Recovery of lithium and transition metals from spent LIBs using low concentration ammonia media

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The exponential growth in the consumption of lithium-ion batteries (LIBs) necessitates the development of environmentally benign recycling technologies to address the impending surge in end-of-life waste. This study presents a novel, sustainable hydrometallurgical approach for the recovery of critical metals (Li, Ni, Co) from spent NMC/LCO cathode materials utilizing a low-concentration ammonia system. In contrast to conventional methods relying on high ammonia concentrations (4-6 M), this work demonstrates efficient metal leaching using only 0.5 M NH_4OH buffered with ammonium sulfate, employing sodium sulfite (Na_2SO_3) as a reducing agent to facilitate the breakdown of the oxide matrix.

Through systematic optimization, the optimal process parameters were established: 0.5 M NH_4OH, 0.273 M $(NH_4)_2SO_4$, and 0.8 M Na_2SO_3 at pH 10.5 and 80°C. Under these conditions, the system achieved leaching efficiencies of 99.6% for Ni, 96.4% for Li, and 89.1% for Co. A distinctive feature of the developed process is the selective retention of manganese; unlike acid leaching, this method retains 75.9% of manganese in the solid residue, significantly simplifying downstream purification and target component separation. The proposed method offers an eight-fold reduction in ammonia consumption compared to conventional ammoniacal schemes, substantially lowering both operational costs and the carbon footprint of the recycling process.

Keywords: lithium-ion batteries; waste recycling; hydrometallurgy; ammoniacal leaching; electrode mass.

Концентрациясы төмен аммиак орталарын қолдана отырып, қолданыстан шыққан ЛИА-дан литий және ауыспалы металдарды тұрақты гидрометаллургиялық бөліп алу

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Литий-ионды аккумуляторларды (ЛИА) қолданудың экспоненциалды өсуі қалдықтар көлемінің алдағы күрт артуы мәселесін шешу үшін экологиялық қауіпсіз қайта өңдеу технологияларын әзірлеуді талап етеді. Бұл зерттеуде төмен концентрациялы аммиак жүйесін қолдана отырып, пайдаланылған NMC/LCO катодтық материалдарынан маңызды металдарды (Li, Ni, Co) бөліп алудың жаңа, тұрақты гидрометаллургиялық тәсілі ұсынылған. Аммиактың жоғары концентрацияларына (4-6 M) негізделген дәстүрлі әдістерден айырмашылығы, бұл жұмыста оксидтік матрицаның ыдырауын жеңілдету үшін тотықсыздандырғыш ретінде натрий сульфитін (Na_2SO_3) қолдана отырып, аммоний сульфатымен буферленген небәрі 0,5 M NH_4OH қолдану арқылы металдарды тиімді шаймалау мүмкіндігі көрсетілген.

Жүйелі оңтайландыру және термодинамикалық талдау барысында процестің оңтайлы параметрлері анықталды: pH 10,5 және 80°C температурада 0,5 M NH_4OH, 0,273 M $(NH_4)_2SO_4$ және 0,8 M Na_2SO_3. Бұл жағдайларда жүйе Ni үшін 99,6%, Li үшін 96,4% және Co үшін 89,1% шаймалау тиімділігіне қол жеткізді. Әзірленген процестің ерекшелігі – марганецтің ішінара ерімеуі; қышқылдық шаймалаудан айырмашылығы, бұл әдіс марганецтің 75,9%-ын қатты қалдықта сақтайды, бұл мақсатты компоненттерді тазарту және бөліп алудың кейінгі сатыларын айтарлықтай жеңілдетеді. Ұсынылған әдіс дәстүрлі аммиак схемаларымен салыстырғанда аммиакты тұтынуды сегіз есеге азайтуды қамтамасыз етеді, бұл қайта өңдеу процесінің операциялық шығындарын да, көміртегі ізін де айтарлықтай төмендетеді.

Түйін сөздер: литий-ионды аккумуляторлар; қалдықтарды қайта өңдеу; гидрометаллургия; аммиакты шаймалау; электродтық масса.

