laboratory reagent mixture. Comparison of the performance of cells from Batches I, IIIA and IIIB, Table 10, shows no significant difference between Batches IIIA and IIIB, but a significant difference between Batch III and Batch I.

The difference between air cooling and water cooling therefore does not seem to be significant. There is no obvious explanation for the large decrease in potentials in Stream C after Day 19. If Streams A and B had behaved in the same way it would indicate that dosing with 0.4 mg/l of zinc, in combination with orthophosphate at 0.16 mg P/l, is an ineffective treatment for this water, but dosing at 0.8 mg Zn/l
### Table 10.
Results from Water 1 comparing cells of different batches

<table>
<thead>
<tr>
<th>Batch</th>
<th>Stream</th>
<th>Days 1-20</th>
<th>Days 21-29</th>
<th>Days 32-40</th>
<th>Days 1-40</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Zn (mg/l)</td>
<td>Mean potential (mV)</td>
<td>Zn (mg/l)</td>
<td>Mean potential (mV)</td>
</tr>
<tr>
<td>IIIA</td>
<td>A and B</td>
<td>0</td>
<td>133.6</td>
<td>0.4</td>
<td>62.3</td>
</tr>
<tr>
<td>IIIB</td>
<td>B and C</td>
<td>0</td>
<td>121.0</td>
<td>0.4</td>
<td>79.5</td>
</tr>
<tr>
<td>I</td>
<td>C</td>
<td>0</td>
<td>85.3</td>
<td>0</td>
<td>38.3</td>
</tr>
</tbody>
</table>

### Table 11.
Summary of results from measurements without treatment on Water 1 (=Water D2), 1984-5

<table>
<thead>
<tr>
<th>Month</th>
<th>Year</th>
<th>Period (days)</th>
<th>Cell batch</th>
<th>Mean potential (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Jan</td>
<td>1984</td>
<td>30</td>
<td>I</td>
<td>62.8</td>
</tr>
<tr>
<td>Jan</td>
<td>1985</td>
<td>30</td>
<td>I</td>
<td>53.1</td>
</tr>
<tr>
<td>Apr/May</td>
<td>1985</td>
<td>20</td>
<td>I</td>
<td>85.3</td>
</tr>
<tr>
<td>Apr/May</td>
<td>1985</td>
<td>40</td>
<td>I</td>
<td>60.0</td>
</tr>
<tr>
<td>Apr/May</td>
<td>1985</td>
<td>20</td>
<td>IIIA</td>
<td>133.6</td>
</tr>
<tr>
<td>Apr/May</td>
<td>1985</td>
<td>20</td>
<td>IIIB</td>
<td>121.0</td>
</tr>
</tbody>
</table>
(orthophosphate at 0.32 mg/l) produces a more marked effect. The trial was continued beyond Day 40 but with no significant change in potentials. (It must be noted that the effectiveness of treatment applied sometime after the exposure of a corrosion surface to untreated water might not be as great as if the treatment is applied from the start of exposure of the surface to the water.)

The results of all measurements carried out on Water 1 in which no treatments were applied are summarised for convenience in Table 11.

The quality of Water 1 was similar throughout all periods of measurement. No cells from Batch II have been used for measurements on Water 1. However, the results of Tables 9 and 11 suggest that cells from Batches II and III tended to produce voltages approximately twice as high as those from Batch I, perhaps because of differences in the composition of the solder. This again indicates that the materials and methods of manufacture of the cells require further standardisation.
Figure 1. Flow diagram for Water 4
Figure 2. Flow diagram for each stream of five cells
Figure 3. Corrosion potentials, Water 1
Figure 4. Corrosion potentials, Water 2
Figure 5. Corrosion potentials, Water 3
Figure 6. Corrosion potentials, Water 4
Figure 7. Corrosion potentials, preliminary measurements on Water 4
Figure 8. Corrosion potentials for test, using Water 1, comparing cells of different batches
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