

<https://doi.org/10.18321/ectj1698>

Limitations of Acid-Induced EDTA Recovery from Citrate-Based Metal Leaching Solutions

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Article info

Received:

2 July 2026

Received in revised form:

27 August 2026

Accepted:

24 September 2026

Keywords:

Acid-induced precipitation;
Pregnant leach solution;
Metal–EDTA complexes;
Black mass; Spent lithium-ion
batteries; Chelating agent;
Hydrometallurgy

Abstract

This study investigates acid-induced precipitation of ethylenediaminetetraacetic acid (EDTA) from citrate-based solutions relevant to spent lithium-ion battery leaching. Three systems were evaluated to assess the impact of matrix composition: an aqueous Na_2EDTA solution (E), Na_2EDTA in a citrate buffer (CBE), and a simulated pregnant leach solution containing Na_2EDTA , citrate, and Li, Co, Ni, and Mn ions (CBEM). Increasing matrix complexity hindered EDTA precipitation. While the simple E system achieved 95–98% EDTA removal from the liquid phase at pH 2.7–1.5, the citrate-containing CBE system required a lower pH (2.0–1.0) to reach 90–96% removal. In the metal-containing CBEM system, maximum removal was approximately 65% at pH 0.5. Analytical methods confirmed H_4EDTA formation in the E and CBE systems, whereas the CBEM precipitate exhibited an unidentified phase composition with trace amounts of transition metals. These findings show that precipitation behavior observed in simple solutions cannot be directly extrapolated to complex, metal-containing leachates and indicate the need to evaluate preliminary metal removal or solution purification before EDTA regeneration.

1. Introduction

The increasing volume of spent lithium-ion batteries (LIBs), associated with the development of electric vehicles (EVs), portable electronics, and energy storage systems, intensifies the need to develop efficient recycling technologies. At the same time, spent LIBs are regarded not merely as environmentally significant waste, but as a secondary source of valuable metals, including Li, Co, Ni, and Mn. The reintroduction of these metals into the production cycle aligns with the principles of a circular economy and mitigates dependence on primary mineral resources [1–4].

Among the existing approaches to LIB recycling, hydrometallurgical methods have garnered particular attention due to their high metal extraction efficiency and the feasibility of subsequent component separation [5]. Traditional leaching schemes

for black mass are frequently based on the use of mineral acids, including H_2SO_4 , HCl, HNO_3 and H_3PO_4 [6, 7]. Despite their high efficiency, such processes are associated with highly corrosive environments, significant reagent consumption, and the generation of secondary effluents. Consequently, increasing attention is being directed towards milder leaching systems based on organic acids [8, 9].

However, the efficient leaching of transition metals from cathode materials frequently requires the introduction of reducing agents, such as H_2O_2 , NaHSO_3 , $\text{Na}_2\text{S}_2\text{O}_5$, which facilitate the conversion of Co(III), Ni(III), and Mn(IV) into more soluble divalent forms [10]. Among organic reagents, citrate systems are of practical interest, as citric acid and its salts combine availability, biodegradability, and complexation capacity [11]. However, simple citric acid-based systems frequently require elevated concentrations of citric acid (2–4 mol/L), temperatures of 70–90 °C, and significant amounts of H_2O_2 (1–10 vol %) to achieve high metal recovery rates [12].

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To overcome these limitations, a leaching system based on a citrate buffer, H_2O_2 , and Na_2EDTA has been proposed [13]. In this system, H_2O_2 acts as a reducing agent, the citrate buffer maintains the specified mildly acidic pH range, and EDTA stabilizes the transition metal ions in solution through the formation of stable chelate complexes. This approach enables the leaching process to be conducted under relatively mild conditions: a pH of 5.0, 50 °C, a citrate buffer concentration of 0.778 mol/L, 0.05 mol/L Na_2EDTA , 1.211 vol % H_2O_2 , and a solid-to-liquid (S:L) ratio of 1:20. Under these conditions, the extraction efficiencies achieved for Li, Co, Ni, and Mn were 100.0%, 98.65%, 90.69%, and 82.87%, respectively. The high efficiency of this system is largely attributed to the role of EDTA as a strong polydentate ligand. EDTA forms stable complexes with a variety of transition metals, including Ni^{2+} , Co^{2+} , and Mn^{2+} , which facilitates the retention of metals in solution and prevents the formation of poorly soluble hydroxide or oxide phases.

