Corrosion due to Tuberculation in Water Systems

I. The Effect of Calgon on the Potential of Iron Electrodes in Differential Aeration Cells with Running Tap Water

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It was the purpose of this work to show in what way Calgon interferes with the mechanism of corrosion due to tuberculation in water pipes. Primary experiments[1] showed a definite effect of minute concentrations of Calgon on the avoidance of rusting of an iron surface exposed to laminar flow of water. In the absence of Calgon we got rusting in the form of well pronounced patterns. When plates had been run with tap water containing increasing amounts of Calgon, the "lines" of rust gradually became less pronounced, and at a concentration of about 20 parts per million (ppm.), the lines did not appear at all.

So far, in our preliminary, short-term experiments, we had been able to show that only the Calgon addition simultaneous with the start of the experiment, completely inhibited the formation of the rust patterns. The addition of Calgon after the patterns had been formed did not remove them, and only high Calgon concentrations (over 100 ppm.) seemed to inhibit the further development of rust lines (streaks).

A surface of iron run with water containing Calgon remained bright for rather a long time, showing only some interference colours indicating the formation of a very thin protective layer.

All these facts together with indications in literature[2] show that the inhibitive effect of Calgon is due to the adsorption of this compound on the iron surface, and that Calgon belongs to the class of adsorption inhibitors[3].

But we were interested in the details of the inhibitive effect of Calgon, and especially in the effect of Calgon on the electrochemical potentials of electrodes in the differential aeration cell (DA-cell) with running tap water.

There exists a rather comprehensive literature[4] about measurements of the potentials of corroding metals and about the influence of inhibitors on the potential of electrodes in bimetallic cells. The measurement of the potentials of the corroding metals has mostly been made either in solutions with well defined, rather high concentrations of the respective metallic ions, or in strong acid, alcaline or salt solutions. In many cases in measurements of the potentials of iron rather little attention has been paid to the influence of oxygen on the potential. Some potential measurements have also been made in natural waters, but either at rather short intervals or without taking into account the division of the metallic surface into anodic and cathodic zones.

Beginning with the experiments of Chyżewski and Evans[5] many measurements have been made of the changes of potentials due to inhibitors. Much literature is quoted by Shih-Jen Ch'iao and Mann[6]. But as far as we know, no experiments have been made on the influence of the inhibitors on the potentials of the electrodes in a DA-cell. Herzog and Chaudron[7] have studied the influence of some inhibitors but only on the current generated by a DA-cell.

DA-cells have been studied mostly in the form first built by Evans[8] *. The form of DA-cell that naturally occurs (tubercles in water pipes — Fig. 1a) or its laboratory modifications (Fig. 1b) have as far as we know never been studied in laboratory until the appearance of the work of Olsen and Szybalski[9].

For this reason we thought that it would be of some interest to study the influence of the inhibitors on the potentials of the anode and cathode of the DA-cell of a shape normally met in tuberculation of water pipes. In this case the concentration of oxygen in the cathodic space will be constant, because the water is saturated with oxygen and the water flow is kept constant; the oxygen concentration on the anodic side will be automatically controlled by the corrosion process. The influence of the atmospheric oxygen is in this way eliminated. This arrangement makes it possible to test natural waters directly from the municipal supply. Also the pressure and temperature of the tested water might be controlled. In order to get well defined potential-time curves we used an automatically recording multipoint instrument, and the potentials of the electrodes of all the cells, simultaneously tested and run with water from a 30 ton storage tank, were measured against one calomel standard electrode. For the determination of the influence of Calgon we have registered simultaneously the potentials of at least four cells i. e. two with Calgon and two without Calgon, and the reproducibility of the parallel experiment was within

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* Dr. F.L. LaQue drove kindly our attention to two early papers of Adie[21] and Viard[22], describing the differential aeration effect.
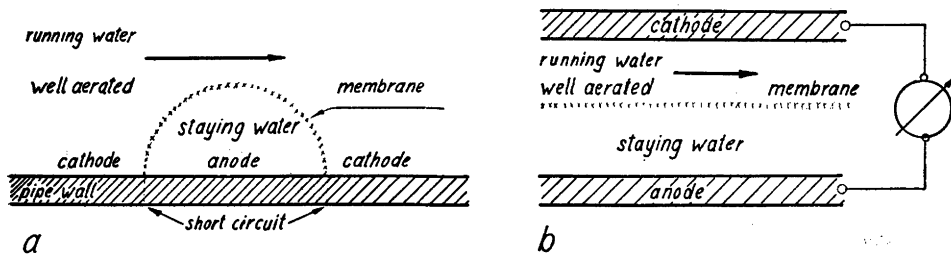
Fig. 1. Schematic comparison of the conditions (a) during pitting with tubercle formation
and (b) in laboratory model of DA-cell (after Olsen and Szybalski).

the limits of 1—5 mV. The equipment used allowed us to extend our measurements on a single cell to some months.