Извлечение лития и переходных металлов из отработанных ЛИБ с использованием низкоконцентрированных аммиачных сред

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Экспоненциальный рост использования литий-ионных батарей требует разработки экологически безопасных технологий переработки для решения проблемы надвигающегося резкого увеличения количества отходов. В данном исследовании представлен новый, устойчивый гидрометаллургический подход к извлечению критически важных металлов (Li, Ni, Co) из отработанных катодных материалов NMC/LCO с использованием низкоконцентрированной аммиачной системы. В отличие от традиционных методов, основанных на высоких концентрациях аммиака (4-6 М), в данной работе демонстрируется эффективное выщелачивание металлов с использованием всего 0,5 М NH_4OH, буферированного сульфатом аммония, с применением сульфита натрия (Na_2SO_3) в качестве восстановителя для облегчения разрушения оксидной матрицы.

Благодаря систематической оптимизации были установлены оптимальные параметры процесса: 0,5 М NH_4OH, 0,273 М $(NH_4)_2SO_4$ и 0,8 М Na_2SO_3 при pH 10,5 и 80°C. В этих условиях система достигла эффективности выщелачивания 99,6% для Ni, 96,4% для Li и 89,1% для Co. Отличительной особенностью разработанного процесса является частичная нерастворимость марганца; в отличие от кислотного выщелачивания, этот метод сохраняет 75,9% марганца в твердом остатке, что значительно упрощает последующие стадии очистки и выделения целевых компонентов. Предложенный метод обеспечивает восьмикратное снижение потребления аммиака по сравнению с традиционными аммиачными схемами, что существенно снижает как эксплуатационные расходы, так и углеродный след процесса переработки.

Ключевые слова: литий-ионные батареи; переработка отходов; гидрометаллургия; аммиачное выщелачивание; электродная масса.

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Article

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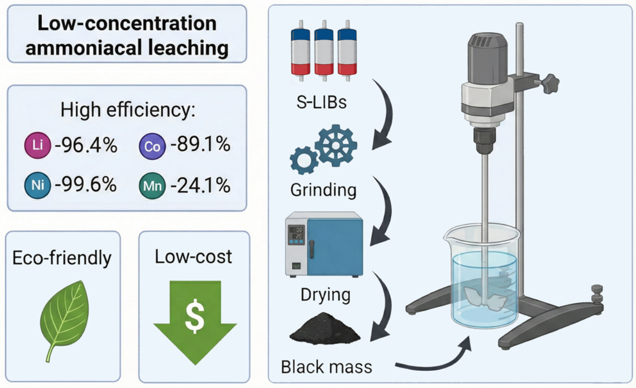
Graphical abstract



1. Introduction

The rapid expansion of the global electric vehicle and consumer electronics markets has created a critical need for the development of sustainable recycling technologies for spent lithium-ion batteries (LIBs) [1]. Projections indicate that approximately 140 million electric vehicles will be in operation by 2030, resulting in the generation of more than 11 million metric tons of battery waste [2]. Despite the global scale of this challenge, worldwide recycling rates for LIBs remain low [3].

Such a disparity between waste generation and recycling rates poses multifaceted challenges across environmental, economic, and strategic dimensions. Improperly disposed LIBs are a significant source of soil and water contamination, introducing transition metals and hydrogen fluoride (HF), a toxic compound generated by electrolyte hydrolysis, into the ecosystem [4]. From the perspective of economic security, the global battery industry is highly vulnerable to geopolitical disruptions. According to data from the United States Geological Survey (2025), the geographic concentration of primary reserves – a factor that will dictate the industry's future reliance on resource-holding nations – is distributed as follows: Co – Congo (54.55%), Li – Chile (31.00%), Mn – Australia (29.41%), Ni – Indonesia (42.31%), and graphite – China (27.93%) (Figure 1) [5]. Recycling is regarded as a fundamental instrument for achieving carbon neutrality targets, since converting mixed-stream lithium-ion batteries into battery-grade materials reduces environmental impacts by at least 58% [6].

The modern LIB recycling industry utilizes three fundamentally different approaches. Pyrometallurgy, which involves high-temperature processing exceeding 1000°C in specialized furnaces, yields metal-rich alloys and lithium-containing slags. This method is characterized by technological simplicity and the absence of requirements for preliminary battery sorting; however, conventional pyrometallurgical methods encounter drawbacks of excessive energy

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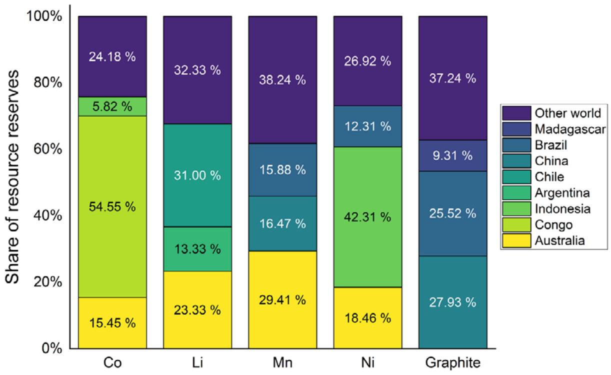

