CONTAMINATION OF WATER BY DOMESTIC PLUMBING FITTINGS (M2186C)

JULY TO DECEMBER 1980

R.J. Oliphant

December 1980

8-E

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DOE CONTRACT REFERENCE: DGR/480/250
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SUMMARY

a) Work to determine the relationship between the galvanic corrosion current, measured by the corrosion cell technique, and the total amount of lead oxidised (corroded) is reported.

b) Further results are presented that support the correlation between the amount of lead contaminating a sample of water, containing a solder/copper couple, and the galvanic corrosion charge generated by that couple.

c) Results are presented which show that progressively more of the metal being oxidised appears in the liquid as the cumulative charge passed by the couple increases.

d) The effects of flux residues, silica, phosphates and sulphate on the corrosion of tin/lead soldered joints is reported.
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OBJECTIVES

The objectives of this project are:

1) To investigate the aggressiveness of different types of water to materials used in plumbing systems.

2) To study chemical, microbiological and organoleptic deterioration of water quality in whole plumbing systems and relate this to the type of material used, the environment and period of detention.

1. INTRODUCTION

The work reported here covers items a, c, e, f and g of the work programme, see Appendix I. Thus apart from items h) (which is not now being pursued, see report for January to June 1980) and i), the proposed laboratory work has been completed. In the time remaining some of the items are being repeated, usually under slightly different conditions, to broaden the scope of the results obtained to-date. The results from this work will be in the final contract report, as will the conclusions under items 1. i) and 3. of Appendix I.

2. THE RELATIONSHIP BETWEEN THE GALVANIC CORROSION CURRENT, MEASURED BY THE CORROSION CELL, AND THE TOTAL AMOUNT OF LEAD OXIDISED (CORRODED)

A possible error with the corrosion cell arises because the galvanic corrosion current measured represents only a proportion of the total corrosion current. The solder will corrode by 'internal' cathodes, i.e. on the solder electrode surface itself, resulting in oxidation of metal without contributing to the current in the external (measuring) circuit that joins the solder to the copper 'external' cathode. From previous results it is known that, with a couple corroding in 0.5% nitric acid, five times the quantity of metal appears in solution than is to be expected by a Faraday's law calculation on the measured galvanic current, i.e. under these circumstances the galvanic current is only 20% of the total corrosion current.

In figure 1 the total amount of lead oxidised, for lead and 40/60
solder electrodes, are plotted against the charge \( \ast \) generated by the galvanic current for couples in a soft (40 mg CaCO\(_3\) \( l^{-1} \) hardness) high chloride water (60 mg \( l^{-1} \) Cl\(^-\)). The lines drawn are those to be expected from theory (i.e. Faraday's law) where the current is assumed to be oxidising lead only (100% theoretical) and where only 60% is assumed to represent lead oxidation (60% theoretical). To obtain the total lead figures the electrodes had to be cleaned using 1% boiling acetic acid.

New uncorroded electrodes were subjected to the same procedure to obtain a maximum blank correction figure for the attack of the acid on uncorroded material.

The results indicate very good agreement with theory. The higher than expected levels for lead at high charge values arose from the progressive disintegration of the electrodes because of the large amount of corrosion. Thus it would appear that, in solutions that form some sort of film on the anode, e.g. natural waters but not nitric acid, the galvanic current does represent something approaching 100% of the total corrosion current and, therefore, the measurement obtained from the galvanic cell does not greatly underestimate the amount of corrosion. This result is not too surprising when it is remembered that the corrosion currents typically obtained from galvanic couples represent corrosion rates of (for lead) \( 5 \text{ mdd} \) \((5 \text{ mg dm}^{-1} \text{ day}^{-1})\) and that rates for the corrosion of the non-galvanically coupled metal in similar solutions are of the order 0.3 mdd.

If these rates remained the same after the galvanic couple has been made (in point of fact the second figure would be depressed further because of the change in potential of the lead), the galvanic corrosion current would

\[ \text{charge Q (in coulombs)} \]

\[ \text{galvanic corrosion current (in amps) \times time (in seconds)} \]

\[*\] Charge or galvanic charge is given by:

Thus:

96,500 coulombs (1 Faraday of charge) oxidises 1 gram equivalent (old style) of material.

or 1 gram mole divided by the number of electrons per atom involved in the charge transfer.