EXPERIMENTAL

Three types of DA-cells were tested: cell I with laminar water flow and cells II and III with turbulent water flow (Fig. 2). In all the cells we had the metal surface divided into two regions insulated from each other: anode and cathode. Between the anode and cathode we always had a filter-paper membrane (Schleicher Schuell No. 589—2) to protect the anode from direct access of the water stream. In cell I the membrane was attached with synthetic resin glue to the insulation i between the electrodes. In cells II and III filter paper was fixed between parts b and c. In this way the cathodic surface of
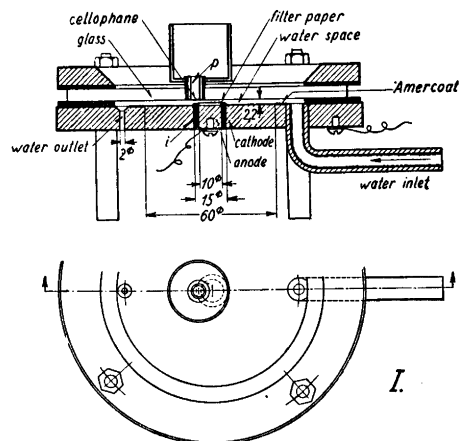

Fig. 2 I. DA-cells for experiments with
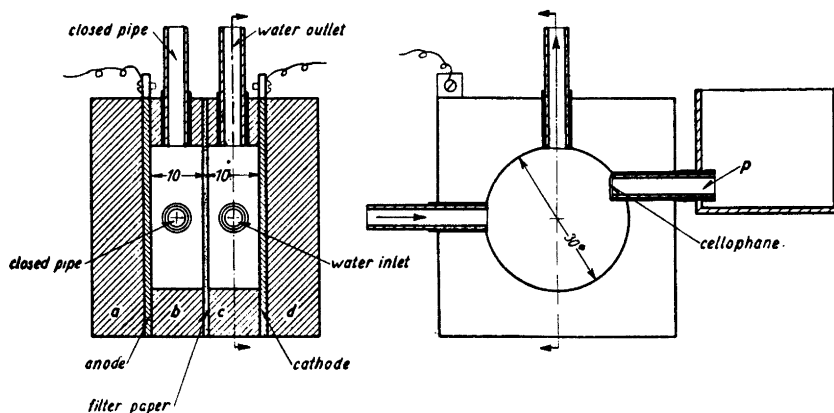running tap water. Cell type I.

Fig. 2 II. Cell type II.

the metal was always violently washed with aerated water; in the anodic space water was stagnant, and consequently we had a strongly reduced access of oxygen, which moreover was quickly used up for (i) the oxidation of ferrous ions, for (ii) the depolarization of the micro-cathodic regions of the anode (due to the micro-cell structure of the anodic surface) and for (iii) direct oxidation of metallic iron.

For cell I (with the dimensions in mm shown in Fig. 2) we worked with a water flow of 300 ml/min, which gave a laminar flow pattern over the main part of the metal surface (Reynolds number — Re = 100). The water flow was the same in cells II and III, but due to the design of the cells the flow pattern was turbulent, which could be directly observed. As electrode material we used S.M.-steel with approximately 0.15—0.18 % C.
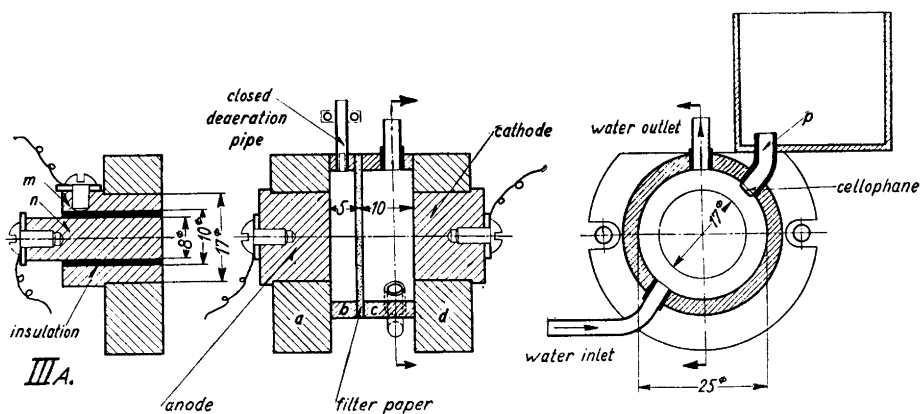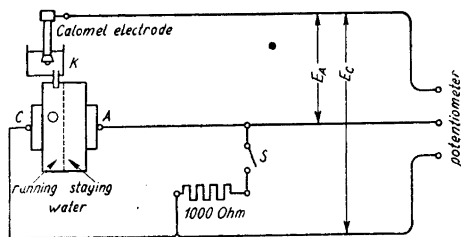

Fig. 2 III. Cells type III A and type III.

Fig. 3. The diagram of electric connections for automatic potential registration in a DA-cell.

