junction structure during processing. Bonding agents of pure Al or Al-Si eutectic were applied to the Mo sheet by rolling accompanied by a substantial thickness reduction to promote the formation of atomic bonds between newly formed Al-Mo interfaces. The Si bonding temperature cycle must be carried out in either an inert or reducing atmosphere. The maximum temperature is limited by the reaction of Al with the Mo, and the cooling rate is limited by the necessity for relieving stresses in the bimetallic structure without inducing fracture. When Si is added to the Al bonding material, considerably more stringent alloying conditions must be used to obtain a satisfactory bond.

### Acknowledgments

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Any discussion of this paper will appear in a Discussion Section to be published in the June 1959 JOURNAL.

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# Electrolytic Reduction of Cyanamide

## II. The Nature of the Reduction of Cyanamide and Formamidine

**Keijiro Odo, Eiichi Ichikawa, Katsujiro Shimogai, and Kiichiro Sugino**

*Laboratory of Organic Electrochemistry, Department of Chemical Engineering,*

*Tokyo Institute of Technology, Tokyo, Japan*

ABSTRACT

Two consecutive steps in the electrolytic reduction of cyanamide have different natures from the viewpoint of organic electrode process. The first step is catalytic and the second step is voltage-controlled. Therefore, the most active cathode for one step may not be the most effective for another. Tin was an effective cathode for the over-all reduction process.

In the course of the reduction of formamidine to methylamine and ammonia, the existence of methylenediamine as second intermediate was verified.

On the electrolytic reduction of cyanamide the isolation of formamidine as intermediate and the confirmation of methylamine and ammonia as final products was reported (1). In the present work, the effect of cathode materials and other electrolytic conditions on the yield of each product was studied. Also, the reduction of formamidine at various cathodes was investigated in order to clarify the over-all reduction mechanism. The results are reported here along with some unusual phenomena observed in the course of this study.

### Experimental

The apparatus used was the same as that already described (1). However, the cell was covered in order to measure the H evolution.

Crystalline cyanamide was freshly prepared from commercial calcium cyanamide by an improved procedure (2), and its purity was determined by the usual method (as silver cyanamide) before use.

Formamidine sulfate was prepared by the catalytic reduction of cyanamide with Pd catalyst (3), mp 156°-158°C.

*Separation of the reduction products of cyanamide.*—The separation of each product was carried out more rigidly than previously (1).

After reduction, the catholyte (about 110-120 cc) was neutralized with a small amount of $H_2SO_4$ (or $NH_3$) and diluted to 200 cc; 10 cc was used as the determination of unconverted cyanamide. The remaining part was evaporated to dryness at 50°-60°C under diminished pressure and the residue was dried for 24 hr in a vacuum-desiccator over $P_2O_5$. This was extracted twice with 50 cc isopropyl alcohol to remove unconverted cyanamide. The residue was again extracted twice with 50 cc absolute

methanol. The final residue was dried at 100°C and weighed (ammonium sulfate).

The methanol extract[1] was evaporated to dryness and the residue was dissolved in 100 cc water. Then, a suitable amount of picric acid (2% excess based on converted cyanamide) was added to it, the mixture was warmed to make a clear solution, and allowed to cool overnight. The precipitate was filtered off, washed with 50 cc water, and dried. Then it was purified by extraction with absolute ether to remove free picric acid, dried at 100°C, and weighed (formamidine picrate). Solubility correction was applied.

After removing the dissolved picric acid by acidification with HCl and extraction with ether, the filtrate was concentrated to 100 cc. The concentrate of isopropyl alcohol extract was added to it, and the mixture was poured into a Kjeldahl flask and heated with 20 g NaOH/50 cc water solution. Methylamine was distilled into N-HCl and the resulting solution (100 cc) was evaporated to dryness and allowed to stand in a vacuum desiccator over $P_2O_5$ overnight. The residue was extracted twice with 50 cc butanol at 50°C. The butanol extract was concentrated to 10 cc and allowed to stand in an ice box. Methylamine hydrochloride crystals which separated out were filtered off, dried at 100°C, and weighed. Some methylamine hydrochloride was recovered from the mixture of the filtrate and the wash.