However, the application of EDTA in such systems imposes technological, economic, and environmental limitations. On one hand, the high stability of metal–EDTA complexes, which is beneficial during the leaching stage, can complicate subsequent metal separation and the purification of pregnant leach solutions [14, 15]. On the other hand, EDTA constitutes a substantial reagent burden; at an Na_2EDTA concentration of 0.05 mol/L and an S:L ratio of 1:20, the consumption of the complexing agent amounts to approximately 0.34–0.37 kg per 1 kg of black mass [13]. Even at an estimated cost for EDTA salts of \$1.3–1.5/kg, this equates to additional costs of approximately \$0.45–0.55 per kilogram of the processed material [16]. Therefore, for the practical application of citrate-EDTA-containing systems, it is essential to evaluate the feasibility of EDTA regeneration and its subsequent reuse [17].

One of the most straightforward approaches to the regeneration of EDTA is acid-induced precipitation. Lowering the pH protonates the ligand and promotes its precipitation as the sparingly soluble free acid, H_4EDTA [18]. This approach is technologically appealing, as it does not require complex equipment and can potentially be integrated into a closed-loop scheme for the utilization of the complexing agent. Acid-induced EDTA precipitation has previously been investigated in soil-washing solutions, leachates of spent Ni–Mo catalysts, and process solutions generated during phosphate ore processing [19–22]. These studies show that precipitation depends on both pH and solution composition, particularly the

identity and concentration of dissolved metals and coexisting components. However, the acid-induced precipitation behavior of EDTA has not previously been investigated in a multicomponent matrix representative of LIB black-mass leachates, in which EDTA coexists with citrate species, Li, Co, Ni, and Mn ions, salts, and products of side reactions. Upon acidification, the concurrent protonation of EDTA and citrate shifts the complexation equilibria and changes the distribution of EDTA between protonated and metal-bound species. These changes affect supersaturation with respect to H_4EDTA and possible coprecipitation, influencing both EDTA removal and the composition of the solid phase.

The aim of the present work was to evaluate how the composition of a model matrix representative of citrate-EDTA-containing leach solutions affects the acid-induced precipitation of EDTA. Three model systems were therefore examined: an aqueous EDTA solution, a citrate-containing EDTA solution, and a metal-containing solution simulating a pregnant leach solution and comprising EDTA, citrate buffer, and transition-metal ions. The results demonstrate that the precipitation behavior of EDTA observed in simple solutions cannot be directly extrapolated to citrate- and metal-containing pregnant leach solutions, because the matrix composition substantially affects both EDTA recovery and the nature of the precipitated solid phase.

2. Experimental

To evaluate the effect of solution composition on EDTA precipitation, three series of model systems were prepared: E, CBE, and CBEM. In all experiments, the initial concentration of the disodium salt of ethylenediaminetetraacetic acid (Na_2EDTA) was approximately 50 mmol/L. The initial solution volume was 100.0 mL in each experiment.

Series E consisted of an aqueous EDTA solution without additional components and was used as a baseline system to evaluate the precipitation of free EDTA at various pH values.

Series CBE contained EDTA in a 0.8 M citrate buffer with an initial pH of 5.00.

Series CBEM additionally contained metal ions to simulate the composition of a pregnant leach solution obtained by leaching black mass from spent lithium-ion batteries. The metal concentrations were selected based on the composition of the pregnant leach solution obtained in the citrate buffer- H_2O_2 - Na_2EDTA system [13]. In the model solution of the CBEM series, the metal concentrations were as

follows: Ni, 17.9 mmol/L; Mn, 15.2 mmol/L; Co, 44.8 mmol/L; and Li, 89.5 mmol/L. The EDTA concentration (approximately 50 mmol/L) was lower than the total concentration of Ni, Co, and Mn (77.9 mmol/L); therefore, only a fraction of the transition-metal ions could be complexed by EDTA. The exact distribution of EDTA among the individual metals was not determined because citrate also competed for metal-ion complexation.