In order to have a rather even water flow over the whole metal surface in cell I we worked only with the central part of the plate; the periphery was covered with a highly water-resistant coat of low electrical conductivity (Amercoat No. 23 — South Gate, Calif.). For the same reason we later changed from cell II to III, because, in cell II on the aerated side in the corners between "Etronax"-wall (c) and the metal plate, the water moved very slowly in comparison with the central part of the cathodic surface. In cell III the surface of the cathode did not reach these dead corners. Another difference between cell II and III was that the central part (b, c) of cell III consisted of a plexiglass tube permitting the experimenter to observe changes in the cell during the experiment. The distance between the electrodes was reduced in cell III in order to get lower internal resistance, and the symmetry of the cell shape was sacrified. In all the cells the metal surfaces (excluding the anodic and cathodic surfaces) which might get in contact with water and could have some influence on the measured potentials were covered with Amercoat. Amercoat was also used for the tightening of cells II and III. The electrolytic connection between running water and the standard calomel electrode (saturated KCl) was made by a saturated KCl solution; the water and the KCl-solution were separated from each other by a thick cellophane membrane. Air from the glass pipe p had been sucked out with a thin plastic pipe so as not to damage the membrane. The insulation i (Fig. 2 I) and the parts a, b, c, d (Fig. 2 II) a, d (Fig. 2 III) consisted of linen-bakelite laminate "Etronax".

The first experiments were made by continuous measurement of the current between the cathode and anode and, only occasionally, by measurement of the potential of the electrodes against a standard calomel half cell. But it was soon found that it would be necessary and more convenient to register the potentials automatically. For this purpose we used the "Multipoint Potentiometric Recorder — SPEEDOMAX" of Leeds and Northrup Cat. No. 60358 with the scale range extended to 1000 mV and registration frequency 6 times per minute. The diagram of connections is shown in Fig. 3. We were able to measure the potentials of the anode and cathode either when they were con-
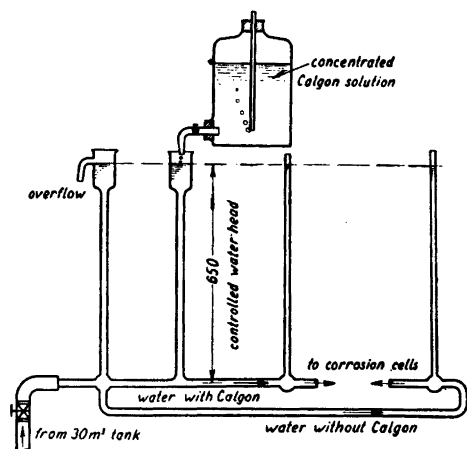
Fig. 4. The diagram of water-connection arrangement for experiments with DA-cells.

nected through a 1 000 ohm resistance or when disconnected. If many cells were used, connections between the calomel electrode and the respective cell cups (K — Fig. 3) were made with saturated KCl-agar bridges, rather thick and as short as possible, because the resistance in the potentiometric circuit must not exceed 10 000 ohms. This feature of the potentiometer used was rather inconvenient for our work. The diagram of the arrangement of the water-connection and the feeding of Calgon is given in Fig. 4.

The used tap-water shows the following average analysis:

Saturation index (pH−pH$_s$)	−0.1−+ 0.1	pH	7.5	SiO$_2$	15−17 ppm
Total hardness	18.3−18.8° H	Cl⁻	81−93 ppm	Fe⁺⁺	0.01−0.03 ppm
Permanent hardness	1.2− 2.0° H	SO$_4^{--}$	71−72 ppm		
Dissolved solids	560−571 ppm				
Water was air-saturated at atmospheric pressure (8° C).					

EXPERIMENTAL RESULTS

1. The measurement of the corrosion current and internal resistance of the DA-cell

Measurement was made with cell I. Only in this experiment we used "The Electroflo Recording Instrument" No. 10306 and the scheme of connections is shown in Fig. 5. By the reading of v_1 and v_2 (switch s in position 1 or 2, respectively) we could calculate the internal resistance of the cell:

Fig. 5. The diagram of electric connections for automatic measurement of the corrosion current and internal DC-resistance in a DA-cell.
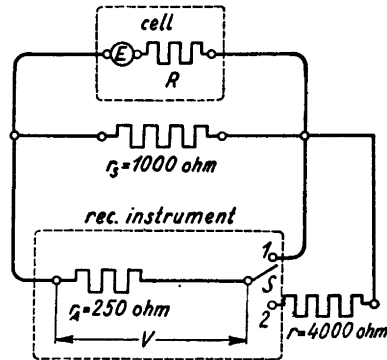
$$R = \frac{v_2 r - (v_1 - v_2)\, r_A}{(v_1 - v_2)\, (\dfrac{r_A}{r_S} + 1) - v_2 \dfrac{r}{r_S}}.$$