Thus 96,500 coulombs will oxidise 103.5 g lead or a galvanic corrosion current of 1 \( \mu A \) passed for 24 hours oxidises \( \sim \) 100 \( \mu g \) lead (100% current efficiency).
represent ~ 94% of the total corrosion current. Uncoupled lead has a low corrosion rate precisely because the film that rapidly develops over the surface is a poor cathodic surface; however, provide an external cathodic surface that remains active, and the corrosion rate will be greatly stimulated and the current that flows between the two surfaces will represent the major proportion of the total corrosion current.

3. RELATIONSHIP BETWEEN AMOUNT OF LEAD CONTAMINATING THE LIQUID PHASE AND THE GALVANIC CORROSION CHARGE GENERATED BY A 40/60 SOLDER/COPPER COUPLE

Figure 2 extends the results and confirms the conclusions, drawn in the previous report, that the amount of lead that appears in the water, whether in true solution or as a precipitate, can be correlated to the charge generated by the couple. The results were obtained by placing corrosion cells, previously aged for a minimum of four weeks, in 11 samples of solution at 20°C under static conditions and measuring corrosion currents passed between the electrodes over different time periods (8 hours to 7 days). The electrodes were then carefully removed, so as not to lose material from the corrosion product layer built up over a much longer period of time, and the solution acidified with nitric acid prior to analysis. The results represent the minimum amount of contamination that could be expected (in the absence of flowing water that would mechanically remove the not very adherent deposit). The points above the 60% theoretical line show higher results than can be explained by theory and, given the work reported in section 2 above, must arise from some mechanical loss of corrosion product during the handling of the couple. Ignoring these points makes the correlation between the lead in the water phase and the galvanic corrosion charge quite obvious. Most of the figures were obtained for solutions containing nitrate, but results from other solutions, e.g. containing phosphate fit quite well on the same line.

4. PROPORTION OF THE LEAD OXIDISED APPEARING IN THE WATER PHASE

The results shown in figure 3 were obtained as explained in section 3 above except here new electrodes were used without any preaging. What the curve indicates is that during the initial stages very little of the oxidised lead appears in the water (except of course through solubility effects), but rather goes to build up the corrosion product layer on the
surface of the electrode. Gradually, however, as this surface film thickens a growing proportion of the material appears in the water. When the curve becomes parallel with the 60% theoretical line (drawn on the left hand side of the graph) the corrosion product layer has reached its maximum thickness and all the lead subsequently oxidised goes into the liquid phase. Thus even in the absence of a mechanical scouring effect, a limit to film growth can be expected at which point the galvanic corrosion current will measure the amount of lead entering the water and the rate at which this occurs.

5. **EFFECT OF FLUX RESIDUES**

In none of the experiments in which galvanic couples were corroded in the presence of flux residues was an increase in the rate of corrosion observed. Large quantities of flux were used ($\sim 2$ g) and either, melted and run around the walls of the boiling tube so as to give an exposed surface area of $\sim 53 \text{ cm}^2$ or, daubed directly above the anode on the plastic mounting sheet so that material entering solution might stream down the face of the electrode. An intermittent flow regime was resorted to leaving the cell static overnight. None of the stratagems produced the expected result. In only two of the cells did the chloride level rise above 30 mg l$^{-1}$ (from 5 mg l$^{-1}$ in the original solution) and the pH never fall below 7 (from an initial value of $\sim 8$, carbonate hardness $\sim 60$ mg l$^{-1}$ CaCO$_3$).

In a previous experiment, using water with a hardness of 30 mg l$^{-1}$ CaCO$_3$, it was possible to reach a pH of 6.8 and a chloride level of 90 mg l$^{-1}$ over an initial 3 day extraction period. After a further 10 days and 3 successive extractions, a 7 day extraction produced a pH of 6.1 and chloride of 47 mg l$^{-1}$. However, all these results were obtained by extracting 2.2 g flux with an exposed surface area of $\sim 55 \text{ cm}^2$ into 23 ml of solution!