Determination was not carried out for nonnitrogeneous hydrolytic products of intermediate compounds, such as formic acid and formaldehyde.

*Separation of the reduction products of formamidine.*—After reduction, the catholyte (110-120 cc) was neutralized with a small amount of $H_2SO_4$ (or $NH_3$), evaporated to dryness at 50°-60°C under diminished pressure, and the residue was dried for 24 hr in a vacuum desiccator over $P_2O_5$. This was refluxed twice with 50 cc absolute methanol, and the insoluble residue was filtered off from the hot solution. The residue was dried at 100°C and weighed (ammonium sulfate).

The methanol extract was worked up to separate unconverted formamidine as picrate and then to collect methylamine hydrochloride just as in the separation of the reduction products of cyanamide. However, in the case, 25 g picric acid was added with 50 cc water to 100 cc aqueous solution made from the evaporation residue of the methanol extract for the separation of unconverted formamidine.

As for nonnitrogeneous hydrolytic products of starting material and the intermediate product, the determination of formaldehyde with formic acid was carried out in some cases as described later.

## Results and Discussion

### *Reduction of Cyanamide*

The yield of each reduction product at various cathode materials is shown in Table I.

[1] In the case of the reduction at Pd, the methanol extract was concentrated and allowed to cool to give formamidine sulfate. After separating these crystals, the filtrate was diluted to 100 cc with water and worked up by the same procedure.

**Table I**

Anode: Pt; anolyte: 60 cc 5% $H_2SO_4$; catholyte: 10.0 g cyanamide (purity: 96-98%) in 100 cc 8% $(NH_4)_2SO_4$. pH range adjusted at 2-7 by adding small amount of $H_2SO_4$ during the electrolysis; temp: 12°-15°C; current density: 5 amp/dm²; amount of current: 38 amp-hr (6 faradays/mole)

| Run No. | Cathode | Cyanamide converted g | Cyanamide converted % | Yield: Formamidine picrate g | Yield: Formamidine picrate % | Yield: Methylamine HCl g | Yield: Methylamine HCl % | Yield: $(NH_4)_2SO_4$ g |
|---|---|---|---|---|---|---|---|---|
| 1 | Sn | 5.1 | 53 | 4.1 | 13 | 0.7 | 9 | 2.7 |
| 2 | Pb | 1.9 | 20 | nearly zero | — | 0.2 | 7 | 0.9 |
| 3 | Hg | 2.8 | 30 | nearly zero | — | nearly zero | — | 1.0 |
| 4 | Cu | 3.1 | 32 | 0.30 | 1.5 | 0 | — | 0.8 |
| 5 | Pd black on Pd. | 8.7 | 90 | sulfate* 8.3 +picrate 7.0 | 52 | 0 | — | 3.7 |

* Of the total yield of formamidine, 8.3 g was obtained as sulfate and 7.0 g was obtained as picrate.

The reduction of cyanamide occurred at all cathodes used (1). It was confirmed that Sn was an effective cathode material for over-all reduction process. Pb and Hg, which have a high H overvoltage, were not so effective in this reduction. Especially at Hg, methylamine was scarcely obtained and ammonia was the only nitrogeneous product. It was noticed that formamidine was not obtained at these two cathodes. This is due to the effectiveness of these cathodes on the reduction of formamidine as described below. Cu, a low H overvoltage metal, was also an active cathode leaving a small amount of formamidine as product. Pd black cathode was seen to be very effective for the formation of formamidine. However, at Pd, methylamine could not be obtained at all.

*Current efficiency at various cathodes.*—Since several products were obtained in the reduction of cyanamide, H evolution at the cathodes was measured to observe the differences in current efficiency of the cathodes (except Hg[2]). The measurement was carried out at intervals of several minutes till the theoretical amount of current (6 faradays/mole) was passed. Results are shown in Fig. 1.