All the time the cathode and anode were connected through a resistance of 1 000 ohms. The calculated internal D. C. resistance of the cell was at the beginning of the experiments of the order of 1 000 ohms. Curves R and R_c (Fig. 6) show the changes with the time of the internal resistance of the cell. The curves i and i_c show the corrosion current. We see that if the Calgon is added just from the beginning of the experiment, when the iron surface is still uniformly bright, it has a very strong influence on the increase of the internal resistance of the cell and on the decrease of the corrosion current. It is obvious that the decrease of the corrosion current cannot be explained only on the basis of the increase of the resistance. The current not only decreases but also changes its direction. That means that Calgon must change the potentials
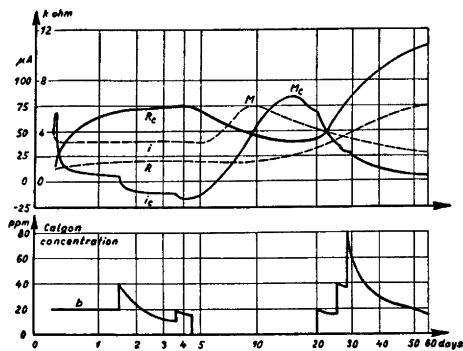

Fig. 6. Time-corrosion current (i, i_c), time-internal DC-resistance (R, R_c) and time-Calgon concentration (b) curves for DA-cells type I with $(i_c\ R_c)$ and without (i, R) addition of Calgon. Rate of water flow 300 ml/min.

of the electrodes. The peaks M and M_c also indicate some changes in potentials. For this reason, in further experiments we have measured the potentials, trying on this basis to explain the mechanism of the action of Calgon.

Curve i_c in its beginning shows very characteristic sudden falls at the points of the increase of the Calgon addition. Curve R_c shows continuous changes. After the discontinuation of the Calgon addition on the fifth day we see that the inhibitive effect of Calgon is fully reversible. The next addition of Calgon for a 20 days old cell shows the same changes as in the beginning but much slower and smaller (the apparently great slope of i_c and R_c curves is due only to the logarithmic time scale). The reversal of the corrosion current was unobtainable in the case of old cells. Curves R and i show that also without the addition of Calgon we get an increase of the resistance and decrease of the corrosion current in the cell probably due to the formation of some compact layers on the cathode, as has been shown by capacity and A. C. and D. C. resistance measurement (Olsen and Szybalski [9]).

After finishing the experiment we opened the cell, removed the filter-paper membrane and examined the anodic and cathodic surfaces. The anodic space under the membrane was filled with rust which could easily be washed off with a water stream; then appeared the iron surface evenly corroded and of a dull metallic lustre. The cathodic surface outside the anode was covered almost completely with a thin, strongly adherent layer, but in some places elevated rust paths appeared, which it was possible to remove by washing and gently brushing. They then showed an underlying iron surface just as under the filter-paper membrane. These rustpaths appeared in places where there was a slower stream of water and consequently smaller aeration than in the neighbouring areas. This tubercle formation on the cathodic surface certainly interfered with the reproducibility of our experiments, but with this shape of the cell and with laminar water flow it was impracticable to get a quite even water flow over the whole surface and consequently an even aeration. For this reason, and because when using a slow stream of water we have had rather small measured potential differences between the anode and cathode, we decided to change over to cells of another shape using turbulent water flow.

2. The measurement of potentials

In the measurement of the potentials of the electrodes we had two alternatives: 1) The anode and cathode short-circuited through a low resistance; the situation would then be just the same as in a natural "tubercle", but it would be impossible independently to measure true potentials of the cathode and anode. 2) The anode and cathode disconnected; we were then able to measure
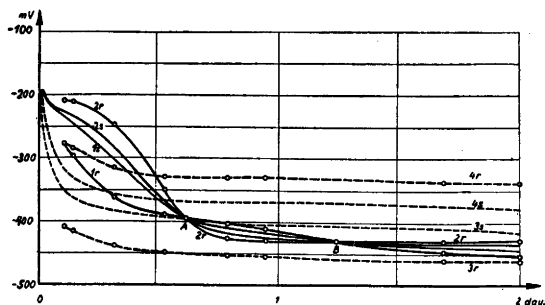
Fig. 7. Time-potential curves for the aerated (2, 4) and non-aerated (1, 3) electrodes of DA-cells type I with (1, 2) and without (3, 4) addition of Calgon. Electrodes connected through a 1 000 ohm resistance (s) or disconnected (r). Rate of water flow 300 ml/min.

the true potentials independently, but the conditions in such a cell are different from those in a real tubercle. We chosed a combination of both. During most of the time of the experiment the electrodes were connected through a 1 000 ohm resistance and only from time to time the circuit was opened so that the true potentials against the calomel electrode were registered.

Diagram (Fig. 7) shows the potential-time curves of two cells of type I with a water flow of 300 ml/min. The electrodes of both cells were connected through a 1 000 ohm resistance (switch S closed — Fig. 3). Curves 3s and 4s show that the potential of iron in contact with water is falling from about — 200 mV to — 370 mV for an aerated and to — 405 mV for an unaerated electrode (normal hydrogen-electrode scale) in the course of 24 hours. The decrease after that time is much slower. The potential difference between the anode and cathode is rather pronounced from the first hours of experiment. From curves 1s, 2s (water with 10 ppm. Calgon-product of Albright and Wilson, Birmingham) it is seen that the potential first falls slower, then quicker and finally reaches a level more negative than curves 3s, 4s. Moreover in the latter half of the first day the potential of the aerated electrode was more negative than of the unaerated one. That is in good agreement with the reversal of the corrosion current on the diagram in Fig. 6. In experiments with higher Calgon concentrations it was possible to get reversed and still greater potential differences and keep them for many days.

