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Electrodeposition of Catalytically Active Cobalt Powder from Aqueous Sulfate Electrolytes

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The electrodeposition of cobalt powder was investigated from aqueous sulfate solutions containing 0.0125—0.0500 $CoSO_4 \cdot 7H_2O$ (I), 0.23—1.00 $(NH_4)_2SO_4$ (II), 0.1 H_3BO_3 and 0.07 mol dm^{-3} $Na_2SO_4 \cdot 10H_2O$. The effects of the bath composition, the pH, the deposition current density and the duration of electrolysis on the cathodic polarization and the efficiency of cobalt electrodeposition, as well as on the morphology and the catalytic activity (towards the decomposition of 0.4% H_2O_2 solution) of the as-deposited cobalt powders were discussed. X-Ray diffraction studies proved that cobalt powders were very pure and deposited in the hexagonal close-packed structure with the orientations (100), (002), and (101). Cobalt powder deposited with an efficiency of 32% and had a catalytic activity approaching 100% could be obtained from the above-mentioned bath formula containing 0.05 mol dm^{-3} (I) and 0.46 mol dm^{-3}(II). The optimum operation conditions to achieve these characteristics were: pH 4.78, j=10 A dm^{-2} and t=15 min.

Little use has been made of pure cobalt deposits and this seems to be due to commercial and technical reasons.1) However, cobalt powder is important in metalloceramics industry2) and in manufacture of alloys characterized by a desired protective, decorative, and magnetic properties.3,4)

The electrochemistry of cobalt is not well established, the number of contributions on the subject is low, and the data on this process is incomplete.2) However, the electrodeposition of cobalt powder was investigated from sulfate5) and tetrafluoroborate6) aqueous solutions. On the other hand, the deposition of cobalt powder is favored by nonaqueous media and has been investigated in a two-layer bath.7) The electrolyte was an aqueous solution of $CoCl_2 \cdot 6H_2O$ and the organic medium was 0.5% solution of oleic acid in toluene. The process was further developed to yield cobalt powder proper for use in the production of magnets.8)

The present study was undertaken to investigate the electrodeposition of cobalt powder in dilute aqueous sulfate solutions. The process may be suitable for recovery of Co^{2+} ions from industrial effluents in form of fine grained powder of beneficial use as a catalyst.

Experimental

The baths used for electrodeposition of cobalt were prepared in distilled water using AnalaR grade chemicals (BDH). The symbol, composition, pH, and specific conductance of each of these baths are given in Table 1. The experimental arrangement for electrodeposition consisted of a Perspex cell with a copper cathode positioned midway between two plane parallel platinum anodes; all electrodes were of the same geometrical area. The anodes were surrounded by asbestose diaphragms to preclude oxidation of Co^{2+} ions and errors in the measured potentials caused by the oxygen evolved at the anodes.

The cathodic polarization curves were measured relative to the saturated calomel electrode (SCE) by means of a Wenking potentioscan model POS 73 and recorded automatically with a Philips x-y recorder model PM 8132. The cathodic efficiencies (f%) were determined by the use of a standard copper coulometer. The morphology of the as-formed cobalt powders was examined with a scanning electron microscope (JEOL model JSM 35). X-Ray diffraction studies were carried out by a Philips X-ray diffractometer PW 1390 with a nickel filter and copper radiation. The percentage decomposition (D%) of 0.4% H_2O_2 solution (at 40 °C) on the surface of the electrodeposited powders was considered as a measure for their catalytic activity. Therefore, a definite volume (50 ml) of the H_2O_2 solution was passed (single-pass) over a fixed bed (0.15 g) of the test powder with a constant flow-through rate (150 ml h^{-1}) by the aid of a MICROPERPEX peristaltic pump (LKB Bromma model 2132). D% was calculated by measuring the exact concentrations of H_2O_2 spectrophotometrically before and after its passage over the powder.