EDTA precipitation was induced by acidification with 16 M sulfuric acid (H_2SO_4). Acidification was performed in a thermostated reactor at 21 °C under constant magnetic stirring at 450 rpm. The pH was monitored using a glass electrode. To evaluate the dependence of EDTA removal from the liquid phase on solution acidity, the pH of the solutions was sequentially reduced to target values from 5.0 to 0.5. Measurements at pH values below 0.5 were not conducted, as highly acidic media can cause the glass electrode response to deviate significantly from the linear Nernstian relationship. This phenomenon, known as acid error, reduces the reliability of pH measurements.

Once the target pH was reached, a 3.00 mL sample of the suspension was collected. The sample was allowed to stand for 3 min, then centrifuged at 6000 rpm for 20 min to separate the EDTA precipitate from the liquid phase. The resulting precipitate was isolated by vacuum filtration using polyvinylidene fluoride (PVDF) membrane filters. The precipitates were washed with a small volume of acetone to remove residual mother liquor and then dried overnight in a vacuum oven at 80 °C.

After separation of the precipitate, a 1000 μL aliquot of the mother liquor was withdrawn. The aliquot was transferred into a 50.0 mL volumetric flask containing 4.00 mL of a 0.048 M Fe^{3+} solution and diluted to the mark. The resulting solution was then sequentially diluted 10-fold and 5-fold. The total dilution factor was 2500. The residual EDTA concentration in the filtrates was determined by UV–Vis spectrophotometry based on Fe–EDTA complex formation, using a UV-1900i spectrophotometer (Shimadzu, Japan). The Fe(III)–EDTA complex is considerably more stable ($\log \beta = 25.0$) than the corresponding Ni(II), Co(II), and Mn(II) complexes ($\log \beta = 18.52$, 16.26, and 13.81, respectively) [14]. Furthermore, Fe^{3+} was introduced at a molar ratio of 3.84:1 relative to the maximum possible amount of EDTA in the aliquot. Therefore, EDTA was unlikely to remain in solution in forms undetectable after Fe^{3+} addition.

The calibration curve was constructed using a series of standard EDTA solutions processed according

to the same procedure. The concentration range of the standard solutions was 0.010–0.070 mmol/L. Absorbance was recorded in quartz cuvettes with a 10 mm optical path length. Quantitative determination was performed at a wavelength of 263 nm, corresponding to the absorption maximum of the Fe–EDTA complex. The EDTA concentration in the analyzed solutions was calculated using the equation of the calibration curve, taking into account all dilution steps [23]. Potential background absorbance from the matrix was evaluated using EDTA-free blank solutions containing all other components of the corresponding systems and subjected to the same Fe^{3+} addition and dilution procedure as the analyzed samples. Their absorbance at 263 nm did not exceed the background level.

The degree of EDTA removal from the liquid phase was calculated based on the change in the amount of the complexing agent in the solution before and after precipitation, accounting for the change in the system volume upon the addition of acid and sequential sampling:

$$\delta = \left(1 - \frac{C_i \times V_i}{C_0 \times V_0 \times \prod_{j=1}^n \frac{V_{j-1} - 3}{V_{j-1}}}\right) \times 100\% \quad (1)$$

where C_i ($\text{mmol} \times \text{L}^{-1}$) is the EDTA concentration in the mother liquor at the i -th stage of the experiment, determined spectrophotometrically taking dilution into account; C_0 ($\text{mmol} \times \text{L}^{-1}$) – initial concentration of EDTA in the model solution; V_i (L) is the volume of the solution at the i -th step; V_0 (L) is the initial volume of the model solution; $\prod_{j=1}^n \frac{V_{j-1} - 3}{V_{j-1}}$ is a correction factor accounting for the decrease in solution volume due to sequential sampling.

All measurements of EDTA removal from the liquid phase were performed in triplicate. The results are presented as the mean with a two-sided 95% confidence interval. The margin of error (ε) was calculated as:

$$\varepsilon = t_{0.975, n-1} \times s/\sqrt{n}, \quad (2)$$

where s is the sample standard deviation; n is the number of independent replicate measurements; $t_{0.975, n-1}$ is the critical value of Student's t -distribution.

