

Corrosion due to Tuberculation in Water Systems

II. The Effect of Calgon on the Potential of Zinc and Copper Electrodes in Differential Aeration Cells with Running Tap Water

J. L. MANSA and WACLAW SZYBALSKI

Mechanical Engineering Laboratory, Technical University of Denmark, Copenhagen, Denmark

In the previous paper¹ we have studied the time-potential curves of iron electrodes in differential aeration cells (DA-cells) with running tap water. We have tried to advance a general theory for the explanation of the tuberculation properties of corrosive and non-corrosive waters.

In domestic water supply systems we very often meet galvanized *i. e.* zinc coated pipes, besides black iron pipes. Therefore it was interesting to study the electrochemical behaviour of zinc and zinc coatings in the zinc-zinc and zinc-iron DA-cells.

The construction of cells, electric and other equipment, have been described in the previous paper¹. In the experiments described below similar cells (type III) were used except that the iron electrodes were replaced by zinc, zinc-coated or copper electrodes of the same construction. All values of potentials are given in millivolts in the normal hydrogen-electrode scale.

ZINC-ZINC DA-CELLS

Curves 3 and 4 (Fig. 1) show the potentials of aerated and unaerated zinc-electrodes connected through a 1000 ohm resistance and measured against a

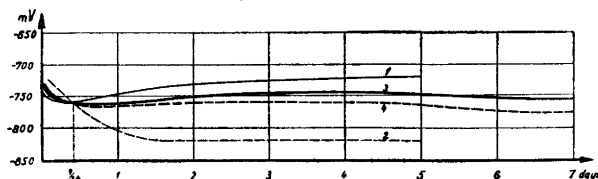


Fig. 1. Time-potential curves for the aerated (1,3) and non-aerated (2,4) zinc electrodes of DA-cell type III. Electrodes connected (3,4) through a 1000 ohm resistance or disconnected (1,2). Rate of water flow 300 ml/min.

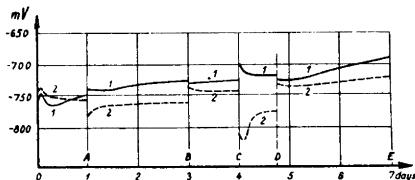


Fig. 2. Time-potential curves for the aerated (1) and non-aerated (2) zinc-coated (galvanized) electrodes of a DA-cell. Electrodes connected (O—A, B—C, D—E) through a 1 000 ohm resistance or disconnected (A—B, C—D). Rate of water flow 300 ml/min.

calomel reference electrode (saturated KCl). Only in the beginning of the experiment the aerated electrode shows a slightly more base potential than the unaerated one. After about 9 hours the potentials change. The potential difference slightly increases during the first days of the experiment. Curves 1 and 2 show the true potentials of the same electrodes disconnected.

Fig. 2 shows the potentials of the galvanized iron electrodes. In the intervals OA, BC, DE the electrodes are connected through a 1000 ohm resistance. In the intervals AB, CD electrodes are disconnected. We can see that after every disconnection the potential difference between the electrodes is decreasing. After the connection the EMF of the DA-cell rises slowly.

The diagrams in Figs. 3 and 4 show the effect of the addition of Calgon on the potentials of the disconnected electrodes of the zinc-zinc DA-cell. We see that the addition of Calgon diminishes the potentials, both the cathode and anode. The effect on the easier accessible cathode is the greater one. The sufficient addition of Calgon may change the direction of the potential difference.

Conclusions: The DA-cell with zinc electrodes shows a qualitative behaviour rather similar to that of a cell with iron electrodes. Quantitative results are more different: The potentials in the beginning of the experiments are much more base (about -750 mV) but show the continuous increase especially with galvanized electrodes. The potential difference in the beginning near to zero or slightly negative increases much slower and remains lower than with an iron cell. That seems to indicate a much smaller oxygen concentration

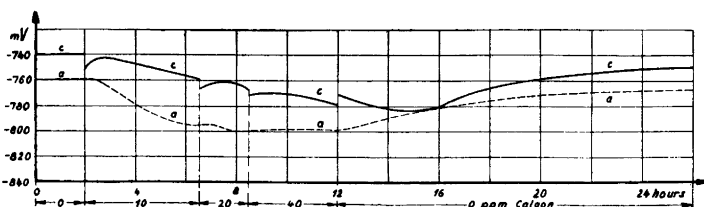


Fig. 3. The effect of various Calgon concentrations on the true potentials of the aerated (c) and the non-aerated (a) zinc-coated electrode, disconnected 8 hours before the start of the experiment. DA-cell type III, one day old. Rate of water flow 300 ml/min.