The electrodeposition experiments were carried out (in a selected bath) at various pH values; current densities, j (A dm^{-2}) and durations, t (min) using stationary electrodes. The pH of the bath was adjusted by additions of concentrated H_2SO_4 (98%) or NaOH solutions. One variable was changed

Table 1. Composition, pH and specific conductance (C) of cobalt deposition baths

Bath Co.	Contents in the bath/mol dm^{-3}				pH	C/ohm^{-1} cm^{-1}
	$CoSO_4 \cdot 7H_2O$	$(NH_4)_2SO_4$	H_3BO_3	$NaSO_4 \cdot 10H_2O$		
1	0.0125	1.00	0.1	0.07	5.43	0.129
2	0.0250	1.00	0.1	0.07	4.94	0.130
3	0.0500	1.00	0.1	0.07	4.72	0.135
4	0.0500	0.46	0.1	0.07	4.78	0.066
5	0.0500	0.23	0.1	0.07	4.85	0.044

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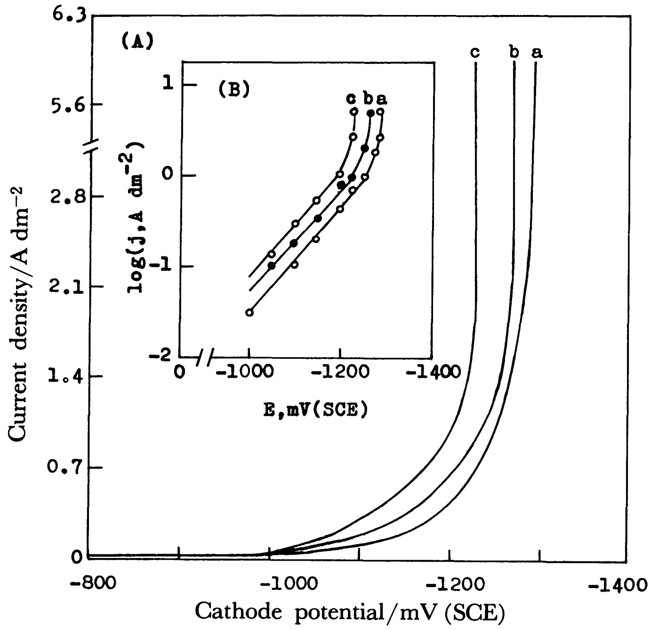


Fig. 1. (A) Polarization curves and (B) Tafel lines for cobalt electrodeposition from Baths: Co. 1 (Curve a), Co. 2 (Curve b), and Co. 3 (Curve c).

while the other two were held constant. Unless otherwise stated, all types of measurements were carried out at 25 °C.

Results and Discussion

Polarization Curves. The cathodic polarization curves for cobalt electrodeposition from Baths Co. 1—3 are shown in Fig. 1(A). The curves are characterized by an initial rapid potential-shift to the more negative values followed by a gradual increase with rise of current density and then the potential remains almost constant. This indicates that the electrodeposition of cobalt is attended by a high activation polarization.[9] This can be seen more clearly in Fig. 1(B) which shows that the Tafel relation holds good within the current density range 0—1 $A\,dm^{-2}$. Furthermore, the Tafel lines and the polarization curves shift to less negative potentials with increase in the concentration of Co^{2+} ion in the bath. This could be attributed to the corresponding decrease in the activation and the concentration polarizations.[10] However, regardless of the concentration of Co^{2+} ion in the bath, codeposition and vigorous evolution of hydrogen could be easily seen.

Decreasing the concentration of $(NH_4)_2SO_4$ in Baths Co. 3—5 which was expected to decrease the cathodic polarization *via* decreasing the stability constants of the Co^{2+}-ammonium complex ions,[11] is in practice found to has the opposite effect, *viz.* increasing the polarization (Figs. 2(A) and (B)). In addition, a corresponding decrease in the specific conductance of these baths is observed (Table 1).

As can be seen in Fig. 3(A), the cathodic polarization increases with increase in the pH of Bath Co. 4 over the range 2.1—9.6. This feature could be ascribed to the corresponding increase in the hydrogen overvoltage[12] and the observed increase in the activation polarization of the cobalt deposition reaction (see Fig. 3(B)). In addition, at a low pH the rate of hydrogen evolution is so high that most of the gas formed escapes as bubbles. Increase in pH produces a state at which bubble formation is not fast enough for the gas to escape and consequently hydrogen adsorption occurs giving rise to an increase in the cathode potential.[6]

