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The decomposition voltage of aluminium reduction cells. The influence of the alumina content in the bath

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The decomposition voltage on 75 kA aluminium reduction cells with Søderberg anodes was measured by extrapolation of current-voltage curves and by use of an aluminium reference electrode. Both methods yielded results in the range 1·50 V–1·85 V, although higher and lower values occasionally occurred. The anode-reference voltage as well as the cell voltage showed a marked increase when the alumina content in the bath decreased below 2 wt%, and the anode effect was approached. This behaviour is in good agreement with theoretical curves based on laboratory data on anodic overvoltage and electrical conductivity.

Introduction

The decomposition voltage (E_D) in aluminium reduction cells depends on several process variables, among which the influence of alumina is very much in evidence, due to the cyclic changes in alumina concentration during cell operation. The E_D can be defined as the difference between the cell voltage U and the ohmic voltage drop through the cell

$$E_D = U - RI \tag{1}$$

encompassing the reversible potential E_{rev} and the anodic (η_{an}) and cathodic (η_{cat}) overvoltages,

$$E_D = E_{rev} + \eta_{an} + \eta_{cat}. \tag{2}$$

For the cell reaction

$$Al_2O_3 + 3/2\ C = 2\ Al + 3/2\ CO_2. \tag{3}$$

the E_{rev} at 980° is 1·18 V, as calculated from thermodynamic data [1] for unit activities of all components. The calculated values have also been confirmed experimentally [2].

The activity coefficient of alumina in cryolite melts is not known. As a rough approximation, it can be taken as the ratio between the actual concentration of alumina and the saturation concentration. In that case, the Nernst equation applied on reaction (3) yields

$$dE_{rev}/d \log (\%\ Al_2O_3) = -\frac{2{\cdot}3\,RT}{6F} = -0{\cdot}06\,V. \tag{4}$$

Laboratory experiments have shown [2] that the anodic overvoltage is of the order of 0·3–0·5 V, but this depends on the alumina content as given by the following relationship

$$d \log i^{\circ}/d \log (\%\ Al_2O_3) = 0{\cdot}56 \tag{5}$$

where i° is the exchange current. The overvoltage on carbon anodes follows Tafel's law, $\eta = a + b \log i$, with an average slope of $b = 0{\cdot}25$, so that

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$$d\eta/d\log(\%Al_2O_3) = -0{\cdot}56 \times 0{\cdot}25 = -0{\cdot}14. \qquad (6)$$

The cathodic overvoltage is lower than the anodic, and it appears to be independent of the alumina content [3]. The variation in decomposition potential can then be evaluated as a function of the alumina content by adding equations (4) and (6). This is shown in Fig. 1, Curve I for the case of an anodic overvoltage of 0·4 V at 10 wt% Al_2O_3 in the melt.

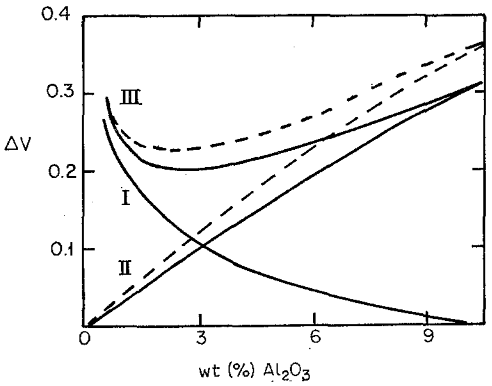

Fig. 1. Calculated variations in decomposition voltage (I), ohmic voltage drop (II) and cell voltage (III) by changing the alumina content in the bath. The total ohmic voltage drop in the bath equals 1·5 V (full lines); the current is increased by 20% (dotted lines).

In equation (1) the resistance R represents the total ohmic resistance of the cell. Under given conditions only the resistance of the bath needs to be considered as a variable. At constant temperature and fluoride composition, the specific conductivity of the melt decreases with increasing alumina content, showing an almost linear relationship at low alumina contents [4, 5]. The variation in the ohmic voltage drop through the bath is given in Fig. 1, Curve II, based on a RI value of 1·5 V in the pure fluoride melt.