The precipitates were characterized by powder X-ray diffraction (XRD) using a Tongda TD-3700 diffractometer (Tongda, China). The diffractometer was equipped with a copper-anode X-ray tube ($\lambda_{\text{CuK}\alpha_1} = 1.54056 \text{ \AA}$ and $\lambda_{\text{CuK}\alpha_2} = 1.54439 \text{ \AA}$). Infrared spectra were recorded on an Alpha II Fourier-transform infrared (FTIR) spectrometer (Bruker, Germany) using

an attenuated total reflectance (ATR) accessory over the wavenumber range of 300–4000 cm^{-1} . To evaluate metal coprecipitation, the precipitate obtained from the CBEM system at the highest degree of EDTA removal was analyzed for Ni, Co, and Mn by atomic absorption spectrometry (AAS) using an AA-7000 spectrometer (Shimadzu, Japan).

3. Results and Discussion

The effect of pH on EDTA precipitation in a simple system was evaluated using series E, which contained solely an Na_2EDTA solution. This approach enables the investigation of the fundamental acid-base nature of the process without the interference of matrix components.

As shown in Fig. 1a, in the pH range of 5.0–3.5, the precipitation of H_4EDTA is virtually negligible; EDTA removal from the liquid phase remains low, not exceeding 10–15%. This indicates that EDTA is predominantly retained in soluble ionic forms. Concurrently, large errors reaching ± 15 –19% are observed at specific points within this region. This is likely attributable to the fact that, under conditions of marginal precipitation, δ is calculated based on a small difference between the initial and current Na_2EDTA concentrations. Consequently, even minor errors in sample preparation, dilution, and spectro-

photometric determination can significantly impact the calculated value of δ .

Subsequently, a sharp increase in EDTA removal is observed as the pH decreases from approximately 3.2 to 2.7. In this region, δ rises to approximately 95–97%, indicating the attainment of conditions for the intensive formation of the H_4EDTA precipitate. Once the region of intensive precipitation is reached, δ remains high over a wide pH range. In the pH range of approximately 2.7–1.5, the values are sustained at around 95–98%, with a comparatively narrow variance typically not exceeding ± 3 –7%. This indicates the virtually complete and reproducible precipitation of EDTA from the solution in the form of H_4EDTA .

Upon further decreasing the pH to the 1.0–0.5 range, a slight decline in δ to 80–90% and an increase in the scatter of experimental points to ± 15 –25% are observed. This is most likely attributable to the increased uncertainty of pH measurements using a glass electrode in the highly acidic region.

The observed dependence is consistent with the acid-base properties of EDTA and the differences in the solubility of its species. According to literature data, the pK_a values for EDTA, corresponding to acid-base transitions in the acidic region, are approximately 2.0 and 2.7 [18]. These values do not directly dictate the precipitation pH, but they indicate the region of active redistribution of the protonated and