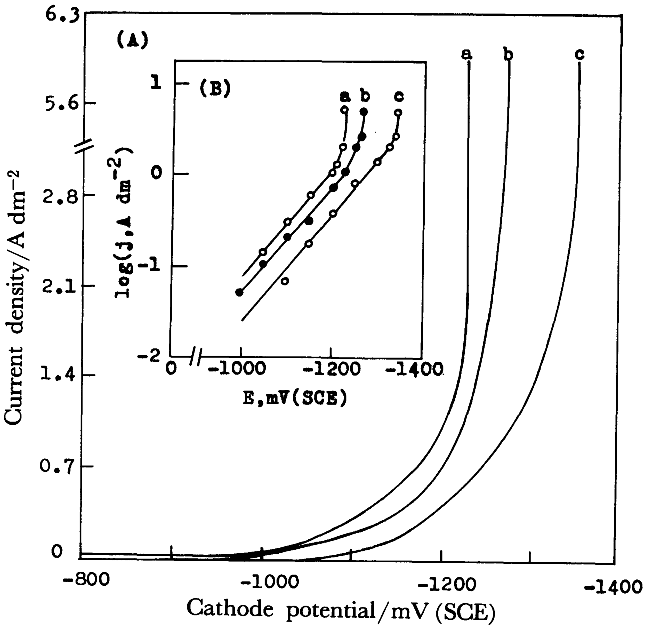


Fig. 2. (A) Polarization curves and (B) Tafel lines for cobalt electrodeposition from Baths Co. 3 (Curve a), Co. 4 (Curve b), and Co. 5 (Curve c).

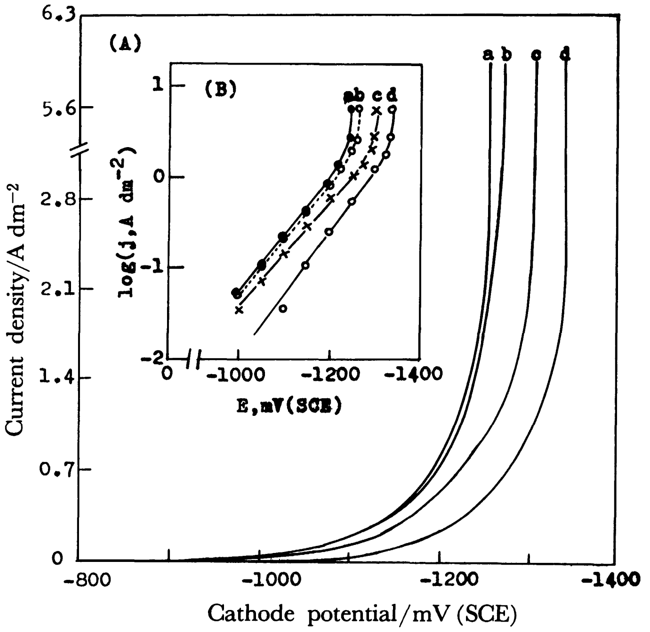


Fig. 3. (A) Polarization curves and (B) Tafel lines for cobalt electrodeposition from Bath Co. 4 at pH 2.1 (Curve a), pH 4.78 (Curve b), pH 7.7 (Curve c), and pH 9.6 (Curve d).

Current Efficiency. The percentage current efficiency (f%) of cobalt deposition increases with increase in the concentration of Co^{2+} ion in Baths Co. 1—3

Table 2. Effect of the Bath Composition on the Efficiency and the Catalytic Activity of Cobalt Deposits

Property	Bath Co.				
	1	2	3	4	5
f %[a)]	10.65	20.04	30.49	32.22	34.79
D %[b)]	82.45	89.55	94.97	97.62	95.86

a) j=6.6 A dm^{-2}, t=10 min. b) j=10 A dm^{-2}, t=30 min.

Table 3. Effect of pH in Bath Co. 4 on the Efficiency and the Catalytic Activity of Cobalt Deposits

Property	pH			
	2.1	4.78	7.7	9.6
f %[a)]	31.33	32.22	29.70	21.56
D %[b)]	94.50	97.62	95.35	96.20

(a) and (b) are the same as in Table 2.