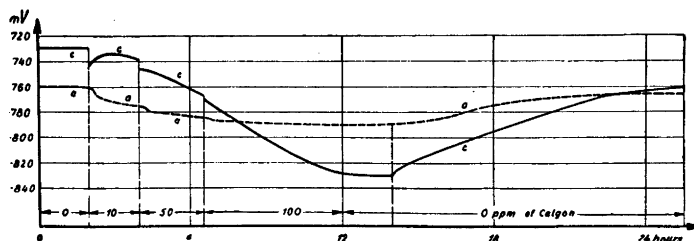


Fig. 4. The effect of various Calgon concentrations on the true potentials of the aerated (c) and the non-aerated (a) zinc electrode disconnected 8 hours before the start of the experiment. DA-cell type III, three days old. Rate of water flow 300 ml/min.

gradient between the cathodic and anodic surfaces which could be accounted for by the lack of the anodic secondary reaction consuming oxygen as in the case of the oxidation of ferro to ferri ions.

The quick decrease of the potential difference after disconnecting the electrodes (Fig. 2; C—D) indicates that the reactions going on at the electrodes during the passage of the current play an important role in establishing the potentials. The continuous renewal of the anodic zinc surface due to the dissolution of the anode could be the cause of the decrease of its potential owing to the diminishing of the chemo-adsorption of oxygen.

The potential-depressing effect of Calgon, both on the cathode and anode, could be explained on the basis of the film-forming property of Calgon and consequent decrease of the oxygen transport to the true metal surface. In the zinc cell the effect of Calgon on both electrodes has the same direction (Figs. 3 and 4) because we have not here the secondary reaction of the anodic oxidation as in the case of iron, where the interference of Calgon with this reaction causes the increase of the potential of the anode.

ZINC-IRON DA-CELLS

It is a rather common belief that zinc is always electronegative against iron in the natural water environments. This belief is based on the normal potential series of metals and on short experimental observations of iron-zinc couples. But pitting with overlying tubercles and rusting of galvanized iron pipes indicate the possible changes in potentials, which has been emphasized by Davis², Haase³ and others. Schikorr⁴ has been able to show the cathodic behaviour of zinc versus iron in hot tap water after some hours of measurement. Roters and Eisenstecken⁵ show such a change of the current direction in zinc-iron couples in cold staying tap water after about two months.

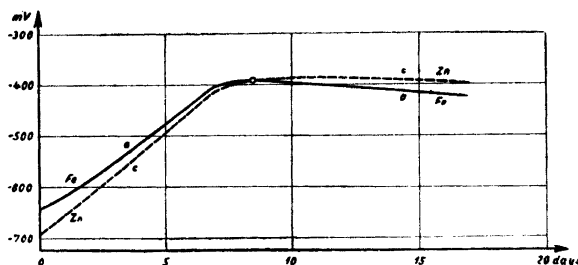


Fig. 5. Time-potential curves for the aerated (c) zinc electrode and the non-aerated (a) iron electrode of a DA-cell. Electrodes connected through a 1 000 ohm resistance. Iron electrode 25 days old (staying water); zinc electrode 15 days old (running aerated water). Rate of water flow 300 ml/min.

Gilbert ⁷, Hoxeng and Prutton ⁸ have also experimentally shown reversals of the zinc-iron potential in hot, respectively in cold water.