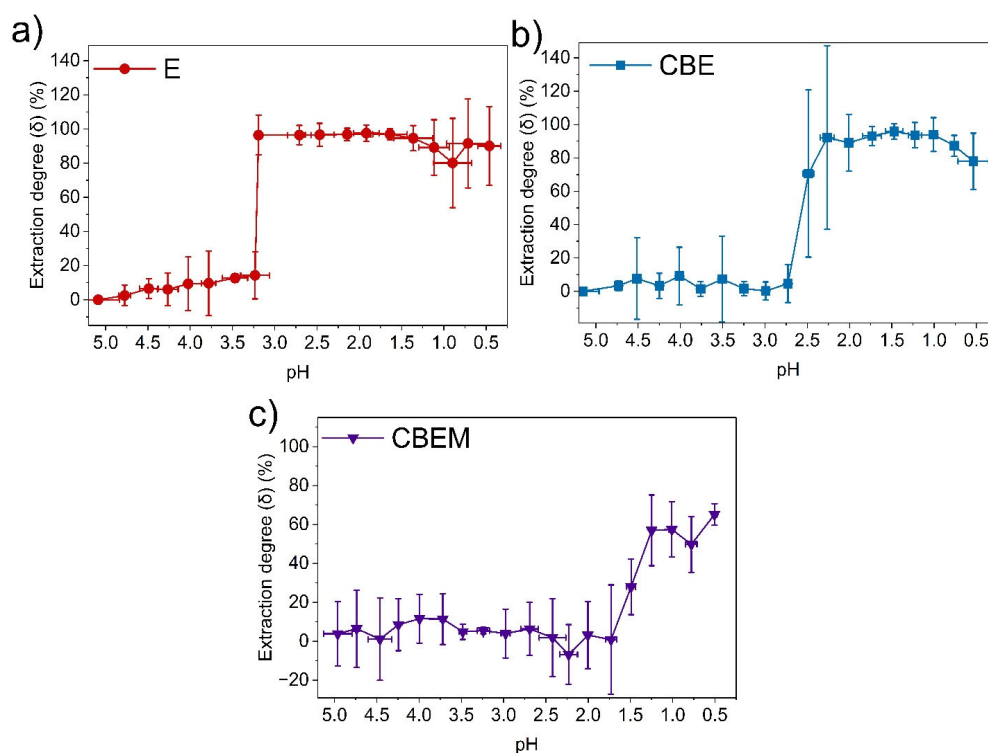


Fig. 1. Dependence of EDTA removal from the liquid phase on pH for the model systems: (a) E, (b) CBE, (c) CBEM. Data are presented as the mean $\pm \epsilon$.

deprotonated species of the ligand. Consequently, upon acidification of the Na_2EDTA solution to a pH of approximately 3 or lower, the fraction of less charged protonated EDTA species increases. Given the low solubility of H_4EDTA , this leads to the supersaturation of the solution and the subsequent precipitation of H_4EDTA .

Thus, the results for series E demonstrate that acidification of a simple aqueous Na_2EDTA solution enables efficient and stable precipitation of EDTA as H_4EDTA over a relatively broad pH range.

The effect of the citrate-containing matrix on the precipitation of Na_2EDTA was evaluated using series CBE, which contained Na_2EDTA in the presence of a citrate buffer. This system makes it possible to determine whether the extent of EDTA removal is maintained upon the introduction of the buffer, as compared to the simple Na_2EDTA system.

As shown in Fig. 1b, in the pH range of 5.0–3.0, EDTA removal from the liquid phase remains low, not exceeding 5–10% at most data points. The increased scatter in this region, reaching approximately ± 15 –25 percentage points, can be explained by the same factors discussed for series E.

A sharp increase in EDTA removal in series CBE was observed upon deeper acidification relative to series E, in the pH range of approximately 2.5–2.2. Within this interval, δ rises from low values to approximately 70–90%. The shift in the transition region can be attributed to the effect of the citrate system on the acid-base equilibria. Upon acidification, not only EDTA species but also citrate species undergo protonation, which alters the solution composition, ionic strength, and the conditions for achieving supersaturation with respect to the sparingly soluble H_4EDTA . As a result, intensive precipitation of H_4EDTA in the CBE system initiates at a deeper level of acidification than in the simple system E. The most pronounced scatter of the experimental data (± 30 –50%) was observed within this transition region. Near the supersaturation boundary with respect to H_4EDTA , minor variations in pH can significantly impact the nucleation rate and the extent of precipitation. Consequently, at similar pH values, some experimental points correspond to incomplete precipitation of H_4EDTA , whereas in other instances, precipitation has already commenced.

Following the transition region, a high-removal zone is established in the CBE system. In the pH range of approximately 2.0–1.0, δ remains at approximately 90–96%, while the scatter of the experimental data decreases to about ± 5 –15%. This indicates effective and relatively stable precipitation of H_4EDTA from the citrate-containing solution.

Upon further decreasing the pH to 0.5, δ declines to approximately 78–80%, and the data scatter increases once again (± 15 –18%). This trend is consistent with the behavior of series E in the highly acidic region.

Thus, the results for series CBE show that the presence of the citrate buffer shifts the effective precipitation of H_4EDTA toward a more acidic pH range but does not prevent high EDTA removal.

The effect of the metal-containing matrix on acid-induced EDTA precipitation was evaluated using series CBEM, which initially contained Na_2EDTA , a citrate buffer, and metal ions characteristic of a pregnant leach solution. This system represents the closest approximation to the actual medium from which EDTA is intended to be regenerated for subsequent recycling back into the technological process.