(Table 2). This effect could be due to the corresponding decrease of the concentration and the activation polarizations of cobalt deposition (Figs. 1(A) and (B)) and the simultaneous inhibition of discharge of H$^+$ ions. However, a general increase in the efficiency with concentration of the depositable metal ion in the bath was reported in previous studies.[10,13)]

As the concentration of ammonium sulfate decreases in Baths Co. 3—5, there is a regular trend of increase in the efficiency of cobalt deposition (Table 2). This could be attributed to the expected decrease in the stability constant of Co^{2+}-ammonium complex ions[11)] and the consequent increase in the concentration of the free Co^{2+} ions in the cathode layer. A similar increase in the efficiency with decrease in the concentration of the complexing agent has been observed during the electrodeposition of other metal powders.[13)]

Bath Co. 4 is distinguished by a comparatively high current efficiency and the produced powder is characterized by the highest catalytic activity. Therefore, this bath was selected to explore the effect of the variables pH, j, and t on the electrodeposition of cobalt powder.

The data of Table 3 show that the efficiency from the as-prepared Bath Co. 4, of pH 4.78, decreases slightly with lowering of the pH to 2.1. This could be due to the competition between Co^{2+} ions and H$^+$ ions for discharge. This result is in good agreement with that obtained for the electrodeposition of cobalt from an acidic chloride bath.[14)] On the other hand, the efficiency decreases considerably with rise of the pH over the range 4.78—9.60. This could be explained by the observed increase in the cathodic polarization with pH (Fig. 3).

The efficiency of cobalt deposition from Bath Co. 4 decreases gradually with increase in the current density (Table 4). This feature may be ascribed to the depletion of Co^{2+} ions in the cathode layer, arising from the increased rate of deposition, and the preferential discharge of hydrogen at high current densities. Similar results have been observed in several acidic plating electrolytes.[15,16)]

Table 4. Effect of Current Density on the Efficiency and the Catalytic Activity of Cobalt Deposits from Bath Co. 4

Property	j/A dm^{-2}			
	2.0	6.6	10.0	13.2
f %[a)]	43.65	32.22	30.35	28.26
D %[b)]	98.15	97.90	97.62	94.32

a) pH=4.78, t=10 min. b) pH=4.78, t=30 min.

Table 5. Effect of Deposition Time on the Efficiency and the Catalytic Activity of Cobalt Deposits from Bath Co. 4

Property	t/min			
	10	15	20	30
f %[a)]	32.22	32.18	28.41	11.04
D %[b)]	100.00	99.00	98.10	97.62

a) pH=4.78, j=6.6 A dm^{-2}. b) pH=4.78, j=10 A dm^{-2}.

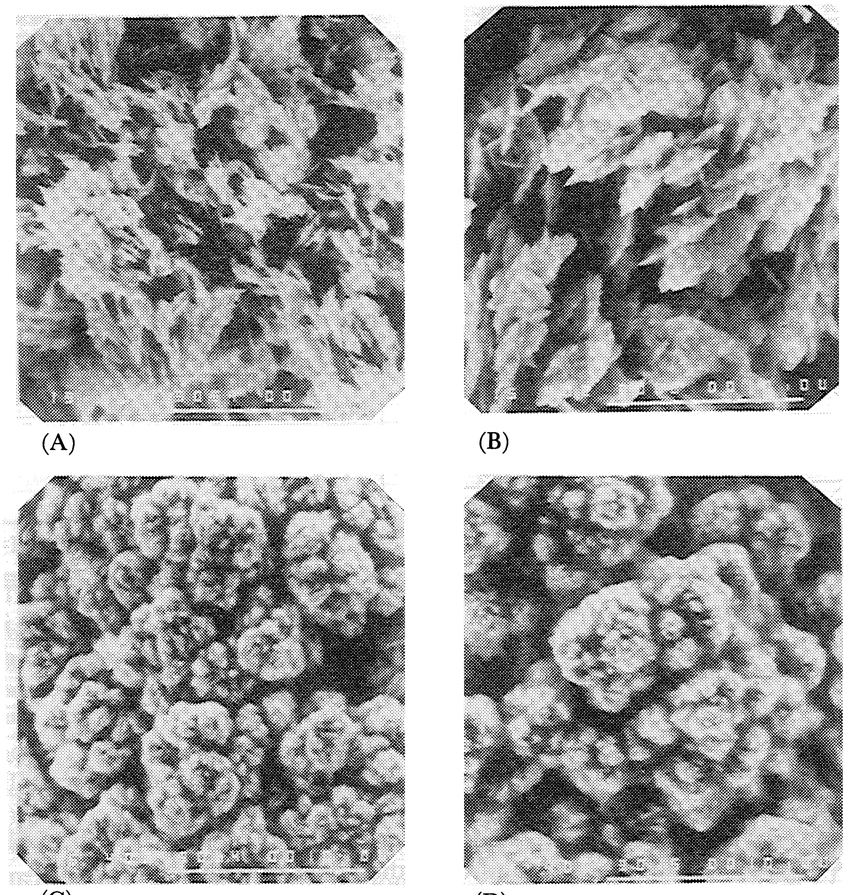
A regular trend of decrease in efficiency with increase in deposition time is represented in Table 5. Actually, this is an unfavourable feature and could be avoided by using soluble cobalt anodes or replenishing the Co^{2+} ions in the bath.

