

Purification of Manganese Chloride with Chelating Resin Containing Iminodiacetate Groups in Ammonium Chloride Solution

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The demand for high-purity Mn is growing in the field of advanced electronics devices. Chromatographic separation using chelating resins is useful for pre-concentration of metal ions prior to the determination of metallic elements by chemical analysis. This separation technique can be applied to the recovery of hazardous substances from industrial waste. In the present study, this separation technique was applied to the purification of Mn for the first time. Separation was carried out in an ammonium chloride medium because Mn can be recovered by electrowinning in the final step. Ammonium chloride added to the electrolyte is useful for improving the current efficiency during electrowinning of Mn. The optimum separation process was examined according to the recovery ratio of Mn and the elimination ratio of each impurity derived from the elution curves. [doi:10.2320/matertrans.MRA2007183]

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1. Introduction

The recent remarkable development of the advanced electronics industry requires increasingly higher-purity materials. For instance, high-purity Fe for β -FeSi₂, which is regarded as a promising material for optical devices,¹⁾ high-purity Co for CoSi₂, an alternative to TiSi₂ used in ULSI,²⁾ High-purity Mn is also essential as a raw material for CuMn alloys used as interconnection in ULSI,³⁾ for FeMn, PtMn, PtPdMn and GaMnAs alloys used as anti-ferromagnetic substances or magnetic semiconductor^{4,5)} and for CdMnTe used as an optical isolator.⁶⁾ Thus, the demand for high-purity Mn continues to grow rapidly.

Purification of Mn by anion-exchange separation was reported by M. Nardin.⁷⁾ This Mn still contains a few mass ppm of transition metal elements, so it is not sufficiently pure for use in advanced electronic materials.

Purification processes generally consist of several steps involving hydrometallurgical and pyrometallurgical techniques, such as purification of electrolyte, electrowinning or electrorefining, distillation or sublimation, and melting. The hydroelectrometallurgical route yields relatively pure Mn. This electrolytic Mn usually has a nominal purity of 99.4–99.8% and contains a few hundred mass ppm of S contamination because electrowinning of Mn generally involves the use of a sulfate electrolyte.⁸⁾ Further purification of Mn requires the removal of metallic impurities before electrowinning.

Chelating resins are widely used and are commercially available worldwide. Their applications are separation and pre-concentration of metal ions prior to analysis or recovery of harmful substances from industry waste. Their absorption mechanism and various characteristics have been investigated by many researchers.^{9–11)} The characteristics of ion exchange resins, whose functions are similar to those of chelating resins, have also been investigated and employed in the purification of various metals using the column method.^{12–17)}

Thus, this paper deals with the application of separation using chelating resins to the purification of Mn in a chloride medium, which is used as an electrolyte after separation. Chloride was selected instead of sulfate because the chloride electrolyte prevents S contamination. In the case of the chloride electrolyte, NH₄Cl needs to be added to improve the current efficiency.¹⁸⁾ The addition of NH₄Cl after separation causes additional contamination, thus, NH₄Cl should be added prior to separation. However free Cl[−] and NH₄⁺ ions are formed in the aqueous phase, and the effect of these ligands should be considered.

Figure 1 shows the concentration of metal ions absorbed on the chelating resin UNICELLEXTM UR-30, whose functional group is iminodiacetate,¹⁹⁾ from hydrochloric acid solution as a function of pH. The absorption of some ions on the chelating resins is equal to desorption of the H⁺ ions. Thus, there is the difficulty that the pH would decrease and the absorption behavior would be affected when a large concentration of some ions are absorbed. But the change of pH during the separation is expected to be suppressed because the concentrations of metal ions that can be absorbed

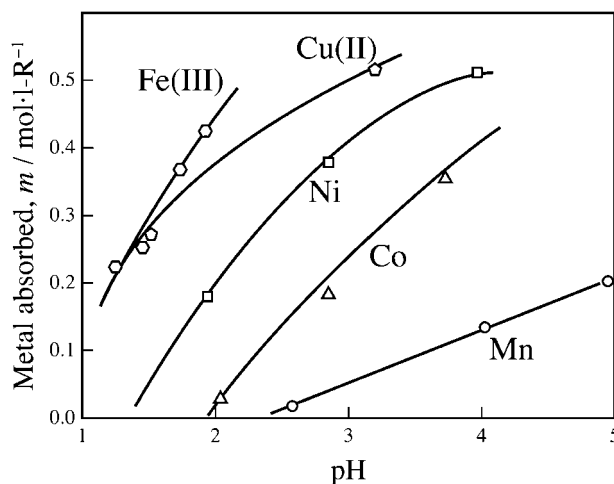


Fig. 1 Sorption of certain metals on a chelating resin whose functional group is iminodiacetic acid as a function of pH.