As shown in Fig. 1c, in the pH range of 5.0–2.0, EDTA removal from the liquid phase remains low, not exceeding 10–15% at most data points, which indicates the absence of pronounced H_4EDTA precipitation within this pH range. The errors at individual points reach approximately ± 10 –25%. Similar to series E and CBE, such variability at low precipitation levels can be attributed to the high relative calculation error associated with the small difference between the initial and current Na_2EDTA concentrations.

The onset of a noticeable increase in EDTA removal in series CBEM is observed only upon deeper acidification. According to the experimental data, precipitate nucleation becomes pronounced at pH 1.5. In this region, δ rises to approximately 25–30%, indicating the initial dissociation of a portion of the metal–EDTA complexes and the accumulation of protonated ligand species capable of converting into the sparingly soluble H_4EDTA .

Upon further decreasing the pH, δ continues to increase; however, it does not reach the values observed for series E and CBE. The maximum removal in the CBEM system is approximately 65% at pH 0.5.

Thus, the results for series CBEM show that the metal-containing matrix substantially hinders acid-induced EDTA precipitation, necessitating deeper acidification and preventing near-complete recovery of the complexing agent.

The precipitates obtained at the maximum EDTA removal in series E, CBE, and CBEM were further investigated by powder X-ray diffraction and IR spectroscopy. The objective of this stage was to qualitatively confirm the formation of EDTA-containing precipitates and to evaluate the effect of the solution composition on the nature of the precipitated solid phase.

Figure 2a presents the powder diffraction patterns of the isolated precipitates. For samples E and CBE, the positions of the main reflections are in good agreement with the reflections of H₄EDTA (CCDC No. 1148826), confirming the formation of crystalline ethylenediaminetetraacetic acid. Differences in the relative peak intensities may be attributed to crystallization features and preferred crystallite orientation. In contrast, the diffraction pattern of the CBEM series precipitate does not correspond to H₄EDTA. A search of available crystallographic databases did not allow for unambiguous phase identification. Given the composition of the initial solution, it can be assumed that the CBEM precipitate represents a metal-containing EDTA product or a mixture of coordination phases for which reference powder diffraction data are unavailable.

The IR spectra of the isolated precipitates are presented in Fig. 2b. A similar spectral pattern is observed for samples E and CBE, corresponding to identical compounds. The spectra exhibit C–H stretching vibration bands of the methylene groups

in the 2800–3022 cm^{−1} region, intense stretching vibration bands of the carbonyl groups $\nu(\text{C}=\text{O})$, at 1660 cm^{−1} for E and 1685 cm^{−1} for CBE, as well as bands in the 1388–1309 cm^{−1} range assigned to the vibrations of C–O and carboxyl groups ($\nu_s(\text{COO})$). In the low-wavenumber region, there are signals corresponding to the bending vibrations of O–H 959 and 961 cm^{−1} and C–H (861 and 867 cm^{−1}), and the skeletal vibrations of C–C, C–N, and C–O in the 420–770 cm^{−1} range. The presence of these bands confirms the existence of functional groups characteristic of H₄EDTA, which is consistent with the powder X-ray diffraction results.

The spectrum of the CBEM sample differs significantly from those of E and CBE. In the 2500–3450 cm^{−1} region, a broad band is observed, which may be associated with O–H groups participating in a hydrogen bond network, as well as with the presence of bound and/or sorbed water. The $\nu(\text{C}=\text{O})$ band of the carboxyl groups appears at approximately 1730 cm^{−1} and is shifted to a higher-frequency region compared to samples E and CBE. This indicates a change