Palladium was the most effective from the viewpoint of current efficiency. However, even at Pd, the efficiency decreased markedly with time.[3] At Sn, the efficiency was not so high at the beginning, but it was maintained at about the same level. At Pb, the efficiency once reached to the same level as at Sn but it decreased greatly after 2 hr[4] and came down to zero after 6 hr. At Cu, the efficiency was very low and it reached to zero at the end. These observations coincided well with the results in Table I.

*Influence of pH and current density on current efficiency at tin cathode.*—The influence of pH and current density on current efficiency was then examined at the Sn cathode for a typical run. Results are shown in Fig. 2.

[2] At Hg, accurate measurement was difficult due to the formation of ammonium amalgam.

[3] This might be due to poisonous action of cyanamide on the catalyte activity of Pd.

[4] It may be possible that this is due to the formation of an insoluble film on the cathode surface, resulting from the action of cyanamide with lead.

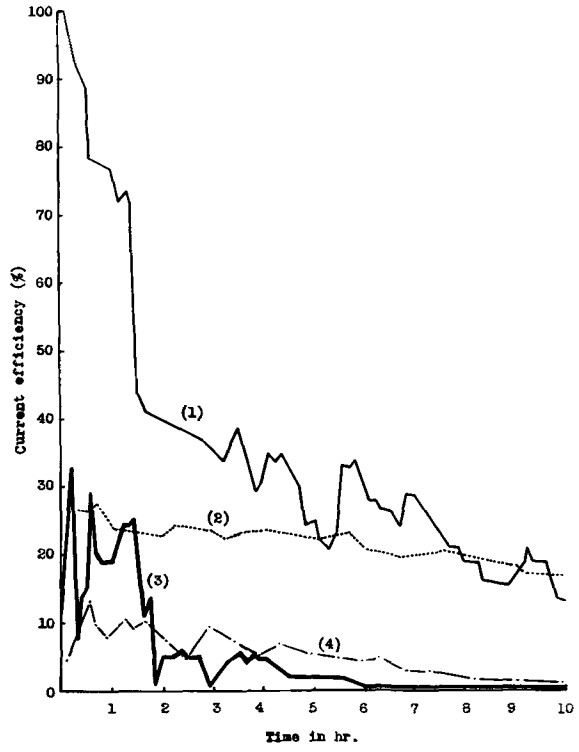


Fig. 1. Current efficiency at various cathodes (reduction of cyanamide): 1, Pd; 2, Sn; 3, Pb; 4, Cu; conditions: same as in Table I.

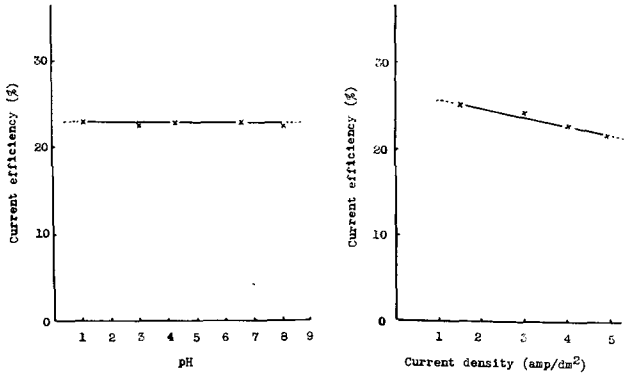


Fig. 2. Effect of pH and current density on current efficiency at Sn (reduction of cyanamide); conditions: same as in Table I.

The change of pH from 1 to 8 had no effect on the current efficiency. As for the influence of current density, the efficiency had a tendency to decrease slightly with increasing current density from 1 to 5 amp/dm$^2$.

### *Reduction of Formamidine*

The yield of each reduction product at various cathode materials is shown in Table II.