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on the chelating resins are small in the aqueous phase and Mn is not absorbed strongly. Thus, the effect of pH variation is negligible during the purification procedure.

On the basis of the above observations, a novel purification process of electrolyte used for Mn electrowinning from NH_4Cl media is proposed. An aqueous solution of electrolytic Mn or MnCl_2 is prepared and the pH is adjusted for chromatographic separation by chelating resins. This separation technique is intended to remove metallic impurities; it is hoped to allow the extraction of high purity Mn by electrowinning directly from the collected effluent.

In this study, purification of MnCl_2 with chelating resins in NH_4Cl media was investigated and optimized for the purification of Mn in particular.

2. Experimental

Chromatographic separation tests were carried out in order to examine the effect of pH and flow rate on the separation efficiency.

Commercial special grade chemical reagents, and distilled and de-ionized water with a resistivity above $18\text{ M}\Omega$ were used throughout this work, and all experiments were conducted at room temperature. The chelating resin used as a stationary phase in this study, UNICELLEXTM UR-30S, whose functional group is iminodiacetate, was supplied by UNITIKA LTD. This is a gel-type chelating resin. The difference between UR-30 and UR-30S is the base material. The base material of UR-30 is polyphenol, while that of UR-30S is polystyrene. They have the same characteristics in terms of metal ion absorption because their functional groups are the same. The resin was packed in a quartz column of 26 mm inner diameter. The height of the resin bed was 260 mm. The resin was rinsed with 1 dm^3 of $2\text{ kmol}\cdot\text{m}^{-3}$ HCl solution and 1 dm^3 of H_2O before separation tests in order to remove organic and inorganic contamination during the manufacturing process.

Eight elements, which are the typical impurities of electrolytic Mn, were selected as test impurities: Al(III), Ca(II), Cr(III), Co(II), Cu(II), Fe(III), Ni(II) and Zn(II). The loading solution for each separation test contained $50\text{ kg}\cdot\text{m}^{-3}$ ($= 0.91\text{ kmol}\cdot\text{m}^{-3}$) of manganese and $\sim 10\text{ g}\cdot\text{m}^{-3}$ each test impurities. These elements were supplied in the chloride form. The loading solution also contained $100\text{ kg}\cdot\text{m}^{-3}$ ($= 1.87\text{ kmol}\cdot\text{m}^{-3}$) ammonium chloride so as to establish the separation as the purification process of the electrolyte used for Mn electrowinning. Finally, the pH of the solutions was adjusted to 2, 4 and 6 by adding NH_4OH solution.

The column was filled with a solution of the same pH as the loading solution prior to the separation. The separation process consisted of three steps: charging the loading solution where Mn just eluted out of the column while impurities would be retained, rinsing with a solution at the same pH as the loading solution, reconditioning with $2\text{ kmol}\cdot\text{m}^{-3}$ HCl solution in order to elute all the impurities remaining in the column. Three flow rates, namely 1, 5 and 10 BV (bed volumes per hour), were tested because chelating reactions generally take a long time so the separation efficiency will be affected by the flow rates. Effluent samples of 50 cm^3 were collected without interruption and analyzed

by inductively coupled plasma atomic emission spectrometry (ICP-AES), using an Optima 3300 manufactured by PerkinElmer, Inc.