When all other variables are kept constant, the dependence of the cell voltage on the alumina content is obtained by adding curves I and II. The resulting curve III predicts a fairly constant cell voltage in the normal operating range from 4 to 2 wt% Al_2O_3, and a rapid rise at lower alumina contents, as the anode effect is approached. A change in operating conditions will also change the shape of the curve to some extent. An increase in current of e.g. 20% will not affect the shape of I appreciably, while II and consequently III are shifted as indicated by the dotted lines. An increase in the anode–cathode spacing will have the same effect.

These curves are based on laboratory data, and on the assumption made on the activity of alumina, so their application on industrial cells may require some modification. Although the general shape seems to be correct, it appears that the voltage rise prior to anode effect in some cases tends to begin at an alumina content somewhat higher than indicated by III. Curves similar to those shown in Fig. 1 have also been presented previously [6–8].

In computer control of aluminium cell operation the variations in cell voltage can be used as a guideline for adjustment of interpolar distance and alumina feeding. Since the cell voltage is the sum of two variables, as shown above, an independent determination of one of them, e.g., the E_D, is desirable. Determination of E_D in industrial cells is associated with considerable difficulties, however. The methods available have been discussed by Arkadev [9] and Ginsberg and Wilkening [10]. In short they are based on (a) the current-voltage relationship [I-V], either (a_1) by extrapolation to zero current or (a_2) by some compensation technique [11, 12]; (b) a reference electrode; and (c) current interruption. The principal shortcomings of these methods are; in the case of (a) that overvoltage is not a linear function of current and that the ohmic resistance may not be constant; in the case of (b) that the resistance term included is difficult to assess, and in the case of (c) that the inductive surge does not permit measurements immediately after the current is interrupted.

In the present work methods (a_1) and (b) were used, i.e., extrapolation of I-V curves and application of a reference electrode. The potential decay at zero current was studied. The investigations were carried out on 75 kA vertical pin Söderberg cells. The temperature of the bath ranged from 960 to 985°C.

Current-voltage curves

The I-V curves were recorded by lowering the current stepwise at 15–30 second intervals. A data logger was used in order to obtain accurate data simultaneously for several cells in the potline. Stable voltage readings were usually achieved in less than one second after the current was changed. When the current was raised again without delay, the descending and ascending curves coincided. If, on the other hand, the current remained disconnected for as long as ten minutes, the ascending curve acquired a rather irregular shape showing higher values, but this was probably due to excessive cooling of the cells.

A normal *I-V* curve is shown in Fig. 2, Curve I. The curves were fairly linear down to 25 kA. The classical method of extrapolation to zero current to determine the so-called extrapolated E_D, in the following denoted $E_{D\,ext}$, yielded values in the range 1·5–1·85 V, the majority falling between 1·60 and 1·75 V. There was a trend towards decreasing $E_{D\,ext}$ by increasing alumina content. A slight tendency to a hump in the *I-V* curves in the range around 20 kA was observed on most curves. In a few cases, this hump was very pronounced as shown by Curve II. Such anomalous curves usually gave abnormally high values of $E_{D\,ext}$.

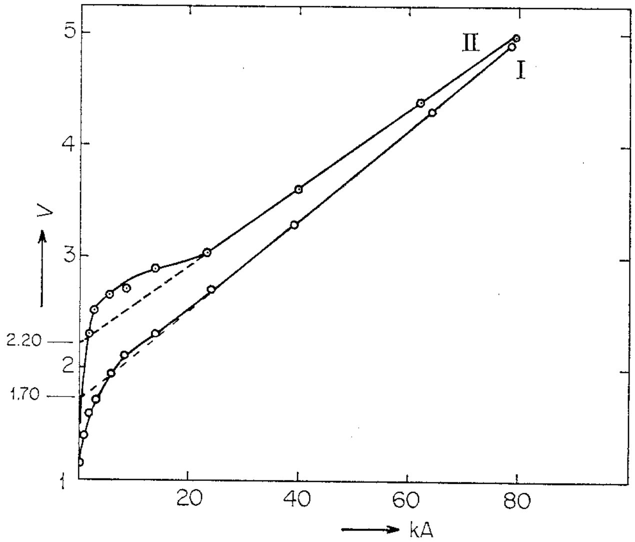

Fig. 2. Current-voltage curves. I, normal shape; II, abnormal curve.