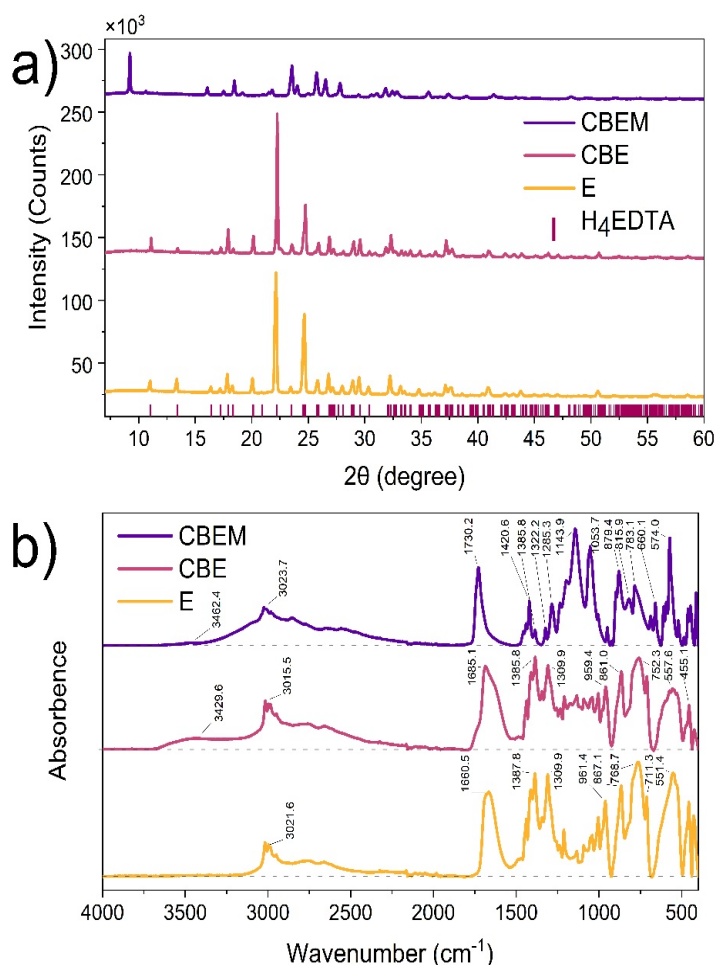


Fig. 2. Diffraction patterns (a) and IR spectra (b) of the precipitates obtained at the maximum EDTA removal in series E, CBE, and CBEM.

Table 1. Comparison of acid-induced EDTA precipitation in the model systems. Data are presented as the mean $\pm$ ϵ

System	Initial matrix composition	pH at maximum EDTA removal	16 M H ₂ SO ₄ added at maximum EDTA removal, mL per 100 mL of initial solution	Maximum EDTA removal from the liquid phase, %	Solid-phase composition
E	Na ₂ EDTA, approximately 50 mmol/L, in water	1.92 $\pm$ 0.15	0.64 $\pm$ 0.06	97.51 $\pm$ 4.84	H ₄ EDTA
CBE	Na ₂ EDTA, approximately 50 mmol/L; citrate buffer, 0.8 mol/L; initial pH 5.00	1.47 $\pm$ 0.10	9.71 $\pm$ 3.57	95.92 $\pm$ 4.59	H ₄ EDTA
CBEM	Na ₂ EDTA, approximately 50 mmol/L; citrate buffer, 0.8 mol/L; Ni, 17.9 mmol/L; Mn, 15.2 mmol/L; Co, 44.8 mmol/L; Li, 89.5 mmol/L	0.50 $\pm$ 0.03	36.36 $\pm$ 10.73	65.18 $\pm$ 5.55	Unidentified phase distinct from crystalline H ₄ EDTA

in the environment of the carboxyl groups relative to free H₄EDTA. Furthermore, a more complex spectral pattern is observed for the CBEM sample in the 1600–1200 cm⁻¹ region. In this range, the vibrations of the –COOH/–COO⁻ groups, as well as the C–O and C–N bonds of EDTA, may overlap. Additional bands may be attributed to the contribution of citrate components present in the initial solution, as citrate also contains carboxyl groups and C–O bonds. Moreover, the position and shape of the bands can be affected by the interaction of carboxyl/carboxylate groups with metal ions.

Thus, the combined XRD and IR spectroscopy data confirm the formation of H₄EDTA in the simple and citrate-containing systems. The increased complexity of the matrix compositions—specifically the presence of transition metals—leads to the formation of a different solid phase. This limits the feasibility of a direct interpretation of the precipitate composition and necessitates a separate structural investigation if the objective is to identify individual crystalline phases.