Given the slow rate at which material leaches from flux, and the large volumes of water flowing through domestic systems, it is unlikely that flux residues will greatly change the composition of most waters, i.e. by raising the chloride and lowering the pH, and thereby increasing the rate of corrosion. One of the functions of the flux is to lower the viscosity of the molten solder so it flows more readily in the capillary space. In the presence of excess flux it is very difficult to avoid running the solder into the bore of the
tube. Use of excess flux is also associated with poor workmanship which may include overheating the joint, further increasing the chance of solder runs. Thus the correlation between unsatisfactory soldered joints and the presence of flux residues may not arise from a direct effect on corrosion rates, but rather by being associated with solder runs in the bore of the tube.

6. EFFECT OF SILICA

Figure 4 shows the effect of silica on the galvanic corrosion rate. With corrosion experiments of short duration it is always difficult to know whether an added agent fundamentally changes the corrosion processes occurring or if it only allows an equilibrium state to be reached more quickly which, in the absence of the agent, would have been attained anyway but over a period longer than the normal duration of the experiments. Certainly electrodes in which the corrosion rate was greatly reduced by the silica tended to retain their bright metallic appearance and, of course, the suppression of the normally high initial rate of corrosion may have its advantages in preventing any contamination problems right from the moment the system is brought into service.

Although the phenomenon, of the effectiveness of silica decreasing with the length of time the experimental solution had been made up, was not observed nevertheless silica freshly dissolved, obtained by running the solution through a column of silicate glass just prior to entering the cell, showed a great deal more activity. Thus corrosion currents as low or lower as those obtained with 40 mg l\(^{-1}\) Si\(_2\)O\(_5\) were obtained with 10 mg l\(^{-1}\) Si\(_2\)O\(_5\) when the latter was freshly dissolved from the column. In previous work, on the dezincification of brass, evidence was obtained which indicated that this behaviour was associated with the slow hydrolysis of silicate ions to silicic acid, the latter having no inhibitory properties.

7. EFFECT OF PHOSPHATES

Ortho and polyphosphates, to a maximum concentration of 2 mg l\(^{-1}\) as P, were tried as corrosion inhibitors under static, flowing and intermittent flowing conditions. On the whole the results were disappointing. A reduction in the galvanic current was achieved, greater for polyphosphate than ortho
and greater under static conditions than flowing. However, the reduction was often not very large and uncertain for any given concentration.

8. EFFECT OF SULPHATE

Figure 5 shows the results for the effect of sulphate on the galvanic current. The pronounced decrease with increasing sulphate may be somewhat exaggerated by the higher than usual values for the controls. However, the trend appears genuine if slightly surprising. Previous results with lead/copper couples support these observations which may be associated in the insolubility of lead sulphate.
APPENDIX I

PROGRAMME FOR PROJECT M2186 - JANUARY 1980 TO MARCH 1981

1. Laboratory work on the corrosion of soldered joints.

a) To determine the relationship between the galvanic corrosion current measured with a corrosion cell and the actual corrosion rate of the metal.

b) Effect of conductivity on corrosion rate.

c) Effect of sulphate on corrosion rate.

d) Effect of nitrate on corrosion rate.

e) Effect of flux residues on corrosion rate, i.e. to identify the individual effects of the changes in pH and chloride ion concentration produced by flux residues.

f) Effect of 'corrosion inhibitors' on corrosion rate and the solubility of the corrosion product layer.

g) To determine the changes in solubility of the corrosion product under the different solution conditions used above.

h) To determine the tendency for thick corrosion product layers to break off the metal surface so giving a particulate contamination problem.

i) To estimate from the above the level of contamination likely to arise from soldered fittings in any given supply.

To continue to participate on the panels of BSI Technical Sub-Committee EPC 44/7 to draw up standard methods for testing new plumbing materials.

Guidelines for good practice in making soldered joints.
Fig. 1. mg Pb oxidised vs. charge passed in external circuit
Fig. 2. mg Pb in liquid vs. charge passed in external circuit (for electrodes after a 4 week ageing process)
Fig. 3. mg Pb in liquid vs. charge passed in external circuit (for new electrodes)
Fig. 4. Average galvanic current (over fourth week) vs. SiO₂ concentration
Fig. 5. Average galvanic current (over fourth week) vs. sulphate concentration
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