Anode potential

The approach of an anode effect (AE) is normally signalled by a rise in cell voltage. Provided that alumina is not fed to the cell, the voltage rise will continue for a period of 15 minutes to two hours, till the AE suddenly occurs. A typical voltage-time curve is shown in Fig. 3, Curve I. Occasionally deviations from this normal pattern were observed. Curve III shows a case where the AE occurred without any preceding voltage rise. This behaviour seems to be typical for unexpected AE's occurring at high alumina contents, e.g. at 4% Al_2O_3, compared to the normal range of 0·5 to 2% Al_2O_3. Another type of abnormal

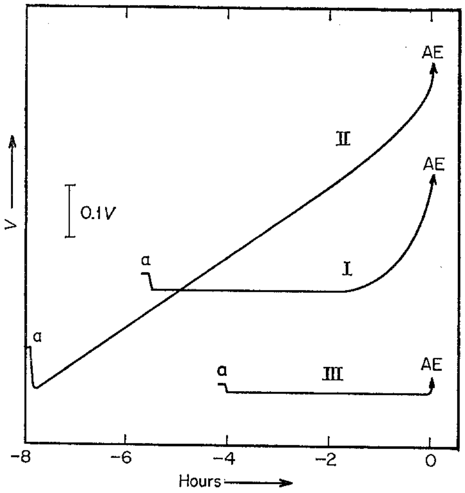

Fig. 3. Cell voltage prior to anode effect (AE). I, normal curve; II, III abnormal curves. Alumina feeding at a.

behaviour is shown by Curve II, exhibiting a remarkably steady voltage increase over a period of several hours.

In tracing the curves, oscillations and short-term erratic fluctuations in voltage were smoothed out. Likewise, fluctuations due to variation in the current were corrected for. The rapid voltage oscillations had an amplitude of around 0·03 V, increasing to 0·05–0·08 V as the anode effect was approached. When alumina was fed to the cells, the voltage usually decreased slightly, as indicated in Fig. 3. The magnitude and duration of this drop seemed to follow a rather complicated pattern. To avoid such variations, all curves shown in the following were recorded in periods when no alumina feedings were made.

The following discussion will be limited to the normal behaviour, as represented by Curve I, Fig. 3. According to Fig. 1, the voltage rise before AE can be attributed to increasing decomposition voltage when the alumina content decreases. In order to substantiate this hypothesis, which was based on laboratory data, an aluminium reference electrode was introduced into the bath to measure the anode potential.

Aluminium reference electrode

The two types of reference electrodes used are shown in Fig. 4. The aluminium E was contained in boron nitride D, and molybdenum wire C served as contact. The bath had access through a 3 mm hole. In one version (a) the boron nitride was shielded by an outer steel tube A. There were no differences in potential between the two types that could be attributed to the difference in design. A laboratory investigation has shown that the aluminium reference electrode acts reversibly and that it has a long-time stability with fluctuations not larger than 2 mV. In this respect it is superior to the alternative reference electrodes that have been used in aluminium cells, i.e. the graphite electrode [13] the C, CO_2 electrode [6] and electrodes based on solid aluminium alloys [14].

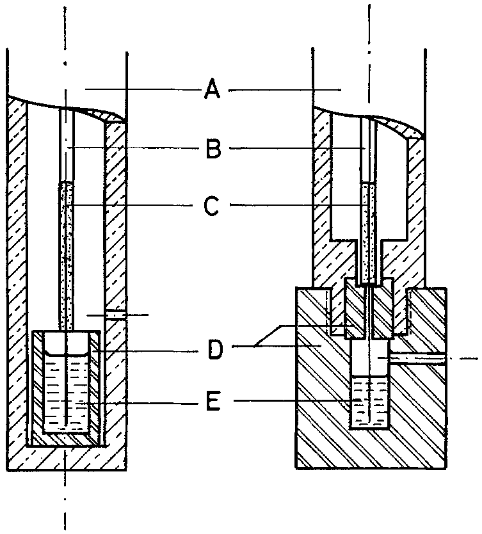

Fig. 4. Aluminium reference electrodes for use in aluminium cells. A, steel tube; B, alumina tube; C, Mo wire; D, boron nitride; E, aluminium.

