

-

Characteristics of a Continuous Denitration by Formic Acid - Electrolytic Trimming of Residual acid with accompanying the precipitation of metal ions.

+, , ,

150, 305-600

-

. Zr, Mo, Nd, Fe

Mo

/

1.65

,

가 0.1M

가

,

Zr, Mo

가

95%,

83%

Abstract

This work has studied the characteristics of destruction of nitric acid and precipitation of several metal ions in a continuous denitration process combining a denitration by formic acid and a residual acid-electrolytic trimming system. The metal ions of Zr, Mo, Fe, and Nd did not affect the electrodes at the step of electrolytic trimming of the residual acid after denitration by formic acid. The Mo ion in electrolytic solution enhanced the generation of nitrite ion during the electrolytic reaction. The mole ratio of formic acid to nitric acid fed into the continuous denitration reactor using formic acid affected much the final acidity, the precipitation yields of metal ions, the precipitate morphology. At the ratio of 1.65, the process had the lowest final acidity of less than 0.1 M, and the precipitation yields of Zr and Mo reached 95% and 83%, respectively as the highest values.

1.

[1-8],

JAERI

[3,4]

가

1.5

가

[9,10]

Zr, Mo

Zr Mo

3 (third phase)

(emulsification)

Zr Mo

가

Zr, Mo, Fe

Nd

2.

[9,10] 125 ml

Pyrex column

96°C

가 .

Ti Ti

voltammogram 가 Fig.1 . Fe, Nd, Zr

i-V 2.0 M background i-V 가

Mo가 -0.2 V -0.4 V

Mo , Mo

20 80 mA/cm² Ti-IrO₂ EPMA

(Electron probe microanalyzer) , Ti

-0.2 V -0.4 V Mo Mo

Mo가 -0.2 V -0.4 V (1) (2) (3)

. [15,16]

$\text{NO}_3^- + 3\text{H}^+ + 2\text{e}^- = \text{HNO}_2 + \text{H}_2\text{O} \quad E_o = +0.94 \text{ (V vs SHE)}$ (1)

$\text{HNO}_2 + \text{H}^+ + \text{e}^- = \text{NO} + \text{H}_2\text{O} \quad E_o = +0.97 \text{ (V vs SHE)}$ (2)

$\text{NO} + \text{NO}_3^- + 2\text{H}^+ + \text{e}^- = 2\text{HNO}_2 \quad E_o = +0.517 \text{ (V vs SHE)}$ (3)

$\text{HNO}_3 + 2\text{NO} + \text{H}_2\text{O} = 3\text{HNO}_2$ (4)

1.0 M 0.5 M voltammogram

가 Fig.2 . Fig.1 Mo가 -0.2 V -0.4

V . Fig.2

Fig.2 -0.2 V -0.4 V (2)

- (4)

(1)

[15,16] Fig.1

Mo

-0.2 V -0.4 V

Mo

(1)

(2)

(4)

Mo가

가 Mo가

(2)-(4)

(2)

(3)

가

가

Mo

0.069

M

0.5 M

2.0 M

voltammogram

Fig.3

Mo

Fig.1

-0.2 V

-0.4 V

가

가

Nd, Fe, Zr

-0.2 V

-0.4 V

가

, Mo가

-0.2 V

-0.4 V

가

Mo

Fe, Nd, Zr

(1)

. Mo

Fe, Nd, Zr, Mo

Ti-IrO₂

400 mA/cm²

15

가 Fig.4

Fe, Nd, Zr

Mo가

2

Fe, Nd, Zr

Mo

Mo

Mo, Zr, Fe, Nd

2.0 M

1.0 ml/min

/

1.75

96°C

100mA/cm²

가

50°C

3 IrO₂-Ti

가

Fig.5

/

[9,10]

가

0.1 M 0.2 M

가 1.5 1.6 가

가

가

Fig.6

1.75

3

가

[9]

30

2.0 M

1.54 M, 0.72 M, 0.42 M, 0.15 M

Fig.7

Fig.6

3

, ,

,

.