Contrary to cyanamide, the reduction of formamidine was found to occur only at cathodes having a high H overvoltage such as Sn, Pb, or Hg. The yield of methylamine based on formamidine converted was the highest at Sn, although it was relatively small. A large amount of ammonia was formed at every cathode. Especially at Hg, the largest amount of ammonia was obtained with a very small amount of methylamine. It was interesting to note that a fairly large amount (40%) of

Table II

Anode: Pt; anolyte: 60 cc 5% $H_2SO_4$; catholyte: 10.0 g formamidine sulfate in 100 cc water (almost neutral). pH range adjusted at 2-7* by adding small amount of $H_2SO_4$ during the electrolysis; temp: 12°-15°C; current density: 5 amp/dm$^2$

| Run No. | Cathode | Amount of current amp-hr | Formamidine unconverted % | Yield Methylamine HCl g | Yield Methylamine HCl % | Yield $(NH_4)_2SO_4$ g | Remarks |
|---|---|---|---|---|---|---|---|
| 1 | Sn | 57.5 | 43 | 0.8 | 18 | 6.2 | |
| 2 | Pb | 57.5† | 0 | 1.1 | 15 | 9.0 | |
| 3 | Hg | 17.3 | 0 | 0.1 | 2 | 11.0 | Urotropine obtained |
| 4 | Cu | 11.5 | 65 | 0 | — | 3.6 | |
| 5 | Pd | 11.5 | 76 | 0 | — | 1.4 | |

* It is well known that formamidine is hydrolyzed very easily to give ammonia and formic acid, especially in alkaline medium.
† In the case of Pb, this amount was more than enough to convert all of the formamidine.

hexamethylenetetramine was found in the product at Hg.[5] This is a characteristic of a mercury cathode and led us to suppose that methylenediamine was formed in the course of this reduction.

At Pd, which has the greatest activity toward the reduction of cyanamide to formamidine, no reduction products were obtained which showed its inactivity toward formamidine. At Cu, no reduction products were also obtained as well as at Pd, but the amount of ammonia formed by hydrolysis was somewhat larger than that at Pd.

*Current efficiency at various cathodes.*—Hydrogen evolution at the cathodes (except Hg)[6] was measured to observe the differences in current efficiency of the cathodes on the reduction of formamidine. The variation of pH of the catholyte was measured by pH test paper at the same time because it had a great influence on current efficiency. The measurement was carried out at intervals of several minutes till the theoretical amount of current (4 frs/mole) was passed. Results are shown in Fig. 3.

Lead showed a high current efficiency at the start, but it decreased with time and reached a small value at the end.[7] On the other hand, at Sn, a moderate efficiency was maintained, as in the reduction of cyanamide. At Pd, at which the efficiency was the highest in the reduction of cyanamide, a definite H absorption due to the reduction was not observed. At Cu, practically zero efficiency was recorded after 1 hr. These observations coincided well with the results in Table II.

*Influence of pH on current efficiency:*[8]—Using a tin cathode, the influence of pH on current efficiency was studied when[9] 17 amp-hr had passed (Fig. 4).

It was found that the current efficiency greatly decreased below pH 2. This was also observed at

[5] The electrolyte close to the cathode might be ammoniacal after ammonia had been formed by reduction or by hydrolysis.

[6] At Hg, accurate measurement was impossible due to the formation of ammonium amalgam, but H evolution could scarcely be observed during the reduction.

[7] This may be due to the disappearance of formamidine. It may be possible that the decomposition of formamidine is affected by current through its discharge.

[8] The influence of current density could not be measured due to the variation of pH with the variation of current density.

[9] At about this time, the variation of pH with current was relatively small.