The electrodes were placed close to the side of the anode, and 5–10 cm above the lower anode surface, as sketched in Fig. 5. The potential was read between the reference and an iron rod driven into the anode above the bath level. The electrodes worked properly for a period of from 6 hours to 2–3 days. The ultimate cause of failure, detected by a rapid decrease in potential, was

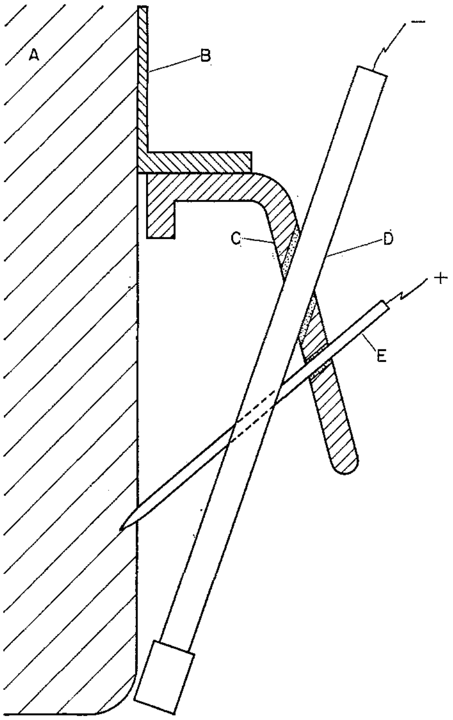

Fig. 5. Positioning of reference electrode. A, anode; B, anode casing; C, gas-collecting skirt; D, reference electrode; E, contact rod.

usually the complete destruction of the lower part of the reference electrode casing. With the aim of developing a more durable arrangement, attempts were made to place the electrode inside a prebaked anode with a hole out to the melt, all encased in boron nitride. However, this type of electrode did not give meaningful and stable readings.

The recorded potentials, in the following designated $E_{D\,\mathrm{ref}}$, encompass the potential of the anode in the area facing the reference electrode, referred to the reversible aluminium electrode, together with an ohmic voltage drop.

The potential decreased when the reference electrode was moved up along the side of the anode, due to the fact that the cd and consequently the overvoltage decreases with increasing distance from the cathode. The ohmic voltage drop included in the readings would generally be lower than 0·1 V. Due to these effects, which act in the opposite direction, the $E_{D\,\mathrm{ref}}$ can differ from the average anode potential of the cell. By assuming that this deviation together with the cathodic overvoltage are practically independent of the alumina content, the $E_{D\,\mathrm{ref}}$ can nevertheless be taken as a measure of the change in E_D of the cell at varying alumina content.

A set of curves displaying the variation in $E_{D\,\mathrm{ref}}$ prior to the AE are shown in Fig. 6. Apart from Curve IV, which corresponds to Curve III in Fig. 3, the curves all exhibit a potential increase. A long duration of this rise was found to be associated with AE's occurring at low alumina contents in the bath; conversely a short duration was typical for AE's at relatively high alumina contents. The initial increase in voltage began at around 2 wt% Al_2O_3 in the bath.

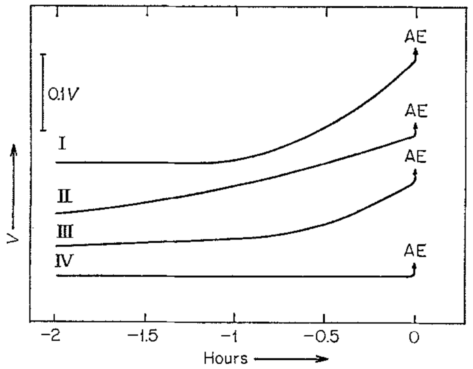

Fig. 6. The anode potential ($E_{D\,\mathrm{ref}}$) prior to anode effect.

Simultaneous recording of cell voltage and $E_{D\,\mathrm{ref}}$ gave sets of curves with rather similar shapes, particularly in the period before AE, as shown in Fig. 7. The corresponding alumina contents in the bath are indicated on the abscissa.

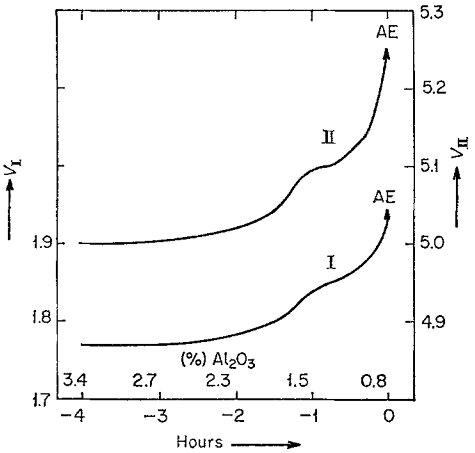

Fig. 7. Anode potential (I) and cell voltage (II) prior to anode effect.