,

[9]

가

10^{-3} M

.

가

(nitrate)

가 pH가

. [9] ,

Fig.8

/

가

가

. Fig.5

/

가 가

가

,

/

가

가

,

IrO₂-Ti

가

1.5

[9,10]

/

가 1.65

가

.

Fig.9

/

가

Zr, Mo, Fe, Nd

가

Zr, Mo

/

가 1.25

70%, 60%

/

가 가

가

1.65 95%,

83%

가

/

가 2.0

가

.

1.65
 가
 Fe 10 15% , Nd 1 4%
 Zr, Mo 100% , Nd 0.1M Fe,
 90% 가 0 M 가
 / 가
 1.65

[7]
 Fig.10 / 가
 morphology SEM 가
 / 가 1.25 ,
 / 가 1.5, 1.65 2 μ m ,
 / 가 2.0 0.1 0.2 μ m 1 3 μ m

Fig.5 Fig.10
 가 0.1M
 0.5 M , Zr,
 Mo

5.

Zr, Mo
 0.1 M Zr, Mo, Nd, Fe
 Mo

가 가 / 가 1.65
 가 가 .
 /
 / 가 1.65 Zr Mo 95% 83%
 Fe 10%, Nd 4%
 /
 / 가 1.5 1.7
 가 .

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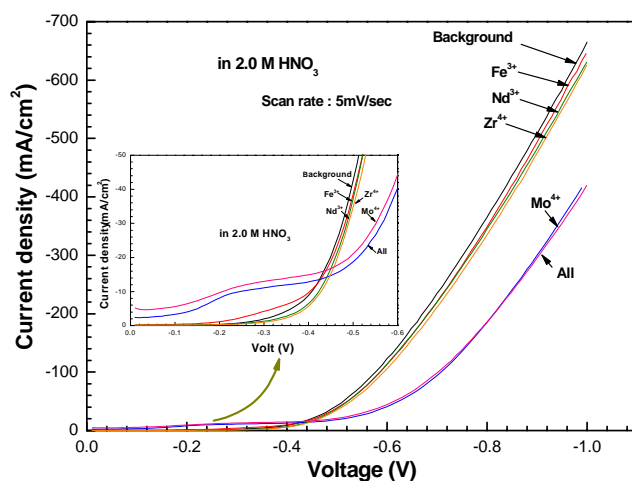


Fig.1 Linear voltammograms of 2.0 M nitric acid solutions with and without metal ions at Ti cathode.

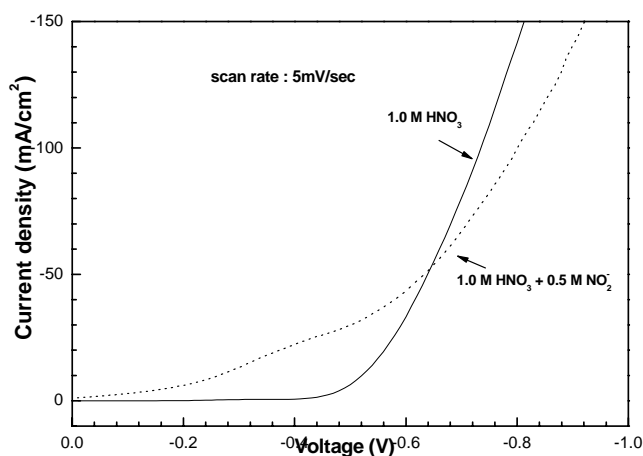


Fig.2 Linear voltammograms of 1.0 M nitric acid solution and of a mixture of 1.0 M nitric acid and 0.5 M nitrite ion at Ti cathode.

