The Influence of Metallic Impurities in the Electrolyte in Sodium Chloride Electrolysis by the Mercury Process. III. Magnesium in the Presence of Cr, Fe, Co, Ni and Cu

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Magnesium was known to be harmful in chlorine-caustic electrolysis by the mercury process when it coexisted with iron or nickel. The authors intended to study systematically the influence of magnesium in the presence of those metals which were reduced to metallic state on cathode and the effect of pH on hydrogen evolution caused by the combination of the metals. Hydrogen evolution was accelerated by the presence of metals but was retarded at low pH value. It is supposed that magnesium hydroxide formed on the mercury surface hinders the deposited metal from migrating and coagulating in small spots, and as a result fine granules of metal attached to hydroxide granules are dispersed over the surface and they take part in hydrogen evolution. At low pH value the hydrogen evolution is retarded due to the increasing solubility and decreasing deposition of the hydroxide.

1 Introduction

The influence of magnesium in the presence of iron or nickel was investigated by Walker, Somiya and G. Angel. The intention of this investigation was to study the influence of magnesium in the presence of those metallic impurities which were reduced to metallic state on mercury cathode and the effects of pH and of mercury added to the electrolyte.

2 Experimental

The experiments were carried out in the same way as described in the previous papers. Hydrogen evolution and cathode potential were measured against time under controlled current electrolysis. The added impurities were magnesium chloride, nickel chloride, ferrous sulfate, cobalt acetate, potassium bichromate and copper sulfate.

The experiments were carried out at pH 6.0~7.0 in case not otherwise stated.

3 Results and Discussion

3.1 Hydrogen evolution did not exceed that of blank in the presence of magnesium less than 1.0 mM/l, in the presence of chromium and the other impurities less than 0.1 mM/l except trivalent chromium ion.

3.2 Magnesium in the Presence of Hexavalent Chromium

The results obtained are shown in Fig. 1. The magnesium concentration was kept constant at 1.0 mM/l while the chromium concentration was varied from 0.04 to 0.004 mM/l.

Neither magnesium nor chromium affected hydrogen evolution and the cathode potential over the concentration range when they were present independently. Marked increase in hydrogen evolution and rise of cathode potential were observed when they were present together. But the hydrogen evolution was retarded at low pH value.

The codeposition of magnesium hydroxide with chromium is supposed to hinder the migration and coagulation of the metal in small spots, and thus dispersed chromium causes the increased hydrogen evolution, because large area of the cathode is covered with magnesium hydroxide to which chromium

a. Relation between cathode potential and time

b. Relation between the volume of hydrogen and time

1~6: Mg 1 mM/l, 7: Mg 0 mM/l, 1: Cr 0.04 mM/l,
2: Cr 0.02 mM/l, 3: Cr 0.01 mM/l, 4: Cr 0.004 mM/l,
5: Cr 0.01 mM/l, pH=3.0, 6: Cr 0 mM/l, 7: Cr 0.04 mM/l,
 $t=14\sim16^{\circ}\text{C}$

Fig. 1 Influence of Mg in the presence of Cr

a. Relation between cathode potential and time

b. Relation between the volume of hydrogen and time

1~6: Mg 1 mM/l, 7: Mg 0 mM/l, 8: Mg 5 mM/l,
1: Fe 0.1 mM/l, 2: Fe 0.04 mM/l, 3: Fe 0.02 mM/l,
4: Fe 0.01 mM/l, 5: Fe 0.002 mM/l, 6: Fe 0 mM/l,
7: Fe 0.1 mM/l, 8: Fe 0.2 mM/l, $t=16\sim18^{\circ}\text{C}$

Fig. 2 Influence of Mg in the presence of Fe

attaches due to its low hydrogen over-voltage. On the contrary, when chromium is present independently, deposited chromium can freely migrate on the surface and coagulate in small spots, and so a large area of clean surface on which sodium ion discharge proceeds. The effect of pH is interpreted as retarded deposition of magnesium hydroxide due to its increase in solubility.

3.3 Magnesium in the Presence of Iron

The cathode potential was observed to rise at the initial stage and then to fall compared with the normal decomposition potential of sodium ion. The deviation of the cathode potential from the normal value increased with increasing concentration. The hydrogen evolution was promoted at the initial stage when the rise of cathode potential occurred, but it was retarded afterward when the potential began to fall.

At low pH value, the phenomenon of the potential rise and successive fall was delayed until the pH value became higher due to the hydrogen evolution. The rapid increase of hydrogen evolution was delayed until the potential began to rise. The hydrogen evolution caused by magnesium in the presence of iron was reduced at low pH value.