The small plateau on the curves is an example of one of the numerous irregularities which can occur without any apparent reason. The $E_{D\,\mathrm{ref}}$ in general showed fewer irregularities than the cell voltage.

By replotting data similar to those given in Fig. 7 versus the alumina content, diagrams as shown in Fig. 8 could be obtained for cells that were in good operating condition. The shape of these curves is very similar to that of the theoretical curves I and III in Fig. 1.

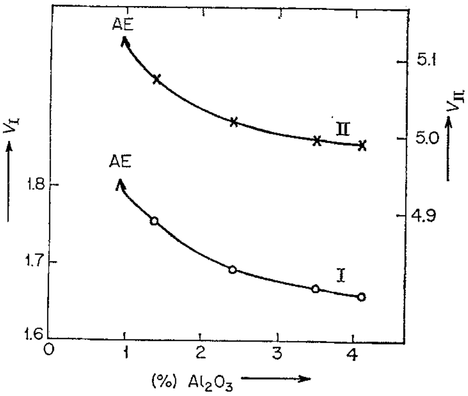

Fig. 8. Anode potential (I) and cell voltage (II) as a function of the alumina content in the bath.

Potential decay by current interruption

The current was lowered gradually to zero and the potential decay was then recorded. The time used to reach zero current varied from ½–3 min, but this did not appear to affect the results significantly. The emf at the moment when the current reached zero ranged from 1·4–1·0 V, as shown in Fig. 9, with most results lying within 1·25–1·10 V. The high values were usually obtained with cells which also showed abnormally high values of $E_{\mathrm{D\,ext}}$.

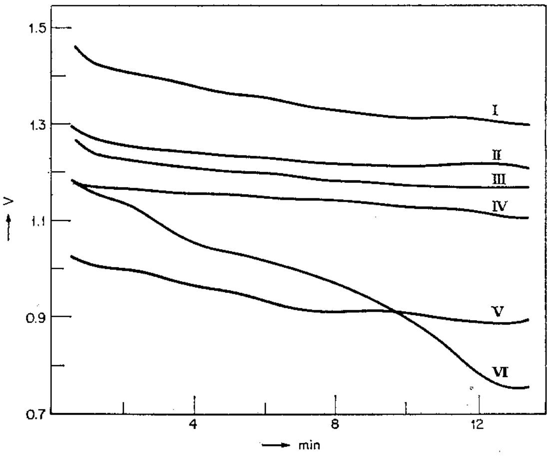

Fig. 9. Variation in cell emf after the electrolysis current was disconnected.

Due to the mode of switching off the current, the results could not be used to determine E_{D} by extrapolation back to zero time. However, the shape of the potential decay curve can possibly render some information on the condition of the cell. The rate of decay was normally in the range 0·01–0·04 V/min, in agreement with previous work [15]. Occasionally a much more rapid decrease was observed, as depicted by Curve VI. Such behaviour indicates the presence of some kind of short circuit between cathode and anode, causing a rapid discharge of the galvanic element which the cell constitutes when the electrolysis is interrupted.

Discussion

As indicated above, erratic short-time voltage fluctuations were smoothed out when tracing the experimental curves. However, sometimes more persistent variations could occur, and no meaningful curves could then be obtained. Still, such phenomena could not mask the very distinct voltage rise prior to AE, while the distinction of the expected small variations at intermediate alumina contents became exceedingly difficult. Since the cells were normally operated at alumina contents below 4–5% Al_2O_3, the presence of a minimum in cell voltage at intermediate contents could not be established unambiguously, although such a trend seemed to exist.

Evidently the E_{D} is not determined by the alumina content alone, even in a potline of identical cells. The variation in the $E_{\mathrm{D\,ext}}$ data clearly indicate the presence of individual variations from one cell to another of the order of 0·2 V. A number of factors may be at play, the temperature and the condition of the anode probably being the most important. There is need to know more about the effect of these and other variables, so that both the differences in E_{D} and the irregularities in the voltage-time curves can be better understood.