Curves 1r, 2r, 3r, 4r show the real potentials of the electrodes which were registered by means of a potentiometer when opening the switch S (Fig. 3) for a short period of time at the points marked on the diagram (Fig. 7). The features shown by curves 1s, 2s, 3s, 4s are here still more pronounced.
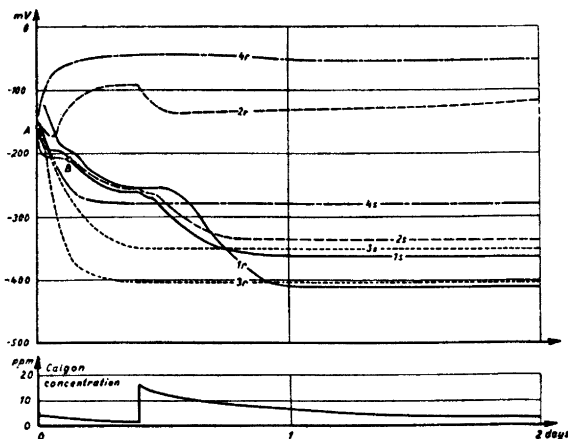
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Fig. 8. Time-potential and time-Calgon concentration curves for DA-cells type III A with (1, 2) and without (3, 4) addition of of Calgon. Aerated (2, 4) and unaerated (1, 3) electrodes connected through a 1 000 ohm resistance (s) or dis-connected (r). Rate of water flow 300 ml/min.

The diagram in Fig. 8 shows the continuous time-potential curves for two cells of type III with double electrodes (fig. 2, III A). Electrodes m were connected through a 1 000 ohm resistance (curves 1s and 2s with Calgon and 3s and 4s without). Internal electrodes n were not connected so that they show their true potentials (curves 1r, 2r with Calgon; 3r, 4r without). It can be seen that a cell of type III shows much greater potential difference and a more noble cathode due to the turbulent flow of water and consequently to
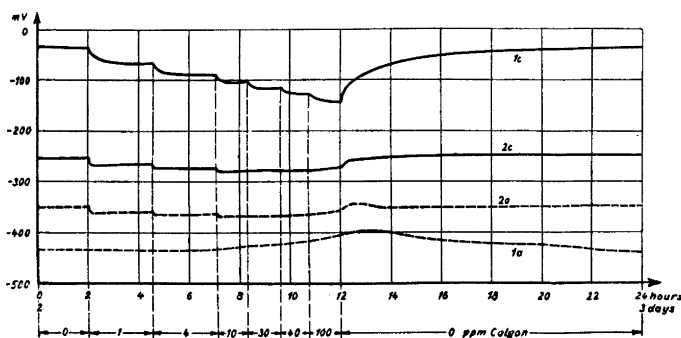

Fig. 9. The effect of various Calgon concentrations on the potentials of an aerated (c) and non-aerated (a) electrode of a two-day-old DA-cell. Electrodes connected through a 1 000 ohm resistance (2) or disconnected (1). Rate of water flow 300 ml/min.
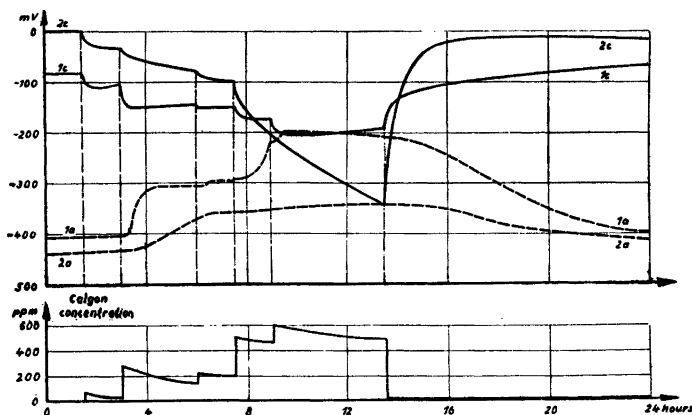
Fig. 10. The effect of various Calgon concentrations on the true potentials of an aerated (c) and a non-aerated (a) electrode in a one-day-(1) and a six-day-old (2) DA-cell. The electrodes disconnected 8 hours before each start of the addition of Calgon. Rate of water flow 300 ml/min.

the greater aeration of the cathodic surface. At this low Calgon concentration it was possible to get the potential difference reversed only during the first hour of the experiment. The potential difference for a cell run with Calgon-treated water is smaller than for a cell without Calgon. The increase of the addition of Calgon causes a very distinct decrease of the cathode potential (2r). A decrease of the addition of Calgon then slowly restores the more noble potential. The influence on the anode is difficult to discuss because the potentials of the electrodes have not yet reached a steady state.