Figure 1 – Distribution of resources required for LIB production by country [5]

consumption, high CO_2 emissions, and substantial lithium loss with lithium in slag and off-gas posing challenges for recovery [7]. Contemporary assessments indicate that pyrometallurgy is economically viable primarily for batteries containing a high proportion of valuable metals, such as nickel and cobalt [8,9].

Hydrometallurgical methods, which are based on processing in solutions of chemical reagents, provide high and selective recovery of metals. The classical approach employs acidic leaching media such as 2 M H_2SO_4 with the addition of H_2O_2, 2-4 M HCl, or mixtures of HNO_3 and HCl. These systems achieve nearly complete dissolution (>98%) of all metals; however, acid utilisation requires specialised conditions and subsequent neutralisation and remediation of the acidic solutions [10].

Direct recycling, which involves the regeneration of cathode materials without complete separation into their primary constituents, represents the most environmentally benign approach, characterized by minimal wastewater generation. However, a key drawback of this technology is its limited technological maturity, which currently hinders the large-scale industrial implementation of direct recycling processes [11].

Within the prevailing dichotomy between non-selective acidic hydrometallurgy and the yet industrially unavailable direct recycling, the search for alternative leaching systems emerges as an optimal solution. A method is required that preserves the high reaction rates inherent to aqueous media while simultaneously enabling a high degree of process selectivity. One promising approach to addressing this challenge is leaching in ammoniacal solutions, where selectivity is governed by the differentiated behavior of individual components. Transition metals (Ni^{2+}, Co^{2+}, Cu^{2+}) form stable ammonia complexes with stability constants of $log\beta_{NH_3}^{(Co,Ni)}(pH) > 8$, whereas aluminum and iron precipitate as hydroxides, $Al(OH)_3$ and $Fe(OH)_3$, at pH = 3.0-5.0 [12,13]. Manganese in ammoniacal media undergoes oxidation to form insoluble MnO_2 or ammonium complex salts [14]. This mechanism enables primary separation of metals directly at the leaching stage, thereby eliminating the need for costly downstream separation operations.

Although the ammoniacal method is well established in conventional hydrometallurgy for copper and nickel ores [12], its application to the processing of spent lithium-ion batteries remains underexplored and warrants systematic investigation. Despite these apparent advantages, the existing literature predominantly focuses on highly concentrated ammoniacal systems (2-6 M NH_4OH) with large excesses of ammonium salts, which compromises the environmental benefits of the approach due to issues related to ammonia volatilization, high reagent consumption, and the complexity of regenerating volatile components [15].

Ammoniacal leaching of lithium-ion battery cathode materials is predominantly carried out in strongly alkaline buffered media with high concentrations of NH_3 and ammonium salts (Table 1), which enables almost complete recovery of Co and Ni, as well as high Li leaching efficiencies at moderate temperatures. [16]. The effectiveness of this process is governed by the formation of stable ammonia complexes and the maintenance of an optimal pH window; however, such a strategy is associated with increased reagent consumption, ammonia volatilization, and greater complexity in gas and