The elimination ratio, E , and recovery of manganese, R_{Mn} , were estimated in order to evaluate the chromatographic separation.

$$E = \frac{\sum m_i}{\sum m_{\text{Mn}}} = \frac{c_{i,\text{load}}}{c_{\text{Mn},\text{load}}} \cdot \frac{\int_{V_s}^{V_e} c_{\text{Mn}} dV}{\int_{V_s}^{V_e} c_i dV} \quad (1)$$

$$R_{\text{Mn}} = \frac{100\text{ pct.}}{\sum m_{\text{Mn}}} \cdot \int_{V_s}^{V_e} c_{\text{Mn}} dV \quad (2)$$

where $\sum m_i$ stands for the loaded, and m_i for the collected mass of the noted elements, determined from the concentrations of the effluent, c_i . The collection range starts at V_s and ends at V_e . Here, the collection range refers to both the range used for the estimation of separation efficiency and the range of effluent to be recovered in practice. Details of the calculation of these characteristics were described in the previous reports.¹⁴⁾

3. Results and Discussion

3.1 Separation at pH 2

Figure 2 shows the elution curves of the separation at pH 2 at the flow rate of 5 BV and Table 1 lists the efficiency characteristics of pH 2 purification process estimated by eqs. (1) and (2). For the calculations, the collection range is

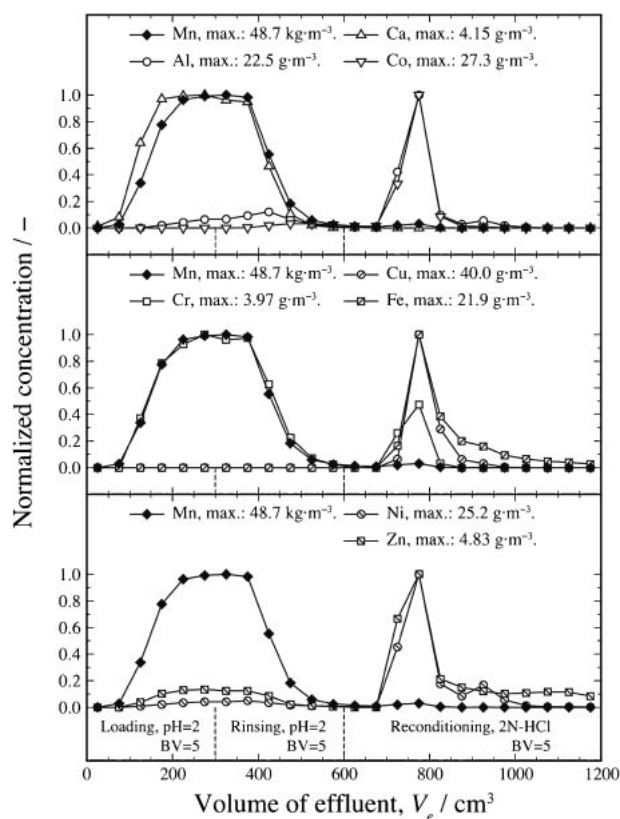


Fig. 2 Elution curves for purification of MnCl_2 in a NH_4Cl solution at pH 2 and a flow rate of 5 BV .

Table 1 The recovery ratio of Mn and the elimination ratio of the tested impurities of pH 2 purification process.

BV	Yield of Mn	Elimination ratio/–							
	$Y_{\text{Mn}}/\%$	Al	Ca	Co	Cr	Cu	Fe	Ni	Zn
1	86.3	15.5	1.01	>1000	1.01	>1000	>1000	>1000	>1000
5	83.6	4.37	1.04	48.7	1.12	>1000	>1000	8.60	4.34
10	81.6	3.01	0.943	10.7	1.13	>1000	>1000	9.18	7.50

taken to be above half the maximum concentration of the Mn elution curve.

Throughout this study, the elution of Mn began at the loading stage, which corresponds to the reported data (Fig. 1) where the Mn absorption is the lowest among the elements tested.

As listed in Table 1, Ca and Cr eluted with Mn at pH 2. This result indicates that Ca and Cr are not able to separate from Mn at pH 2 condition employed in this study. The separation of Al was poor because it always eluted slightly with Mn.

Co, Ni and Zn were completely separated at the flow rate of 1 BV, but with increasing flow rate, the elimination ratios decreased markedly. In other words, these elements were not absorbed sufficiently at the flow rate higher than 5 BV. This indicates that the absorption rates of these elements on the chelating resin were not so fast.

On the contrary, the elimination of Fe was successful at all flow rates. Trivalent Fe ions are strongly absorbed on the chelating resin,^{10,19)} and Fe was added to the loading solution as ferric chloride. Thus, Fe was successfully removed.