Surface Morphology. The powder obtained from Bath Co. 1 consists of fine crystals which have a characteristic fern-like shape (Fig. 4(A)). On increasing the concentration of Co^{2+} ions in Baths Co. 2 and 3, there is a growth habit modification towards the formation of coarser leaf-like dendritic deposit (Fig. (4B)). This change could be due to the decrease in the concentration and the activation polarizations (Figs. 1(A) and (B)) and the increase in diffusion of Co^{2+} ions which enable preferential growth on certain crystallographic planes and directions.[17)]

The inclusion of lower concentrations of ammonium sulfate in Baths Co. 4 and 5 results in the formation of dispersed nodular deposit and better coverage of the cathode surface (Fig. 4(C)). This result is in agreement with the observed increase in the cathodic polarization (Fig. 2) and the correspondingly expected increase in the nucleation sites.[10)]

On lowering the pH of Bath Co.4 from 4.78 to 2.10, there is no remarkable change in the growth morphology of the deposit other than refinement of the crystal size. In contrast, increase in pH of Bath Co. 4 over the range 4.78—9.60 leads to passivation of the cathode and formation of isolated dendritic clusters (Fig. 4(D)). This could be due to the polarization increasing effect with pH (Fig. 3) resulting from the increase in adsorption of hydrogen onto the cathode surface[6)] and the consequent inhibition of Co^{2+} ions deposition.

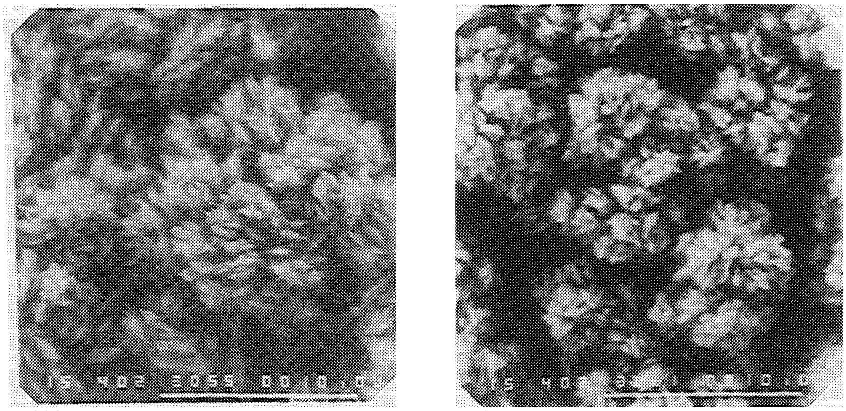
The effects of the deposition current density (1.3—13.2 A dm^{-2}) and duration of electrolysis (3—30 min) on the morphology of cobalt powder from Bath Co. 4 (pH=4.78) were also examined. At a low current density (j=1.3 A dm^{-2}) small dihedral grains randomly oriented at the cathode are obtained (Fig. 5(A)). A regular trend of increasing grain size and transformation to



(A) (B)

(C) (D)

Fig. 4. Electron micrographs of cobalt powders from Baths Co. 1 (A), Co. 3 (B), Co. 4 at pH 4.78 (C), and Co. 4 at pH 7.7 (D); j=6.6 A dm^{-2}, t=10 min and magnification (×4000).