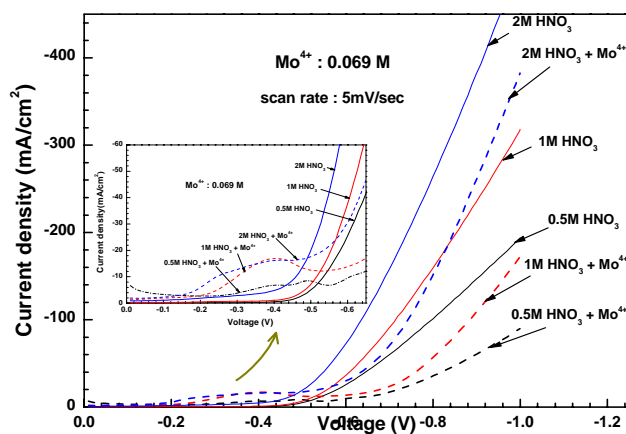


Fig.3 Linear voltammograms of the solutions of several nitric acid concentrations with Mo ion of 0.069 M at Ti cathode.

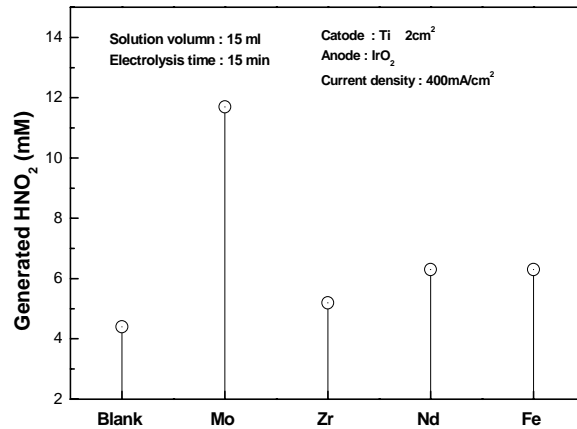


Fig.4 Amounts of nitrite ion generated in 2.0 M nitric acid solutions with each metal ion for 15 minutes by Ti cathode at 400 mA/cm².

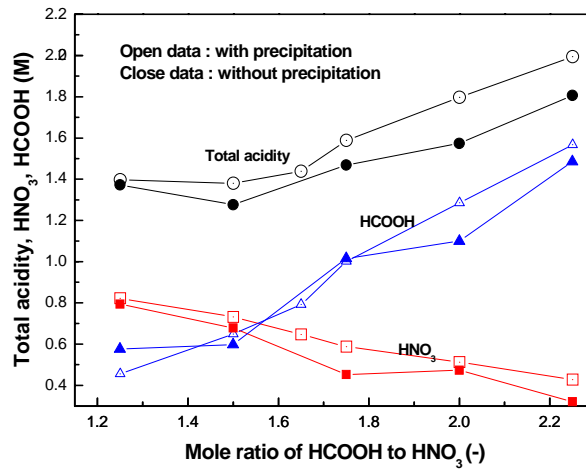


Fig.5 Changes of total acidity, nitric acid, and formic acid at the continuous denitration reactor in the cases with and without the precipitation of metal ions with a change of mole ratio of formic acid to nitric acid.