The promotion of hydrogen evolution is supposed to be caused by the same mechanism as described above (3.2), and the successive retardation of hydrogen evolution is supposed to be due to the growth of magnesium hydroxide in film and iron was included in it and inhibited the evolution of hydrogen.

3.4 Magnesium in the Presence of Cobalt

The rise and oscillation of cathode potential were observed when cobalt was present simultaneously

with magnesium as shown in Fig. 3. The oscillation was accompanied by the rippling of mercury surface. Hydrogen evolution was also promoted. The mechanism of the promotion of hydrogen evolution is supposed to be the same as mentioned previously in the case of other combinations.

a. Relation between cathode potential and time

b. Relation between the volume of hydrogen and time

1: Mg 5 mM/l, 2: Mg 2 mM/l, 3~6: Mg 0.4 mM/l, 1~3: Co 0.04 mM/l, 4: Co 0.02 mM/l, 5: Co 0.01 mM/l, 6: Co 0.04 mM/l, $t = 15 \sim 16^\circ\text{C}$

Fig. 3 Influence of Mg in the presence of Co

3.5 Magnesium in the Presence of Nickel

The results are shown in Fig. 4. Hydrogen evolution was promoted in this combination but at low pH value it was retarded. The cathode potential did not fall or rise in this case.

3.6 Magnesium in the Presence of Copper

Hydrogen evolution was promoted at the initial stage when copper and magnesium were present together but was retarded afterward when the cathode potential became more cathodic, as shown in Fig. 5.

The hydrogen evolution caused by this combination was fairly well retarded by mercury added to the electrolyte, as shown in Fig. 6.

Hydrogen evolution was retarded at low pH value as shown in Fig. 7.

The effect of mercury is supposed to be due to the amalgamation of deposited copper attached to the hydroxide by deposited mercury.

Summary

Magnesium less than 1.0 mM/l, chromium and other impurities less than 0.1 mM/l did not cause hydrogen evolution when they were present independently, but when they were present together with

1~6: Mg 1 mM/l, 1: Ni 0.01 mM/l, 2: Ni 0.02 mM/l, 3: Ni 0.04 mM/l, 4: Ni 0.1 mM/l, 5: Ni 0.1 mM/l, pH=3.0, 6: Ni 0.04 mM/l, pH=3.0

Fig. 4 Influence of Mg in the presence of Ni

a. Relation between cathode potential and time

b. Relation between the volume of hydrogen and time

1~6: Cu 0.2 mM/l, 1: Mg 5 mM/l, 2: Mg 2 mM/l, 3: Mg 1 mM/l, 4: Mg 0.5 mM/l, 5: Mg 0.2 mM/l, 6: Mg 0 mM/l, $t = 31^\circ\text{C}$

Fig. 5 Influence of Mg in the presence of Cu

a. Relation between cathode potential and time

b. Relation between the volume of hydrogen and time

1~8: Mg 0.5 mM/l, Cu 1 mM/l, 1: Hg 0 mM/l,
 2: Hg 0.1 mM/l, 3: Hg 0.5 mM/l, 4: Hg 0.8 mM/l,
 5: Hg 1 mM/l, 6: Hg 1.2 mM/l, 7: Hg 1.5 mM/l,
 8: Hg 3 mM/l, $t=24^{\circ}\text{C}$

Fig. 6 Influence of Hg in the presence of Mg+Cu

supposed to be due to the codeposition of magnesium hydroxide with metal. The hydroxide hinders the migration and coagulation of the metal. The metal attached to the hydroxide is dispersed over the cathode surface and takes part in hydrogen evolution.

At low pH value, hydrogen evolution is retarded due to increasing solubility and to decreasing deposition of the hydroxide.

Retardation of hydrogen evolution in relation with the cathode potential fall observed in the cases of iron and copper in the presence of magnesium is supposed to be due to the growth of the hydroxide in film which includes codeposited metal and hinders it from taking part in hydrogen evolution.

Mercury added to the electrolyte retarded the hydrogen evolution due to copper which is easily amalgamated.

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a. Relation between cathode potential and time

b. Relation between the volume of hydrogen and time

1~4: Cu 0.2 mM/l, 1: Mg 5 mM/l, 2: Mg 2 mM/l,
 3: Mg 1 mM/l, 4: Mg 0 mM/l, $t=31^{\circ}\text{C}$

Fig. 7 Influence of Mg in the presence of Cu (pH=3.0)

magnesium they caused hydrogen evolution. At low pH value, hydrogen evolution was retarded.

The promotion of hydrogen evolution is sup-

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