The influence of Calgon on two-day-old cells, where the cathode and anode have reached some rather stable balanced potentials, is shown on the diagram Fig. 9. Curves 2a and 2c show the potentials of the anode and cathode connected through a 1 000 ohm resistance of a cell of type III. The upper curves 1a and 1c show the true potentials of a parallel cell where the electrodes have been disconnected 8 hours before the start of the addition of Calgon. Every increase of the addition of Calgon gives a decrease of the cathode potential, but low concentrations of Calgon show a relatively greater effect. The effect on the anode is slower and changes the potential in the noble direction. That is the reason why at concentrations higher than 40 p.p.m. the curves 2a and 2c cease to move in the negative direction but change to the noble one.

The diagram in Fig. 10 shows the influence of the age of the cell on the potential-time curves. On both electrodes the calgon-effected changes are slower with an increasing age of the cell. On the anode, moreover, the changes are smaller, but not on the cathode.
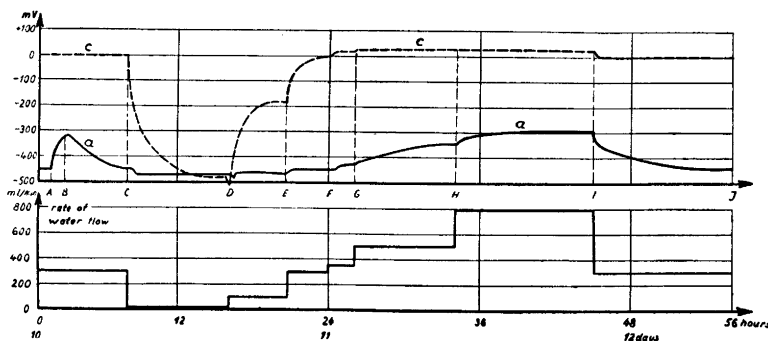
Fig. 11. The effect of the rate of water flow on the potentials of an aerated (dotted line) and a non-aerated (full line) electrode in a six-day-old cell. Explanations in text.

The diagram in Fig. 11 shows the influence of changes of water-flow velocity. The flow of water through the anodic space (the deaeration pipe under the filter-paper membrane (Fig. 2, III) is opened, rate of water flow through it = 2 ml/min.) increases the potential of the anode (A—B); the interruption of this percolation (the deaeration pipe closed) restores the original state but more slowly (B—C). — The interruption of the whole water flow through the cell causes the potentials of the electrodes to be equalized (C—D). The return to the previous velocity of the water flow ennobles the potential of the cathode to the former value (D—E—F). The increase of the water flow first has a great effect on the increase of the cathodic potential and almost none on the anodic potential (D—E—F). The further increase of the water velocity brings the cathodic potential to a constant value and only causes a further increase of the anodic potential (F—G—H). A reduction of the water flow to 300 ml/min. restores the first observed potentials (I—J).

CONCLUSIONS

The most striking feature observed in all experiments was the great range of different potentials shown by iron. The ennoblement of the iron potential is referred to by the term p a s s i v a t i o n. The nature of passivity is still an object of controversy in the literature (*e. g.* Evans [3], Uhlig [10]), but for our purpose we could regard it as a result of some factor which impedes the passage of metal ions from the surface of the crystal lattice to the water solution. Oxygen adsorbed or chemically bound in a reversible manner on the metal surface stabilizes its lattice and diminishes the tendency of the metal to pass into the solution, which means that the potential of the metal becomes more
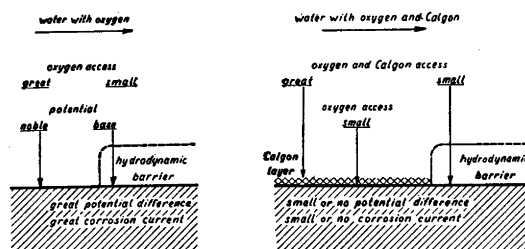
Fig. 12. Diagram of the influence of Calgon on the corrosion due to the action of DA-cells.

noble. The passivity and ennoblement of the iron potential * depend on the
saturation of the metal surface with oxygen, but because the adsorbtion pro-
cess is reversible, and because the oxygen is used all the time for the oxidation
of hydrogen and ferro-ions, we must have a constant supply of oxygen to the
metal surface. The covering of the metal surface with some porous layer
impedes oxygen diffusion to the true iron surface. The saturation of the metal
surface with oxygen decreases and consequently the potential is shifted in the
base direction. This porous layer could be of various kinds. It could be some
deposits of rust or of a microbiological character or any other hydrodynamic
barrier which diminishes the water velocity in some area and consequently
the oxygen transport towards iron surface. But also the adsorbtion layer of
large molecules of Calgon or its complexes with other substances found in
natural waters, seems to have the same depressing effect on the potential of
iron due to the hindrance of oxygen access. But there is some fundamental
difference between the action of Calgon-layers and other hydrodynamic bar-
riers. The situation is shown on the following diagram (Fig. 12). In cathodic
places where water carrying oxygen and Calgon has an easy access to the iron
surface, the Calgon adsorbtion layers are rapidly well developed and conse-
quently do not allow the oxygen diffusion to the true metal surface. In this
way in stead of getting an easier oxygen access to the true iron surface in
places of greater water flow the oxygen access becomes more difficult and the
electro-chemical potential decreases in these places. At a small concentration
of Calgon its transport to surfaces covered by hydrodynamic barriers will be