(A) (B)

Fig. 5. Electromicrographs of cobalt powders from Bath Co. 4 at j=1.3 A dm^{-2} and t=10 min (A) and at j=6.6 A dm^{-2} and t=3 min (B); pH=4.78 and magnifications (×4000).

nodular dendrites is observed with increase in current density, as can be seen in Fig. 4(C). This feature could be attributed to the increase in the rate of discharge of Co^{2+} ions with current density; whereas, the cathodic polarization remains constant (Fig. 2(A)). Such conditions favour enlargement of the crystal size without considerably affecting the nucleation density.[15,18)]

For short deposition times (t=3 min), isolated clusters of fine crystals are formed (Fig. 5(B)). On increasing the deposition time, there is a corresponding increase in the grain size of the cobalt deposit and better coverage of the cathode as shown in Fig. 4(C). These results could be ascribed to the fact that bigger grains are more stable thermodynamically, and if the system has enough time it will reach its most stable state.[19)] This phenomenon would result from redissolution and recrystallization of the deposits, through the formation of local cells between them.[18)] However, similar results and ex-

Table 6. X-Ray diffraction patterns of cobalt deposit from bath Co. 4

Line	2θ	d/Å	I/I_0	hkl	Observed parameters		Standard parameters	
					a/Å	c/Å	a/Å	c/Å
1	41.60	2.1690	20	100	2.505	4.065	2.507	4.070
2	44.50	2.0342	60	002				
3	47.50	1.9120	100	101				

planations were reported for the electrodeposition of cadmium.[15)]

X-Ray Diffractometry. X-Ray structural studies were carried out on the electrodeposited cobalt powders from the under test baths at a current density of $10\,\mathrm{A\,dm^{-2}}$ and duration for 30 min. Table 6 shows as for example the data for the deposit formed in Bath Co. 4. Regardless of the composition or the pH of the examined baths, the obtained data reveal that cobalt powders are deposited in the hexagonal close-packed structure and exhibit the orientations (100), (002), and (101). Moreover, the powders are deposited in a very pure form as could be find out from the good agreement between the values of the calculated and the standard lattice parameters.

Catalytic Activity. In general the catalytic activity (D%) of the electrodeposited cobalt powder, towards the decomposition of 0.4% H_2O_2 solution, is relatively high (82—100%) and this seems to be a specific property. However, the catalytic activity increases with increase of Co^{2+} ions concentration in Baths Co. 1—3 and decrease of ammonium sulfate concentration in Baths Co. 3—5 (Table 2). These effects may be due to the corresponding morphological transformations (Figs. 4A—C) which would result in an increased surface area of the deposit and accordingly increase its catalytic activity.[20)]

The effects of the variables, pH, current density, and deposition time on the catalytic activity of cobalt powders formed in Bath Co. 4 were also examined. A negligible change in the catalytic activity is observed with altering the pH over the range 2.1—9.6 (Table 3). This may be referred to the slight effect of pH on the surface morphology of the deposit (Figs. 4(C) and (D)).

The catalytic activity of the deposited powder at the lowest current density ($2.0\,\mathrm{A\,dm^{-2}}$) and the shortest deposition time (10 min) is almost 100%. However, the catalytic activity decreases gradually with increasing current density (Table 4) and increasing deposition time (Table 5). These results may be due to the corresponding enlargement of the cobalt grain size and formation of clusters rather than disperse deposit as mentioned above in the discussion of the surface morphology. However, it seems probable that the catalytic activity of the cobalt powder is, in general, a morphological-sensitive property.

Conclusions

The electrodeposition of cobalt powder from sulfate electrolytes can be controlled by the bath composition, the pH, the current density, and the duration. The obtained data show that the effects of these variables on the cathodic polarization influence to a great extent the surface morphology of the electrodeposited cobalt powder. In addition, the catalytic activity seems to be a morphological-sensitive property. Accordingly, the optimum bath is found to contain 0.05 $CoSO_4 \cdot 7H_2O$, 0.46 $(NH_4)_2SO_4$, 0.1 H_3BO_3, and 0.07 $\mathrm{mol\,dm^{-3}}$ $Na_2SO_4 \cdot 10H_2O$. This bath yields the best depoit, characterized by a catalytic activity of 99%, with an efficiency of 32% at the most suitable operating conditions: pH$=$4.78, $j=10\,\mathrm{A\,dm^{-1}}$ and $t=15$ min.

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