In our above mentioned experiments with iron and zinc DA-cells we have seen that the potentials of both metals can vary markedly, but we have not observed any overlapping of the zinc and iron time-potential curves. But as the measurement with zinc was a rather short one and the potentials still showed an increasing tendency (Figs. 1 and 2), we built a cell with an aerated zinc electrode and a non-aerated iron electrode. The diagram in Fig. 5 shows that after 8 ½ days the aerated zinc electrode, violently washed by running water, has become cathodic against the iron electrode in stagnant water. After 17 days the cell connected through a 1000 ohm resistance shows EMF equal to 30 mV. In the disconnected 18-day-old cell zinc shows a potential as

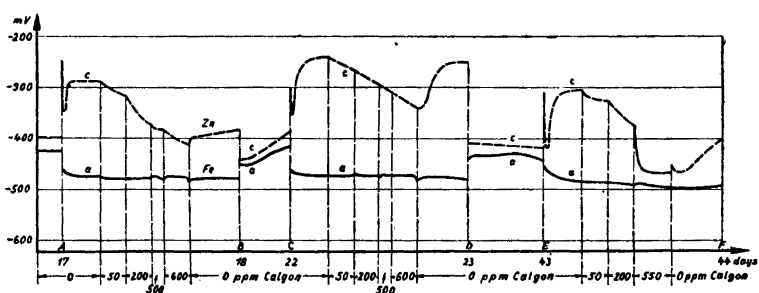


Fig. 6. The effect of various concentrations of Calgon on the potentials of the aerated (c) zinc electrode and the nonaerated (a) iron electrode of a 17 days old DA-cell. Electrodes connected through a 1 000 ohm resistance (O—A, B—C, D—E) or disconnected (A—B, C—D, E—F). Rate of water flow 300 ml/min.

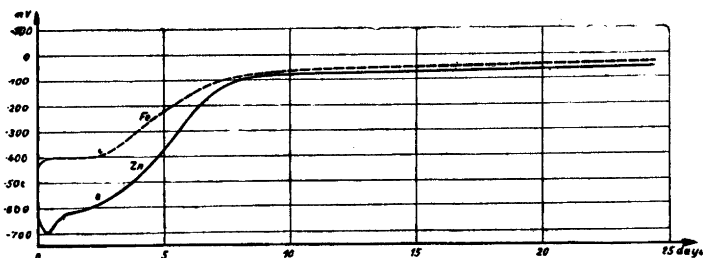


Fig. 7. Time-potential curves for the aerated (c) iron electrode and the non-aerated (a) zinc electrode of a DA-cell. Electrodes connected through a 1 000 ohm resistance. Rate of water flow 300 ml/min.

high as -300 mV and iron -490 mV *i. e.* the potential difference was 190 mV. After 23 days the potential difference of 230 mV was observed.

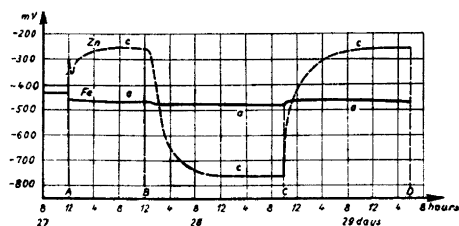
These facts seem to be the adequate explanation for the pitting and tuberculation in galvanized pipes where we have zinc-coated cathodic surfaces against the iron surface at the bottom of pits.

The addition of Calgon (Fig. 6) causes the marked decrease of the cathodic potential. But almost no changes are seen in the potential of the iron anode, which we may explain by the age of iron electrode ($18 + 25 = 43$ days) and a consequently large accumulation of rust in the anodic space that inhibits the diffusion of Calgon into the anodic space.

The cathodic behaviour of zinc against iron seems to be reversible, and after the discontinuation of the water flow across the zinc surface (B, Fig. 8) the potential of zinc falls to a value lower than the value of the potential of the iron electrode. The restoring of the former flow of water (C) brings the zinc potential to the former noble value.

For the sake of comparison we have measured the time-potential curves for the cells with the aerated iron cathode and the zinc anode. The potentials of the electrodes connected through a 1000 ohm resistance are shown on the diagram (Fig. 7). In the course of the first fortnight of the experiment the potentials increase markedly and the EMF decreases. Afterwards the poten-

Fig. 8. The effect of the rate of water flow on the potentials of an aerated (c) zinc electrode and a non-aerated (a) iron electrode of the 27 days old DA-cell. Electrodes connected through a 1 000 ohm resistance (O-A) or disconnected (A-D). Rate of water flow 300 ml/min (O-B, C-D) or 0 ml/min (B-C).