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* The potential difference between two identical electrodes immersed, the one in a staying
and the other in a running "oxygen-free" water solution, has been called Motor-Electric Poten-
tial [11]. But there are various opinions in the literature as to the nature of this effect [12]. Many
authorities believe it could be referred to the action of the omnipresent oxygen. Apart from the
nature of the motor-electric potential, its reported values are negligible in comparison with the
fluctuation of potential observed in our case and caused by the differential aeration effect.

very small and no great changes are supposed to occur there. Consequently on a fresh iron surface, after the addition of Calgon, there will be no great changes in the potential of the anodic areas (we leave out of account the secondary influence of Calgon due to the interference of Calgon with the reaction of the oxygen depletion) and the higher cathodic potential will decrease with a resulting decrease of potential difference and corrosion current.

This smaller corrosion current causes the decrease of the production of ferro-ions at the anode, which allows a greater oxygen diffusion to the anodic surface with a resulting decrease of potential difference and corrosion current. That induces a further reduction of the production of ferro-ions on the anode, etc.

This picture of the influence of Calgon is very clear in the case of rather good differentiation of the iron surface into regions with an exposed clean metal surface and regions covered by some hydrodynamic barriers. The covering of the metal surface with some protective layers or a rather strong development of tubercles change the speed and effectivity of the action of Calgon.

The reported peptization power of Calgon [13] causing the solution and removal of the tubercles must also be taken into consideration, because it means the removal of the well developed hydrodynamic barriers and consequent equalization of the aeration and the potentials of the metal surface.

We can extend the explanation of the cathodic Calgon action in order to explain the tuberculation faculty of natural waters. We can be sure that the aerated water running over an iron surface will always in the beginning cause the formation of differential aeration cells, because the velocity of the water will change from point to point owing to the hydrodynamic properties of the surface. In this way in the places where we have a higher rate of water flow we shall have a better oxygen access and a more noble potential. Non-corrosive waters (Fig. 13b) are able to form quickly some impervious layers in the area where the water velocity and consequently the aeration are greater, which diminishes the oxygen access and turns the potential in the base direction in the same places. In places of a more rapid water exchange the non-corrosive water must show the ability of a so strong protective layer formation that the oxygen access to the true metal surface will be more difficult than in places with lower water flow. That will cause the equalisation or even reversal of the difference of potentials between more and less washed areas, and consequently there will be no tuberculation. This cathodic formation of a protective layer must be quick, before, owing to the primary differential aeration effect, we get well developed rust tubercles in the anodic areas with a consequent very great decrease of potential in comparison with the rather
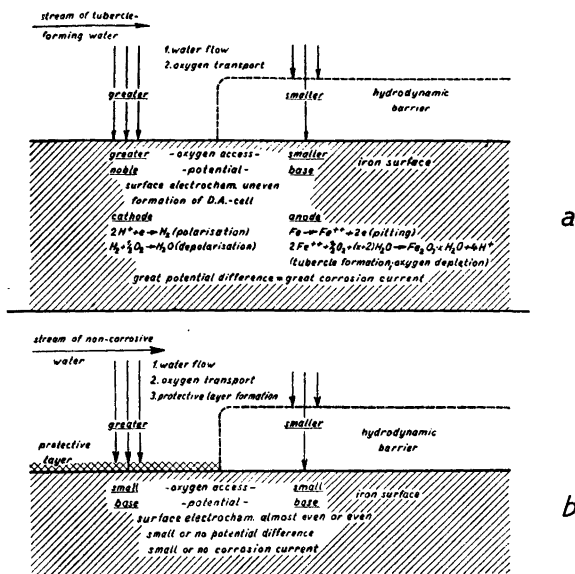
Fig. 13. Diagram of the influence of tubercle-forming (a) and non-corrosive (b) waters on the corrosion due to the action of DA-cells.

small primary potential differences due to the irregularities of the metal surface.

The tubercle-forming water (Fig. 13a) has no ability to form quickly some protective layers in the places of primary better oxygen access. That means that in every anodic area of the primary DA-cells due to the uneven water flow, we get, in a border case, the formation of tubercles. This case is not so very dangerous, because the ratio of the cathodic to the anodic areas is then rather high and because there is a possibility that anodic rust deposits, always extending beyond the anodic surfaces, will all join together, causing an even, small oxygen access to the whole surface. More dangerous is the case when the water has a limited ability to form protective layers. In this case only a few primarily stronger DA-cells will develop tubercles on the anodic surfaces, but because of the high ratio of the cathodic to the anodic surface the pitting might be rather serious.