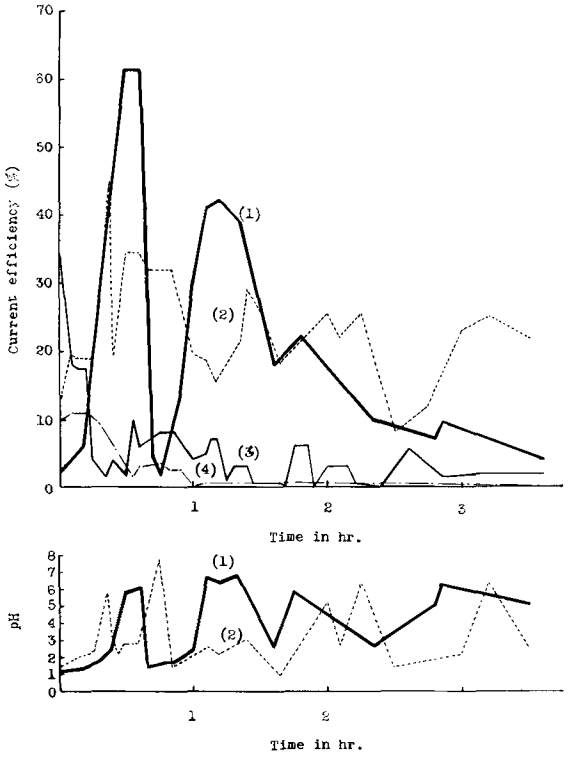


Fig. 3. Current efficiency at various cathodes (reduction of formamidine): 1, Pb; 2, Sn; 3, Pd; 4, Cu; conditions: same as in Table II.

active cathodes other than Sn, as shown in Fig. 3, and was a characteristic of formamidine reduction. This is the reason of great irregularities in current efficiency-time curves in Fig. 3.

### *Formation of Formaldehyde by Reduction of Formamidine; Indirect Confirmation of Methylenediamine as the Intermediate*

In the preceding paper, it was pointed out that in the course of the reduction of cyanamide at Sn, formamidine—the intermediate—was not only reduced to methylamine and ammonia, but hydrolyzed to ammonia and formic acid. In that case, the formation of formaldehyde was very small and barely confirmed. However, as described above, the reduction of formamidine at Hg gave a large amount of hexamethylenetetramine as follows.

Ten grams of formamidine sulfate was reduced at Hg under the same conditions as in Table II. After 13.8 amp-hr passed, the catholyte was worked up according to the procedure described above to the methanol extraction; 8.8 g ammonium sulfate was obtained. The methanol extract[10] was then concentrated to 30 cc under diminished pressure and allowed to stand until it reached to room temperature. Some crystals were separated (0.40 g). The filtrate was again evaporated to dryness to give further crops of the same crystals. The combined crystals were purified from methanol by dilution of a methanolic solution with ether, yield 1.0 g. The characteristic $HgCl_2$ compound was then prepared, mp 225°-230°C dec.

[10] When the methanol extract was allowed to cool, a small amount of brilliant crystals were separated. This was filtered off, washed with methanol, and dried in a desiccator. Yield 0.02 g, mp 215°C, picrate mp 185°-186°C. The identification of this compound has not yet been carried out.

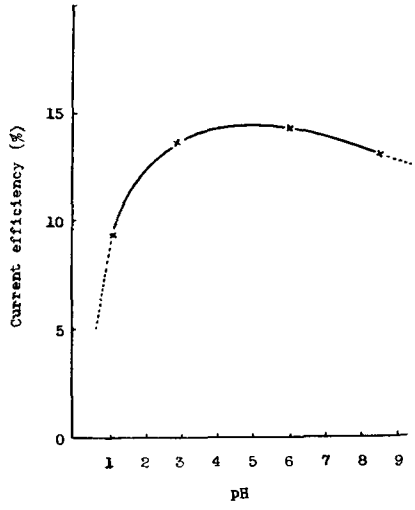


Fig. 4. Effect of pH on current efficiency at Sn (reduction of formamidine); conditions: Same as in Table II.

The isolation of hexamethylenetetramine suggested the formation of formaldehyde in the catholyte. Moreover, a small amount of formaldehyde was also recovered with formic acid from the reduction product at Pb. This may be due either (*a*) to the hydrolysis of methylenediamine which may be the intermediate from formamidine to methylamine and ammonia or (*b*) to the reduction of formic acid formed by the hydrolysis of formamidine itself. The reduction of formic acid [catholyte: 6.8 g ammonium formate in 100 cc 5% $(NH_4)_2SO_4$; other conditions: the same as in Table II] was then carried out at *p*H 2-7 at Sn and at Hg. Hydrogen was evolved quantitatively and no products were obtained after 11.6 amp-hr of current was passed.