Table 1 – Summary of the results of studies of the ammonia leaching process

Cathode material	Leaching agent (concentration)	Reductant (concentration)	Conditions (T, t, S/L)	Leaching efficiency, %	Ref.
LCO	4.0 M NH_4OH +1.5 M $(NH_4)_2SO_4$	0.5 M Na_2SO_3	90°C, 120 min, 10 g/L	Li: 99.5, Co: 96.5	[19]
LCO	4.0 M NH_4OH + 1.5M NH_4Cl	0.5 M Na_2SO_3	80°C, 4h, 1 g/100 mL	Li: 70.8, Co: 98.2	[20]
NMC	6.0 M NH_4OH – 0.5 M $(NH_4)_2CO_3$	0.5 M Na_2SO_3	150°C, 30 min, 10 g/L	Co: 99.5, Ni: 91.1, Li: 87.0, Mn: 2.5	[21]
NMC	4.0 M NH_4OH – 1.5 M $(NH_4)_2SO_4$	0.5 M Na_2SO_3	80°C, 5 h, 10 g/L	Co: 80.7, Ni: 89.8, Li: 95.3, Mn: 4.3	[22]
NMC	120.0 g/L NH_4OH + 75 g/L NH_4HCO_3	Na_2SO_3 ($n_S : n_{Co}$ = 2:1)	80°C, 240 min, 20 g/L	Co: 91.2, Li: 97.57	[23]
NMC	1.0 M NH_4OH – 1.0 M $(NH_4)_2CO_3$	0.5 M $(NH_4)_2SO_3$	80°C, 1 h, 10 g/L	Co: 94, Ni: 37	[24]
NMC	1.5 M NH_4OH – 1 M NH_4HCO_3	1.0 M $(NH_4)_2SO_3$	60°C, 3 h, 20 g/L	Co: 80.99, Ni: 100, Li: 60.53	[25]
NMC	4.0 M NH_4OH +1.0 M $(NH_4)_2CO_3$	0.3 M Na_2SO_3	80°C, 5 h 10 g/L	Li: 98.4, Co: 99.4, Ni: 97.3	[26]

wastewater treatment [17]. The accumulation of ammonium nitrogen in solid residues and effluents further amplifies toxicological and environmental risks and necessitates resource-intensive neutralization technologies [18,19]. In this context, an important research challenge is the development of ammoniacal leaching systems with reduced NH_3 content that can deliver comparable selectivity and recovery of valuable metals while lowering the environmental and technological burden of the process.

The objective of this study is to demonstrate efficient recovery of valuable metals at low concentrations of ammoniacal buffer through precise optimization of thermodynamic parameters (pH, temperature) and the introduction of an effective sulfite-based reducing system. The aim is not merely to prove the conceptual feasibility of the process, but to perform an in-depth optimization of all relevant parameters in order to achieve industrially meaningful recovery rates while minimizing costs and environmental burdens. This work presents the first systematic investigation of ammoniacal leaching of electrode mass from spent LIBs based on LCO/NMC at NH_4OH concentrations ≤ 0.5 M, providing a rationale for achieving high efficiencies (>90%) at reduced reagent consumption and for selecting the leaching regime from the standpoint of the underlying mechanism of metal dissolution in ammoniacal media.

2. Experiment

2.1 Materials and reagents

Analytical grade and chemically pure reagents were used in this study, including aqueous ammonia solution (NH_4OH, 25%), ammonium sulfate $(NH_4)_2SO_4$), ammonium carbonate $(NH_4)_2CO_3$), ammonium chloride (NH_4Cl), sodium sulfite (Na_2SO_3), as well as sulfuric acid (H_2SO_4) and hydrogen peroxide (H_2O_2, 35 wt.%). All solutions were prepared using distilled water. The electrode mass employed in the experiments was obtained from spent prismatic-type lithium-ion batteries.

2.2 Sample preparation

To obtain the target fraction of electrode mass, the spent cells were subjected to a sequence of discharging, crushing, drying, and fractionation steps, as outlined in Figure 2.

Figure 2 – Schematic illustration of electrode mass preparation process

For the leaching process, the fraction with a particle size of less than 100 µm was selected, as it represents the most homogeneous portion enriched with the target components.

2.3 Leaching methodology and optimization

All leaching experiments were conducted in a 150-mL three-necked round-bottom flask equipped with a reflux condenser to prevent evaporative losses. A 1.00 g sample of homogenized electrode mass was introduced into 100.0 mL of ammoniacal buffer solution containing Na_2SO_3 additives at a fixed temperature, with the suspension stirred at 600 rpm. A water bath was employed to control the reaction temperature. To obtain a representative sample and ensure uniform distribution of components within the electrode mass, each test portion was prepared using the "cone and quartering" method.

Optimization was performed using the One-Variable-At-a-Time (OVAT) approach [28,29], investigating the following parameters: NH_4OH concentration (0.1-1.0 M), Na_2SO_3 reducing agent concentration (0.1-1.0 M), solution pH (10.0-11.75), which was adjusted by adding $(NH_4)_2SO_4$, temperature (50-80°C), and leaching duration (2-8 h).

To determine the initial metal content in the electrode mass, a control acid leaching method was utilised using 2 M H_2SO_4 + 5% H_2O_2 as a traditional reagent regime for electrode mass leaching (so-called standard for black mass dissolution). The treatment involved ultrasonic agitation (1 h) followed by stirring (16 h) to ensure complete metal recovery.