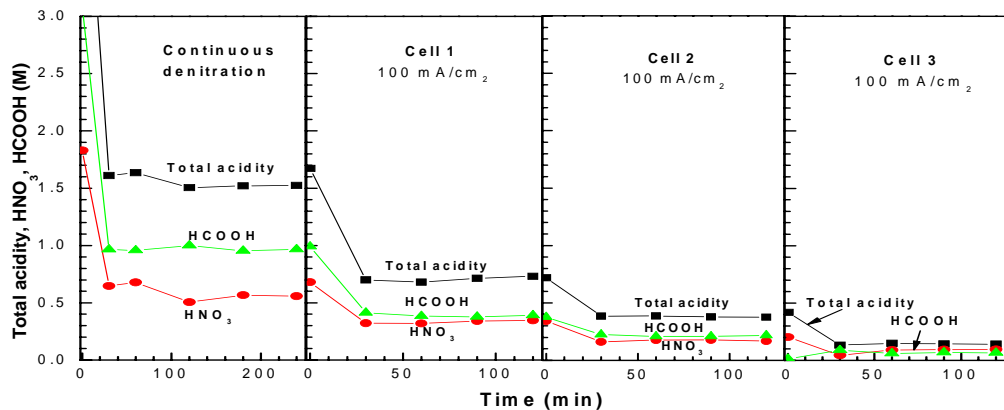


Fig.6 Changes of total acidity, nitric acid and formic acid at each step of the continuous denitration reactor and the electrolytic cells accompanying the precipitation of metal ions with a change of denitration time at a mole ratio of formic acid to nitric acid of 1.75.

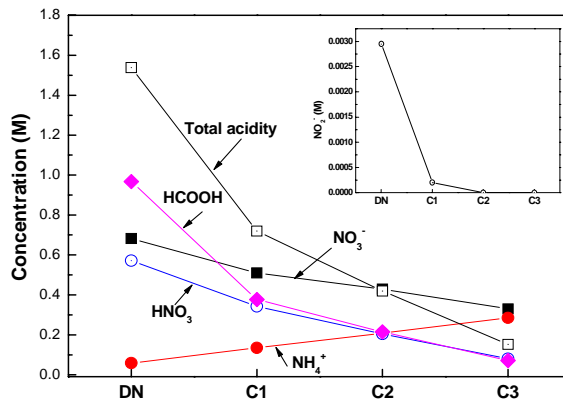


Fig.7 Changes of several species at each step of the continuous denitration reactor and the electrolytic cells accompanying the precipitation of metal ions at a mole ratio of formic acid to nitric acid of 1.75.

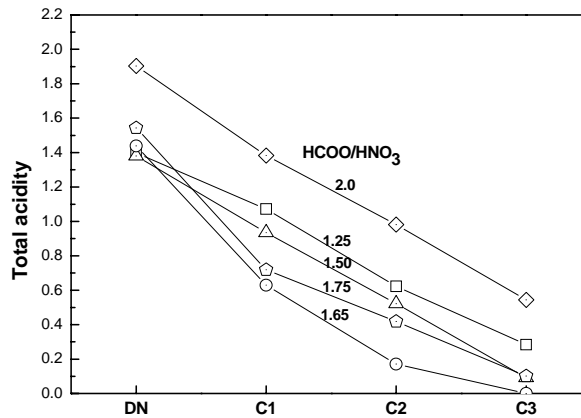


Fig.8 Changes of total acidities at each step of the continuous denitration reactor and the electrolytic cells accompanying the precipitation of metal ions at several mole ratios of formic acid to nitric acid.