It may be seen, therefore, that formaldehyde was formed by the hydrolysis of methylenediamine. To confirm it, methylenediamine was prepared by the procedure of Knudsen (4) and the hydrolysis and the reduction of it were carried out.

Methylenediamine 2HCl, needle crystal

Anal. Calc'd for $CH_8N_2Cl_2$: N, 23.9; Cl, 59.6

Found: N, 24.0; Cl, 60.9

2.3081 g sample in 100 cc water acidified with 2 cc HCl was subjected to distillation. 0.567 g, 98% formaldehyde[11] was found in the distillate (50 cc) by the $Na_2SO_3$ method. 0.648 g, 98% $NH_3$ was recovered from the residue as usual.

This indicated the quantitative formation of formaldehyde and ammonia by hydrolysis as well as the authenticity of the sample.

Then the electrolytic reduction of methylenediamine was carried out at Sn to confirm the formation of methylamine.

After reduction, the catholyte (140 cc) was acidified with HCl and subjected to distillation to give 120 cc distillate. Further distillation of the residue with 30 cc water and 3 cc HCl gave 30 cc second distillate. Formaldehyde in the combined distillate was determined by $Na_2SO_3$ method. The distillation residue was diluted with water and evaporated to

[11] Identified as dimedon derivative, mp 187°-188°C.

**Table III**

Anode: Pt
Anolyte: 60 cc 5% $H_2SO_4$
Catholyte: 5.95 g methylenediamine 2HCl, 8.0 g $NH_4Cl$, 80 cc $CH_3OH$, 50 cc $H_2O$ (initial *p*H 1.2). *p*H* adjusted at 1-7 by adding a small amount of HCl.
Temp: 6°-8°C
Current density: 3 amp/dm²
Amount of current: 7 amp-hr†
Results: Pure methylamine HCl obtained: 0.56 g, 18% (based on methylenediamine used) mp 210°C, picrate mp 200°C; methylguanidine picrate was then prepared, mp 198°C. Formaldehyde (resulted from unconverted methylenediamine and its hydrolytic product): 0.84 g, 56%.

* In the reduction of methylenediamine, keeping *p*H in a desirable range was very easy as compared with that in cyanamide or formamidine reduction.
† The electrolysis was conducted until hydrogen began to evolve quantitatively.

dryness. The solid, after drying overnight in a vacuum-desiccator over $P_2O_5$, was extracted with 50 cc hot butanol. From the extract, methylamine hydrochloride was collected by working up as described above and weighed.

Results are shown in Table III.

5.95 g methylenediamine 2HCl was also reduced at Hg and at Pb under conditions similar to those in Table III. Although the efficiency was smaller than that at Sn, the reduction occurred to give 0.1 g and 0.15 g methylamine hydrochloride after 6.12 amp-hr and 2.68 amp-hr of current was passed, respectively.[12]

These results might be proofs for existing methylenediamine as the intermediate of the reduction of formamidine.

## Polarographic Measurement[13]

Polarographic measurement was carried out for cyanamide and formamidine in order to explain the results obtained by macroelectrolysis more clearly.

[12] In these cases, formaldehyde could not be obtained from the product. At present, this is a problem we still can not understand.

[13] This was carried out by T. Sekine in our laboratory.