From the elution curves and efficiency characteristics at pH 2, the descending order of selectivity on the chelating resin was

$$\text{Cu} \sim \text{Fe} > \text{Co} \sim \text{Ni} \sim \text{Zn} > \text{Al} > \text{Ca} \sim \text{Cr} \sim \text{Mn}. \quad (3)$$

According to the literature,¹¹⁾ the selectivity order should be $\text{Cu} > \text{Ni} > \text{Zn} > \text{Co}$, but the position of Zn is mismatched in Eq. (3). Presumably, a ZnCl_x^{2-x} complex was formed since $\sim 1.87 \text{ kmol} \cdot \text{m}^{-3}$ of Cl^- ions were present in the loading solution, and thus chelation was hindered. On the other hand, Cu, Ni and Co would not form their chloro-complex ion at this concentration of Cl^- ions. This might be the reason why the selectivity for Zn decreased.

3.2 Separation at pH 4

Figure 3 shows the elution curves of the separation process at pH 4 at the flow rate of 5 BV, and Table 2 lists the efficiency characteristics of each purification process.

The elimination ratios of Al and Cr obtained in the case of the separation at pH 4 were slightly improved compared to the values obtained at pH 2. In contrast to these two elements, Ca could not be removed. The elimination ratios of Ni and Zn improved notably. In particular, Ni was removed completely at all flow rates. The separation efficiency of Co was not changed compared with the separation at pH 2.

On the basis of the elution curves and efficiency characteristics at pH 4, the descending order of selectivity on the chelating resin was

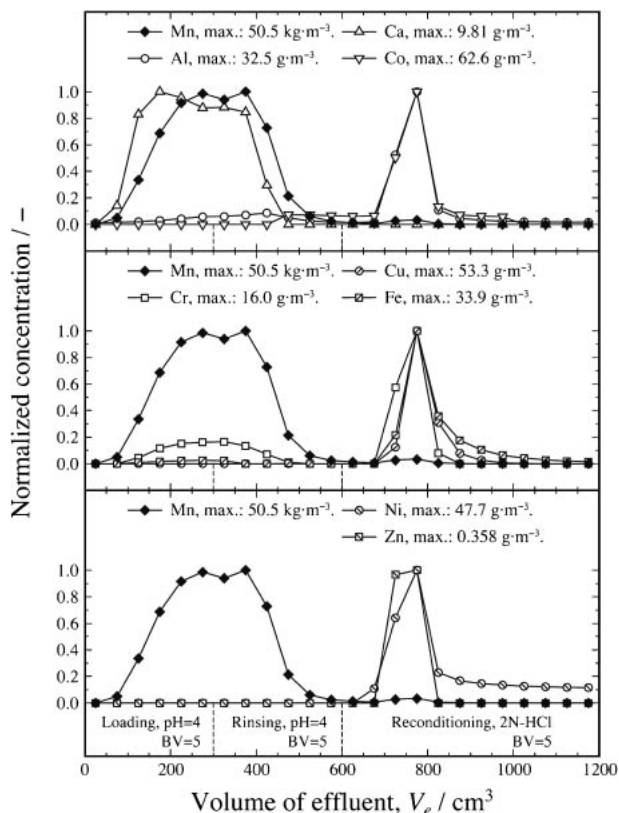


Fig. 3 Elution curves for purification of MnCl_2 in a NH_4Cl solution at pH 4 and a flow rate of 5 BV.

$$\text{Cu} \sim \text{Ni} > \text{Zn} > \text{Co} > \text{Al} > \text{Cr} > \text{Ca} \sim \text{Mn}. \quad (4)$$

Fe was omitted in the above equation, the following gives the reason. Fe eluted slightly with Mn at the flow rates of 5 and 10 BV, as shown in Fig. 3, in the contrast to pH 2 separations. The Pourbaix diagram demonstrates that ferric ion forms hydroxide ion in the high pH region.²⁰⁾ So this is presumably because $\text{Fe}(\text{OH})_x^{3-x}$ ($x = 1, 2$) was formed in the loading solution and this species was hardly to be absorbed.

It has been reported that the absorption of Al on the chelating resin begins at pH 2 and all Al is absorbed above pH 3.5.¹⁰⁾ Hence Al should be eliminated in the pH 4 separation process, however, Al eluted slightly with Mn as Fe, although the elimination ratio was slightly improved in the pH 4 separation process as compared with pH 2. This improvement agreed with the absorption behavior reported; stronger absorption is necessary for complete elimination. The elements that are completely eliminated were absorbed on the chelating resin extremely strongly, compared to Al.