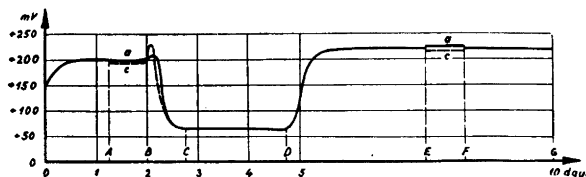


Fig. 9. Time-potential curves for the aerated (c) and the non-aerated (a) copper electrodes of a DA-cell. Electrodes connected through a 1 000 ohm resistance (O—A, C—E, F—G) or disconnected (A—C, E—F). Rate of water flow 300 ml/min (O—B, D—G) or 0 ml/min (B—D).

tials and EMF become rather stable. No exchange of the cathodic and anodic functions of the electrodes occurs and after 25 days the true potential difference of the disconnected electrodes is still very great (about 600 mV). After 40 days the true potentials are — 570 mV (zinc electrode) and — 160 mV (aerated iron electrode).

COPPER-COPPER DA-CELL

The time-potential curves of a DA-cell with copper electrodes are shown on the diagram (Fig. 9). When the electrodes had been connected through a 1000 ohm resistance, the potential difference was not detectable with the potentiometer used. The disconnected electrodes show a potential difference less than 5 mV with a higher potential of the non-aerated electrode. This phenomenon has been described and explained by Evans⁵.

The interruption of the water flow has a pronounced diminishing effect on the potentials of both electrodes. The reproducibility of the measurements was not very good, and the cell shows a high internal resistance which in our case renders the long automatic recording impossible.

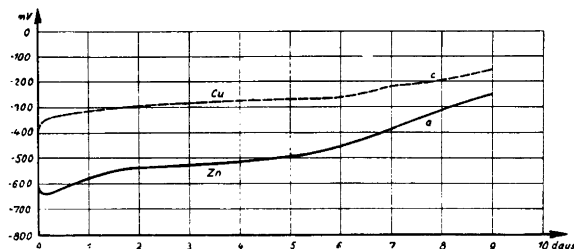


Fig. 10. Time-potential curves for the aerated (c) copper electrode and the non-aerated (a) zinc electrode of a DA-cell. Electrodes connected through a 1 000 ohm resistance. Rate of water flow 300 ml/min.

COPPER-ZINC DA-CELLS

The diagram in Fig. 10 shows the potentials of a DA-cell with a Cu-cathode and Zn-anode connected through a 1000 ohm resistance. The EMF of such a cell is rather high but shows a decreasing tendency. The increase of potentials is due to the ennoblement of the potential of zinc electrode.

SUMMARY

The behaviour of zinc in a DA-cell indicates that the corrosion of the zinc could also be due to the action of the differential aeration currents as in the case of iron. The range of obtained potential differences is smaller than with iron. The addition of Calgon depresses the potentials of both the cathode and anode due to the formation of adsorption layers which inhibit the access of oxygen to the metal surface. Calgon has a greater effect on the decrease of the potential of the cathodic, easier accessible surface and in this way depresses the potential difference or even changes it to negative values, thus eliminating the corrosion.

After some weeks zinc becomes cathodic against iron in the DA-cell where the zinc surface is exposed to an aerated water stream and the iron electrode placed in stagnant water. That explains the tuberculation and pitting in galvanized iron pipes in the same way as described in our previous paper for iron.

The ennoblement of the potential of zinc is reversible when the water flow decreases.

Some other aspects of the DA-cells with zinc, iron and copper electrodes are discussed.

LITERATURE

1. Mansa, J. L., and Szybalski, W. *Acta Chem. Scand.* **4** (1950) 1275.
2. Davis, E. J. *Power* **82** (1938) 831.
3. Haase, L. W. *Metalloberfläche* **1** (1947) 73.
4. Schikorr, G. *Trans. Elchem. Soc.* **76** (1939) 247.
5. Rotters, H., and Eisenstecken, F. *Archiv Eisenhüttenw.* **15** (1941) 59.
6. Evans, U. R. *Metallic corrosion, passivity and protection.* London (1946) p. 365.
7. Gilbert, P. T. *Sheet Metal Industries* **25** (1948) 2003.
8. Hoxeng, R. B., and Prutton, C. F. *Corrosion* **5** (1949) 330.

Received February 24, 1950.