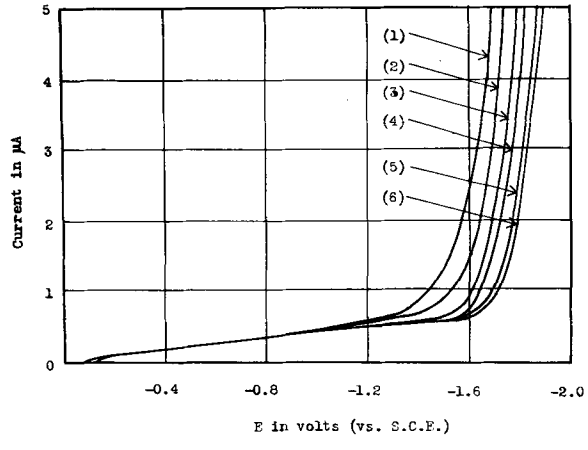


Fig. 5. Polarograms of cyanamide. Concentration of cyanamide: 1, 1.2 mole/l; 2, 2.4 × $10^{-1}$ mole/l; 3, 4.8 × $10^{-2}$ mole/l; 4, 9.5 × $10^{-3}$ mole/l; 5, 1.9 × $10^{-3}$ mole/l; 6, 0 (supporting electrolyte). Supporting electrolyte: 7.456 g KCl/l Sorensen's phosphate buffer solution (pH 6.75); sensitivity of galvanometer: 6.58 × $10^{-8}$ amp/mm; dropping mercury electrode: m = 1.67 mg/sec, t = 2.55 sec ($m^{2/3}$ $t^{1/6}$ = 1.65), h = 72 cm.

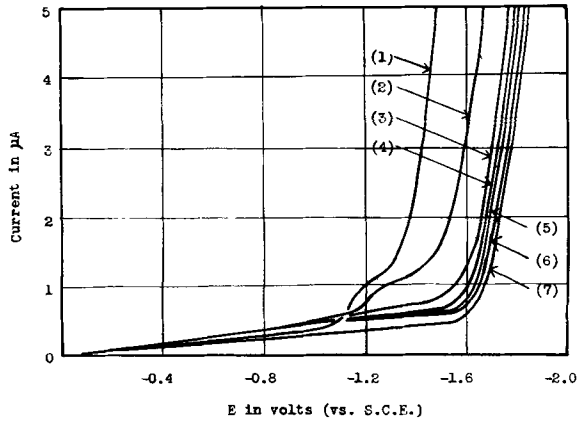


Fig. 6. Polarograms of formamidine sulfate. Concentration of formamidine: 1, 3.5 mole/l; 2, 1.2 mole/l; 3, 2.4 × $10^{-1}$ mole/l; 4, 4.8 × $10^{-2}$ mole/l; 5, 9.5 × $10^{-3}$ mole/l; 6, 1.9 × $10^{-3}$ mole/l; 7, 0 (supporting electrolyte). Supporting electrolyte: 7.456 g KCl/l Sorensen's phosphate buffer solution (pH 6.75); sensitivity of galvanometer: 6.58 × $10^{-8}$ amp/mm; dropping mercury electrode: m = 1.67 mg/sec, t = 2.55 sec ($m^{2/3}$ $t^{1/6}$ = 1.65), h = 72 cm.

Polarograms for cyanamide and formamidine sulfate are shown in Fig. 5 and Fig. 6.

Cyanamide: No distinct wave was detected prior to hydrogen discharge wave. The shift of H wave to a more positive potential with increasing concentration of cyanamide was observed.

Formamidine sulfate: No wave was detected up to the concentration of $10^{-2}$ M in Sorensen buffer (*p*H 6.75). However, in 1M solution, a wave appeared at $E^{1/2}$, —1.20 v (vs. S.C.E.). This is probably due to the reduction of undissociated molecule of formamidine, because this wave disappeared at *p*H 2.2 even in 1M solutions.[14] The shift of H wave to a more positive potential with increasing concentration of formamidine was also observed.

## Nature of Two Successive Reductions of Cyanamide

By combining the results of these studies, it is seen that two successive reductions of cyanamide have different natures from the viewpoint of electrochemical reduction. That is, the first step reduction is an exceptionally slow process and affected by the use of cathode material having catalytic action. On the other hand, the second step reduction may be a voltage-controlled one and affected by the use of cathode material having a high H overvoltage. Thus the most active cathode for one step may not be the most effective for another. For the over-all reduction process, Sn was the only effective cathode material among the cathodes used. This may be a problem in electro-organic reduction.