Biological deposits can be especially active in causing tuberculation either by interference with the cathodic formation of the protective layers or by very quick establishment of highly anaerobic conditions in primarily anodic areas with a so rapid decrease of the potential that the slower cathodic decrease due to the formation of a protective layer cannot equalize the potentials and stop

the tubercle formation. In the literature we very often see that together with tuberculation a growth of iron bacteria has been found [9, 14, 15].

The non-corrosive water must show not only the ability to form protective layers, but this ability must also be 1) quick and energetic 2) differential — i. e. stronger where we have a higher rate of water flow and primary oxygen access, and weaker in the other places.

The nature of the protective layers built by natural waters and acting in the same way as Calgon will not be discussed here.

On this theoretical basis we can now discuss some aspects of the experiments described above.

The decrease of the cathodic potential caused by the increase of the Calgon concentration can be seen in Figs. 9 and 10 curves 1c and 2c. We see that small additions of Calgon to a 1-day-old cell give more rapid changes, which can be explained by an easier Calgon access to the fresh iron surface. A large and a long-term addition of Calgon shows a greater effect on the older cell. It seems that the joint effect of the cathodic covering of the surface by Calgon and by some natural protective layers gives a better protection against the oxygen access, but a somewhat longer time is necessary for the development of such layers.

At the anode a higher Calgon concentration has an influence on the potential opposite to the influence on the cathode. That is more pronounced in young than in old cells, because in old cells the diffusion of Calgon through the membrane toward the anodic surface is strongly impeded by the development of rust in the whole anodic space. This ennoblement of the anode potential by the addition of Calgon we may try to explain in two ways:

1) Calgon has the same effect on the potential as oxygen 2) Calgon interfers with the process of consuming the oxygen for the anodic oxidation processes. Explanation 1) is not very probable, because of the quite different Calgon action on the cathode. Explanation 2) sounds reasonable because if the consumption of oxygen in the anodic space slows down or stops, then the difference in the oxygen concentrations in the anodic and the cathodic space will be slowly equalized with a consequent increase of the anodic potential. The oxygen diffusing to the anodic space is mostly used for (i) oxidation of ferro to ferri ions, (ii) oxidation of hydrogen on the cathodic surfaces of micro-corrosion cells due to the uneven structure of the anodic metal surface and (iii) direct oxidation of metallic iron. We have not investigated if the auto-oxidation of ferro ions is retarded by the presence of Calgon. Nor can we say if Calgon interferes with the two other reactions.

The curve i_c on the diagram in Fig. 6 shows the corrosion current when Calgon is added. The decrease of the current is the result of the decrease of

the potential difference and the increase of the internal resistance of the cell due to the formation of the Calgon layer on the metal surface (curve R_c). At the outset of the experiment it was possible to get a reversal of the current also in the case of a low Calgon concentration, because the highly anaerobic conditions in the anodic space have not yet been established. It is obvious that this reversal of the current is due to the reversal of potentials, which could be seen in Fig. 7 and 8 between points A and B. If the hydrodynamic barrier between the anodic and cathodic surfaces is less developed, and we have a smaller water stream (cell I, Fig. 2), then it is easier to bring about the reversal of potentials by a smaller addition of Calgon than in the better developed DA-cell (cell III, Fig. 3).

Diagram in Fig. 11 shows the great influence of the changes of the water flow (aeration) on the potential of a DA-cell. We see that the ennoblement of the iron potential due to the oxygen content of water is fully reversible. After the interruption of the water flow, when oxygen will be used up in some oxidation processes, we get almost equally base potentials of both electrodes (C—D). First the increase (D—E—F) and afterwards the decrease (F—G—H—I) of the potential difference by the increase of water flow are in good agreement with the phenomenon often reported in the literature of an increase of the corrosion rate and tuberculation with increasing rates of flow to some critical value, after which the corrosion decreases (for inst. Hayn and Bauer[16], Friend[17], Pallo[18] — the apparently different results of Speller and Kendall[19] are discussed by Russell, Chapell and White[20]).

SUMMARY

The influence of Calgon on the potentials of the electrodes in a DA-cell with running tap water has been studied. Calgon decreases the potential of the cathode by the formation of an adsorbtion layer on its surface, which inhibits the oxygen access to the iron surface with a consequent decrease of its passivating action. The potential of the anode rises because Calgon interferes with the anodic depletion of oxygen. Both these effects cause the decrease of the potential difference and corrosion current. The decrease of the corrosion current is also caused by the increase of the internal resistance of the cell due to the formation of protective layers of low electrical conductivity. The peptization power of Calgon must also be taken into consideration.

The attempt at a general theory of tubercle-forming and non-corrosive waters is based on the property of non corrosive waters of the d i f f e r e n-t i a l formation of protective layers in the areas of greater water flow, which decreases the oxygen access in these primary cathodic zones, equalizes the

potentials and causes the corrosion and tuberculation to cease. Some general aspects of the DA-cell are discussed and the phenomenon of critical corrosion rate with a successive increase of water flow is explained.

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