The composition of the solid phase was determined by AAS for the CBEM precipitate obtained at maximum EDTA removal. Ni, Mn and Co account for 0.0930, 0.0134 and 0.0038 wt% (0.016, 0.0024 and 0.0006 mmol/g), i.e. 0.11 wt% in total. Since a metal that is a structural constituent of a coordination compound would contribute several to tens of wt% at any metal-to-ligand ratio, these levels identify the metals as impurities rather than framework components; less than 1% of each metal is transferred to the solid, and Ni, Mn and Co remain almost entirely in solution.

The Ni : Mn : Co molar ratio of 24.6 : 3.8 : 1 shows a marked enrichment in nickel, consistent with the stability of the Ni–EDTA complex ($\log \beta = 18.52$ vs 16.26 for Co and 13.81 for Mn) [14]. The Mn : Co ratio, however, deviates from the stability sequence, pointing to additional factors such as competitive citrate complexation of Co. Together with the XRD and IR data, this indicates that the difference between the CBEM precipitate and free H₄EDTA is most likely due to co-precipitation of organic matrix components, including citrate.

Overall, the obtained results demonstrate that acid precipitation can be an effective method for EDTA regeneration in metal-free systems (Table 1). The introduction of the citrate matrix shifts the region of intensive precipitation to a more acidic region, whereas the presence of transition metal ions not only reduces the extent of EDTA removal but also alters the nature of the precipitating solid phase. Based on the data in Table 1, acid consumption per mole of EDTA removed from solution increased from 2.1 ± 0.2 mol H₂SO₄ in system E to 32 ± 12 mol in CBE and 179 ± 55 mol in CBEM. Thus, the practical application of direct acid precipitation for metal-containing solutions is limited not only by the incomplete recovery of EDTA but also by the necessity for deep acidification. This may diminish the technological advantages of the mild citrate–EDTA–H₂O₂ system and necessitates a separate evaluation of the acid balance, as well as the feasibility of preliminary metal removal.

4. Conclusion

The present study has demonstrated that acid precipitation can be utilized as a straightforward approach for EDTA regeneration from post-leaching solutions; however, the process efficiency is substantially governed by the composition of the initial matrix. In the simple system E, intensive precipitation initiates in the pH region of 3.2–2.7, and the maximum EDTA removal from the liquid phase reaches 95–98% in the pH interval of 2.7–1.5. In the citrate-containing system CBE, the region of intensive precipitation shifts toward lower pH values, with stable removal of 90–96% observed in the pH range of 2.0–1.0. The most pronounced effect of the solution composition was established for the metal-containing system CBEM: noticeable precipitation begins only at a pH of approximately 1.5, and maximum removal efficiency does not exceed 65% at pH 0.5.

Powder X-ray diffraction and IR spectroscopy data confirmed the formation of crystalline H₄EDTA in simple and citrate-containing systems. At the same time, the precipitate isolated from the metal-containing system CBEM differs from free H₄EDTA in both its diffraction pattern and IR spectrum. AAS analysis revealed the presence of small amounts of Ni, Mn and Co in the solid phase. These metals are most likely present merely as an impurity within the precipitate, the bulk of which is likely composed of co-precipitated organic matrix components, including citrate species.

Thus, the results obtained for solutions containing only EDTA cannot be directly extrapolated to actual pregnant leach solutions. Acid consumption per mole of EDTA removed from solution increased from 2.1 ± 0.2 mol H₂SO₄ in system E to 32 ± 12 mol in CBE and 179 ± 55 mol in CBEM. Consequently, direct acidification of metal-containing solutions does not ensure complete EDTA recovery and may substantially offset the advantages of the mild citrate–EDTA–H₂O₂ system for black mass leaching. Nevertheless, the method may remain viable if metals are removed from the solution before EDTA regeneration. Accordingly, the sequence of process steps is critical when developing closed-loop black mass recycling schemes.

CRedit authorship contribution statement

Michail Simonov: investigation, data curation, writing – original draft. **Saken Abdimomyn:** conceptualization, methodology, writing – review & editing. **Artur Grigoryev:** investigation, data curation.

Amirkhan Bekmagambetov: investigation, data curation, visualization. **Fyodor Malchik:** supervision, funding acquisition, project administration, writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgment

This research is funded by the Committee of Science of the Ministry of Science and Higher Education of the Republic of Kazakhstan (Grant BR 27198753).

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