2.4 Analytical methods

The phase composition of the solid products was analyzed by X-ray diffraction (XRD) using a TD-3700 diffractometer (Tongda, China) with Cu-Kα radiation. The elemental composition of the solid phase was assessed by X-ray fluorescence (XRF) analysis using a FOCUS-2M spectrometer.

The concentration of metal ions (Li, Ni, Co, Mn) in the pregnant leach solutions was determined by atomic absorption spectrometry (AAS) using an AA-6200 spectrometer (Shimadzu, Japan).

2.5 Calculation of leaching efficiency

The leaching efficiency was calculated as the ratio of the mass of metal transferred into the solution to its mass in the initial sample (eq. 1):

$$E = \frac{C_{Me}^{solution} \cdot V}{C_{Me}^{solid} \cdot m} \cdot 100\% \qquad (1)$$

Where $-C_{Me}^{solution}$ is the metal concentration in the solution under investigation (mg/L); C_{Me}^{solid} – is the metal content in the electrode mass determined by the standard (section 2.3) method (mg/g), V – is the volume of the diluted solution (L) and m – is the mass of the electrode mass sample subjected to leaching (g).

3. Results and Discussion

3.1 Physicochemical characterization of electrode materials

To determine the composition and structure of the feedstock, a comprehensive set of physicochemical studies was conducted, including elemental analysis and investigation of the phase composition.

Quantitative determination of the major elements was performed by AAS using a wet chemistry (standard acid leaching) procedure. The analysis results, presented in Table 2, indicate that carbon is the dominant component of the mixture (60.2 wt.%), evidencing a high content of graphite (anode material) in the initial mass. Among the valuable metals, cobalt constitutes the largest fraction (23.5 wt.%), followed by nickel (7.0 wt.%) and lithium (5.4 wt.%). The manganese content is 3.9 wt.%. Such a ratio suggests that the processed feedstock represents a mixture of materials, likely based on lithium cobalt oxide and NMC.

Table 2 – Elemental composition of the electrode mass

Element	C	Mn	Co	Li	Ni
wt.%	60.2±1.0	3.9±0.5	23.5±0.6	5.4±0.8	7.0±0.5

To confirm the qualitative composition and identify the crystalline phases, XRF and XRD methods were employed. The XRF spectrum (Figure 3a) clearly exhibits characteristic energy peaks corresponding to the Kα lines of manganese (Mn), cobalt (Co), and nickel (Ni), confirming the presence of these transition metals in the material and corroborating the elemental analysis data. The XRD analysis (Figure 3b) confirmed that the initial electrode mass is a multiphase composite. Quantitative Rietveld refinement identified the presence of two main cathode phases: $LiCoO_2$ (LCO, ~18.4%) and $LiCo_xNi_yMn_zO_2$ (NMC, ~18.1%). In addition to the active cathode components, graphite, which is the primary anode material, is present in significant quantities (~60.6%). All identified crystalline phases are characterized by narrow and intense reflections, indicating a high degree of crystallinity of the starting materials.

3.2 Optimization of the ammoniacal leaching process

The optimization of electrode mass leaching from spent LIBs represents a multi-stage process of identifying the optimal value for each of the investigated factors. The selected initial conditions are averaged values used in previous studies (Table 1): leaching time – 2 h, stirring speed – 600 rpm, temperature – 80°C; reagent concentrations – 4 M NH_4OH + 0.75 M $(NH_4)_2CO_3$, pH = 11.0

3.2.1 Effect of buffer additive anion composition on leaching efficiency

The selection of the optimal composition for the leaching system requires not only determining the ligand (ammonia) concentration but also justifying the nature of the anionic background created by ammonium buffer salts. Given the limited systematic data in the current literature regarding the specific influence of anions on the dissolution of NMC-type cathode materials, a series of comparative experiments was conducted. The effect of three ammonium salts was investigated: chloride (NH_4Cl), sulfate ($(NH_4)_2SO_4$), and carbonate ($(NH_4)_2CO_3$), maintaining the following reagent regime: 4M NH_4OH + 0,75M $(NH_4)_2SO_4$ + 0,5M Na_2SO_3; 4M NH_4OH + 1,5M NH_4Cl + 0,5M Na_2SO_3; 4M NH_4OH + 0,75M $(NH_4)_2CO_3$ + 0,5M Na_2SO_3.