Extrapolation of *I-V* curves does not yield theoretically well-defined results, since the curves are not strictly linear and since part of the overvoltage is included in the $E_{\mathrm{D\,ext}}$. This method may still prove useful for practical applications. A close examination of the *I-V* data revealed some more or less easily discernible deviations from a straight line relationship. When the current was increased above the normal line current of 75 kA, there was in some cases a slight tendency towards an upward bend of the *I-V* curve. In the range 75–25 kA a slight convexity towards the current axis was detected. This was most easily seen by evaluating the ohmic resistance from the equation

$$R_{\mathrm{ext}} = (U - E_{\mathrm{D\,ext}})/I. \qquad (8)$$

The $E_{\mathrm{D\,ext}}$ value giving the best fit was found by computer calculations. The resulting values of R_{ext} showed a slight maximum in the range 40–60 kA.

In the current range 25–7 kA, a slight hump on the *I-V* curve usually occurred, as can be seen in Fig. 2, Curve I, representing the normal type of curve. This behaviour was probably due to an actual increase in ohmic resistance. The magnetic forces acting on the cathode metal may set up a permanent skew in the metal surface. When the current is lowered, the metal surface becomes horizontal, resulting in increased resistance in the bath. The convection in the bath and in the metal will also diminish when the current is lowered.

According to laboratory data [2] the overvoltage follows Tafel's law. The observed slight convexity of the I-V curve in the 75–25 kA range indicates that introduction of a logarithmic term in equation (8) might give a better fit. Normally, the improvement would be particularly evident at low currents, but due to the apparent change in resistance, this range was not available for analysis.

The following equation was tried,

$$U = E'_D + b \log \frac{I}{75{,}000} + RI \qquad (9)$$

where E'_D is the decomposition voltage at $I =$ 75,000 A, and b is the Tafel coefficient, which was given values from 0·20 to 0·30. For a given b the E'_D which gave the best constancy of R was found by trial and error by computer calculations. Since the logarithmic term is much smaller than the RI term, the best value of b could not be assessed with any degree of certainty. Values from 0·20 to 0·26 seemed to give equally good fit. When b was changed from 0·26 to 0·20 the corresponding value of E'_D decreased by 0·05 V. A set of results obtained in this manner by use of equations (8) and (9) are shown in Table 1. The standard deviation of the resistance values calculated from eight recordings in the 20–79 kA range are given. It appears that equation (9) gives a somewhat better fit. This is due to the straightening out of the convexity of the I-V curve.

The persistence of the cell emf by zero current at values above the reversible potential, as displayed by Curves I–III Fig. 9, has also been noted by other workers [11, 16]. It can probably be attributed to formation of relatively stable intermediate compounds at the anode, having a higher free energy of formation than CO_2.

Practical applicability

For most practical purposes extrapolation of the I-V curve is an adequate means of determining E_D. It should be borne in mind, however, that $E_{D\,ext}$ has no strict theoretical meaning as pointed out above. Obviously the current need not be lowered down to zero current; about 60% of full current will suffice. In order to cause as little disturbance in cell operation as possible, only 5–10% variation in current has been suggested [10], but the uncertainty in the extrapolation is then necessarily greater. The same is true for methods based on the accidental variations in the line current [11, 12, 17]. With some refinement, these methods may nevertheless prove to be sufficiently accurate for some applications.

The aluminium reference electrode provides very satisfactory results for the determination of anode potential, and obviously it can also be used for cathode studies. Unfortunately, the short life-time of the electrode limits its use to research purposes.

Acknowledgment

Financial support was received from the Royal Norwegian Council for Scientific and Industrial Research. The experimental work was carried out

Table 1. Calculated values of decomposition voltage and cell resistance

		$E_{D\,ext} = U-RI$ [8]			$E'_D = U-0{\cdot}26 \log (I/75{,}000) \div RI$ [9]		
Cell no.	*%Al_2O_3*	$E_{D\,ext}$ (*V*)	*R* ($\mu\Omega$)	*Stand. dev.*	E'_D (*V*)	*R* ($\mu\Omega$)	*Stand. dev.*
1	3·3	1·80	41·70	0·41	1·90	40·60	0·23
2	2·4	1·82	40·49	0·14	1·99	38·19	0·17
3	3·3	1·70	41·12	0·18	1·85	39·17	0·17
4	2·9	1·70	40·31	0·40	1·82	39·10	0·22
5	6·5	1·65	40·34	0·13	1·81	37·75	0·18

at the aluminium plant of A.S. Årdal og Sunndal Verk, Sunndalsøra. The assistance of Mr Johan Gulbrandsen in carrying out the measurements is acknowledged.

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