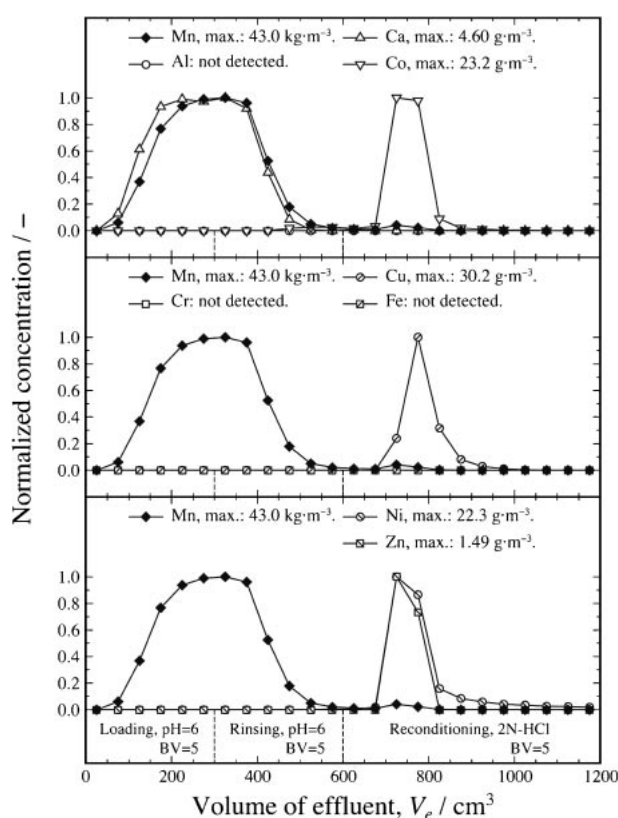
Table 2 The recovery ratio of Mn and the elimination ratio of the tested impurities of pH 4 purification process.

BV	Yield of Mn	Elimination ratio/—							
	$Y_{Mn}/\%$	Al	Ca	Co	Cr	Cu	Fe	Ni	Zn
1	85.8	130	0.980	>1000	1.58	>1000	>1000	>1000	>1000
5	83.4	5.38	1.11	56.7	2.78	>1000	21.7	>1000	>1000
10	79.5	3.09	0.980	79.9	2.74	>1000	8.81	>1000	2.53

Table 3 The recovery ratio of Mn and the elimination ratio of the tested impurities of pH 6 purification process.

BV	Yield of Mn	Elimination ratio/—							
	$Y_{Mn}/\%$	Al	Ca	Co	Cr	Cu	Fe	Ni	Zn
1	86.7	— [†]	0.979	>1000	— [†]	>1000	— [†]	9.22	>1000
5	83.0	— [†]	1.021	>1000	— [†]	>1000	— [†]	>1000	>1000
10	77.7	— [†]	0.965	>1000	— [†]	>1000	— [†]	>1000	>1000

[†]hydrolyzed and precipitated as its hydroxide in the loading solution, so the elimination ratio could not be calculated.

Fig. 4 Elution curves for purification of $MnCl_2$ in a NH_4Cl solution at pH 6 and a flow rate of 5 BV.

3.3 Separation at pH 6

Figure 4 shows the elution curves for the separation process at pH 6 at the flow rate of 5 BV, and Table 3 lists the efficiency characteristics of each purification process. The difference from the separation processes at lower pH was that Al, Cr and Fe were precipitated by hydrolysis in the loading solution due to its high pH. Thus, these elements were removed prior to the separation tests.

The separation efficiency of Co was significantly improved at pH 6 as compared with that at lower pH, as were those of

Ni and Zn at pH 4. Zn could be separated at pH 6 at all flow rates, which suggests that increasing the pH promoted the absorption of Zn. The behavior of Ca and Cu was the same throughout the present experiments. It is obvious that Cu is strongly absorbed on the chelating resin, and Ca is not in the range of pH 2 to 6.

The elution curves and efficiency characteristics at pH 6 suggest that the descending order of selectivity on the chelating resin was

$$Cu \sim Zn \sim Co > Ni > Ca \sim Mn. \quad (5)$$

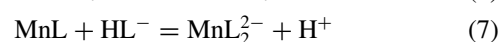
Because Al, Cr and Fe were separated before the separation tests, their selectivity could not be evaluated.