Moreover, the second step reduction was greatly influenced by *p*H. This is the reason for the necessity of adjusting the *p*H between 2-7 in order to carry out the reduction of cyanamide to the final state.

These gained support from the results of polarographic measurement.

## Conclusions

1. The reduction of cyanamide occurred at Pd smoothly to give formamidine in a fair yield. Tin

[14] This accounted for no occurrence of macroreduction below pH 2.

seems to have a mediocre activity toward this reduction, but the reduction could proceed beyond the formamidine level to methylamine and ammonia. Lead and mercury were not so effective for this reduction.

2. The reduction of formamidine, on the other hand, was effected by the use of cathodes having a high H overvoltage, such as Sn, Pb, Hg.

3. For the over-all reduction process, Sn was the only effective cathode material among the cathodes used in this study.

4. The formation of a large amount of formaldehyde at Hg suggested the existence of methylenediamine as second intermediate. This was further supported by the fact that methylenediamine gave methylamine by the reduction at Sn and other cathodes. The complete mechanism is as follows.

$$NH_2CN \xrightarrow{2H} NH_2 \cdot CH{=}NH \xrightarrow{2H}$$

$$NH_2 \cdot CH_2 \cdot NH_2 \xrightarrow{2H} NH_3 + CH_3NH_2$$

Main side reactions are

$$NH_2 \cdot CH{=}NH \xrightarrow{2H_2O} 2NH_3 + HCOOH$$

$$NH_2 \cdot CH_2 \cdot NH_2 \xrightarrow{H_2O} 2NH_3 + HCHO$$

Low yield of the final products was seen to be due to the hydrolysis of two intermediate compounds.

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Any discussion of this paper will appear in a Discussion Section to be published in the June 1959 JOURNAL.

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# The Measurement of Magnetic Fields in Aluminum Reduction Furnaces

**J. H. Kent**

*Research Department, British Aluminium Company Limited, Kinlochleven, Argyll, Scotland*

ABSTRACT

The efficient operation of aluminum reduction furnaces of capacities greater than about 50 KA is affected by electromagnetic forces acting in the molten bath. Measurement of the magnetic fields which give rise to these forces is made difficult because of the high temperature and corrosive nature of the molten bath. A technique is described which overcomes these difficulties. Results are given of measurements made in the baths of furnaces operating at 100 KA with different conductor layouts. It is shown how conductor layout design affects the magnetic characteristics of the furnace.

Electromagnetic forces acting in the molten bath, i.e., both metal and electrolyte, of an aluminum reduction furnace are known to affect the performance of the furnace and reduce its current efficiency (1, 2). Particularly is this so in large furnaces operating at currents above 50 KA. Briefly, their effect is to set the bath in motion and displace the molten metal layer, thus upsetting those stable conditions which are known to be essential for efficient operation. The forces can be divided into two main categories: those that arise from the interaction between the vertical component of the current and the horizontal component of the magnetic fields in the bath, and those that arise from the interaction between the horizontal component of the current in the molten metal and the vertical and horizontal components of the magnetic fields. To reduce the effect of electromagnetic forces it is necessary to reduce as much as possible and make suitably symmetrical the magnetic fields in the bath and to reduce the horizontal component of the current in the metal layer. The magnetic fields can be reduced and made suitably symmetrical by various arrangements of busbars and by magnetic shielding, such as the methods devised by Elektrokemisk (3, 4). Similarly, the horizontal component of the current in the molten metal layer can be reduced by various designs of current feed and collection such as, for instance, the methods of current collection devised by Thayer (5) or Elektrokemisk (6).

An exact calculation of the magnetic fields in the bath of a furnace is made extremely difficult by saturation and temperature effects in the steel parts of a furnace and steel structures close to it. For this reason, a design based on calculations alone may fall far short of achieving minimum magnetic fields in the bath. The use of scale models such as described by Böckman (7) overcomes many of the difficulties. However having laid down an experimental furnace in the furnaceroom to a design