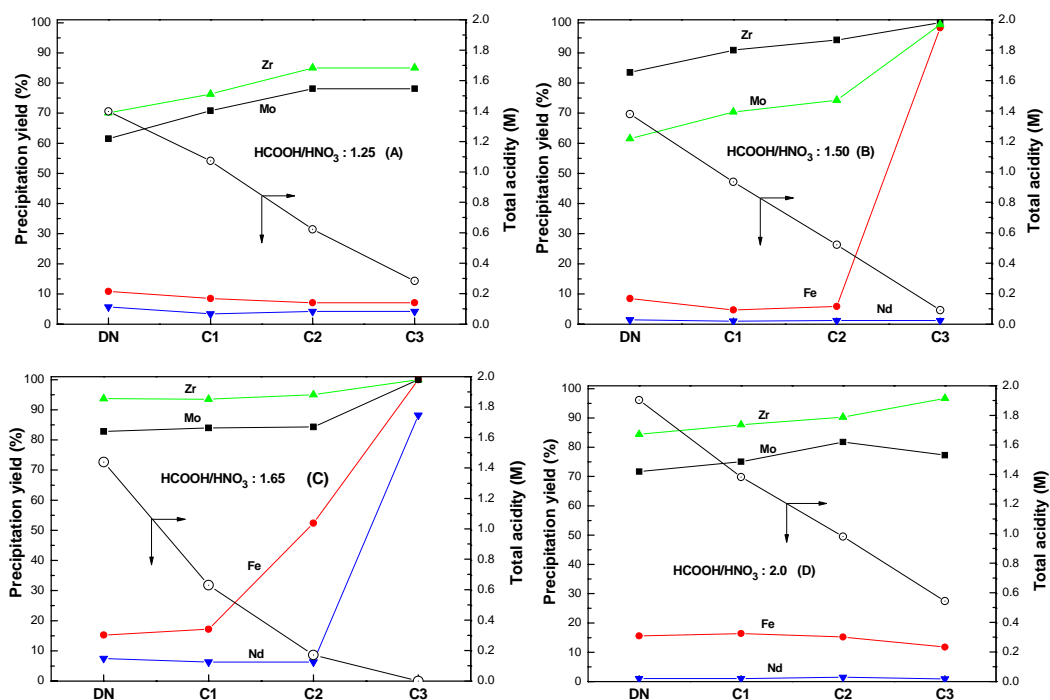
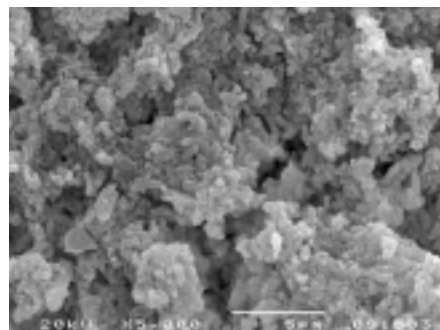
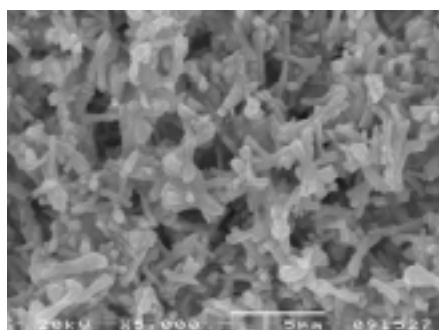


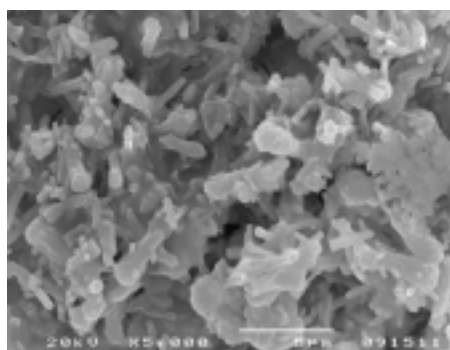
Fig.9 Precipitation yields of metal ions and total acidities at each step of the continuous denitration reactor and the electrolytic cells at several mole ratios of formic acid to nitric acid.



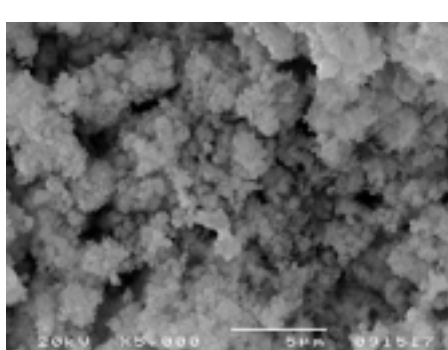
(A) HCOOH/HNO₃ : 1.25



(B) HCOOH/HNO₃ : 1.50



(C) HCOOH/HNO₃ : 1.65



(D) HCOOH/HNO₃ : 2.0

Fig.10 SEM photographs of precipitates generated in the continuous denitration reactor with the mole ratio of formic acid to nitric acid.