Ni exhibited unexpected behavior at pH 6. It has been reported that the absorption of Ni on chelating resin⁹⁾ begins at pH 2 and Ni is completely absorbed over pH 3, so Ni was expected to be removed under all separation conditions. But the results of the elimination ratio indicate that Ni was absorbed less at the slower flow rate. The difference between previously reported data and the present results is the media, where the reported data were obtained using $NaNO_3$ solution without NH_4Cl . Thus, the influence of NH_4Cl on the absorption behavior should be examined in the future.

3.4 Effects of the flow rate on the recovery ratio of Mn

The recovery ratio of Mn decreased with increasing the flow rate in each purification process as listed in Tables 1, 2 and 3. These results indicate that the amount of Mn absorbed on the chelating resin during the loading stage varied: the faster the flow rate, the more the amount of Mn absorbed.

It is presumed that the following chemical reactions take place successively when Mn is absorbed on the chelating resin.²¹⁾



where L denotes the ligand, that is iminodiacetic acid. It is obvious that twice amount of Mn can be absorbed on the equal amount of the chelating resin when the chemical reaction of eq. (6) occurs solely compared with when the

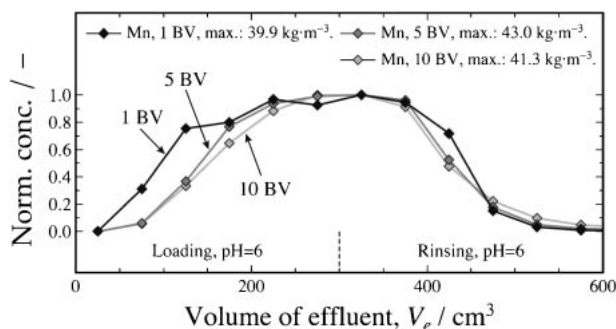


Fig. 5 Elution curves of Mn at pH 6 for different flow rates.

secondary reaction of eq. (7) occurs subsequently. Therefore, it is likely that the whole successive reactions represented by eqs. (6) and (7) occurred at a slower flow rate, while the only reaction represented by eq. (6) occurred practically at a faster flow rate.

Figure 5 shows the elution curves of Mn for pH 6 separations at different flow rates. Generally, an elution curve is broadened and its peak lowers with increasing the flow rate. But in Fig. 5, the elution peaks of Mn showed the reverse trend: the slope of the breakthrough curve was the largest at the lowest flow rate of 1 BV in each separation test. Namely this trend indicates that the less Mn absorbed on the chelating resin and not only the reaction of eq. (6) but also the reaction of eq. (7) occurred in succession at a slower flow rate. On the other hand, the reaction of eq. (7) hardly took place at a faster flow rate, because an increase in the flow rate is equivalent to a decrease in the contact time of the solution with the chelating resin. This consideration is in agreement with that of the recovery ratio of Mn described above.

Although it is confirmed that the reaction of eq. (6) takes place followed by the reaction of eq. (7) from these considerations, the detailed kinetics of each absorption reaction cannot be determined. Almost all investigation on absorption on chelating resins has focused on their equilibrium state; few studies to date have dealt with their kinetics. It is necessary to make the kinetics clear with further examination in the future.

Our experimental results revealed that the separation process at pH 6 at the flow rate of 5 BV had the highest separation efficiency. However, Ca could not be removed by any conditions employed in this study. Thus, Ca must be removed by another method, e.g., electrowinning subsequent to the chromatographic separation, Ar-H₂ plasma arc melting after reduction.

4. Conclusions

Purification tests of MnCl₂ with chelating resins in NH₄Cl

media at various pH and flow rates have yielded the optimal conditions: pH 6 and a flow rate of 5 BV. Using these conditions, Co, Cu, Ni and Zn were separated with chromatographic separation with chelating resins containing imino-diacetate groups, and Al, Cr and Fe were separated by hydrolysis in the loading solution before separation. The recovery ratio of Mn was 83%, which is believed to be enough for practical use.

A MnCl₂ solution containing NH₄Cl was successfully purified in this study; this effluent is suitable for extracting high-purity metallic products by electrowinning.

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