Analysis of the obtained experimental data (Figure 4) demonstrates the absence of a critical influence of the anions' nature on the final leaching efficiency of the target metals. The variability of leaching rates across salts falls within a 5-7% confidence interval, consistent with data from several researchers indicating that the dominant factor in complexation is free ammonia concentration ($[NH_3]$ free) rather than the nature of the anion.

Nevertheless, the ammonia system based on ammonium sulfate ($(NH_4)_2SO_4$) was selected for further process optimization in this work. This choice is dictated by a combination of physicochemical and technological factors that determine the stability, controllability, and environmental compatibility of the

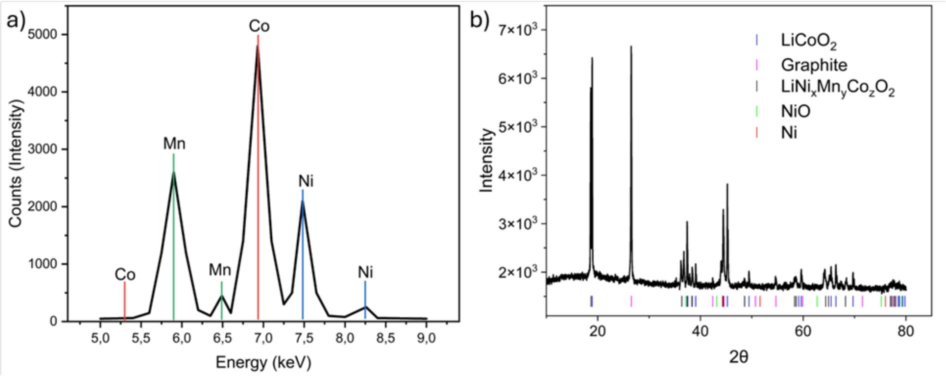

Figure 3 – a) XRF spectrum of the electrode mass, b) XRD pattern of the electrode mass

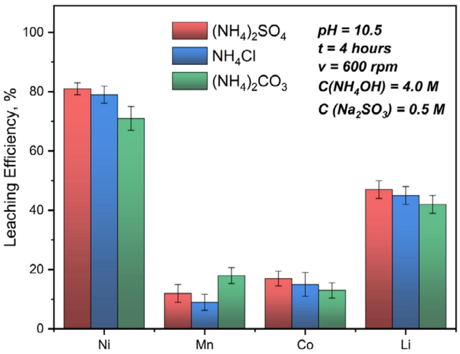

Figure 4 – Comparative diagram of leaching using different ammonium salts

leaching medium. First, ammonium sulfate is characterized by high solubility (approximately 750-760 g/L at 20°C), which allows for the formation of solutions with increased buffer capacity in the NH_3/NH_4^+ system. This is fundamentally important for maintaining a quasi-stationary pH in the range of 9.5-11.5, where, on one hand, a sufficient concentration of free ammonia for complexation is ensured, and on the other hand, intensive hydrolysis of metal ammonia complexes and premature precipitation of hydroxide phases upon NH_3 consumption are prevented [30]. Second, corrosion and operational aspects serve as significant arguments in favor of the sulfate medium. The chloride ion (Cl^-) is an effective initiator of pitting corrosion in stainless steels, necessitating the use of expensive corrosion-resistant alloys (e.g., titanium or high-alloy nickel-containing materials) [31]. Carbonate systems based on ammonium salts, despite their widespread use, possess limited thermal stability: at temperatures above 50-60°C, ammonium carbonate undergoes decomposition with the evolution of gaseous ammonia and carbon dioxide, accompanied by uncontrolled changes in the leaching solution composition and increased specific reagent consumption (eq. 2) [32, 33]:

$$(NH_4)_2CO_3 \xrightarrow{T} 2NH_3\uparrow + CO_2\uparrow + H_2O \qquad (2)$$

This leads to uncontrolled variations in the leaching solution composition and increased reagent costs. Thus, the use of the sulfate system ensures an optimal balance among leaching efficiency, process-parameter stability, and equipment design requirements.

3.2.2 Effect of solution pH on leaching efficiency

The pH of the leaching solution in the ammonia–sulfate system is a secondary parameter determined by the ratio of the free base NH_3 to its conjugate acid form NH_4^+, as well as by the concentration of the ammonium salt, in accordance with the Henderson–Hasselbalch equation (eq. 3) [34]:

$$\mathrm{pH} = \mathrm{p}K_a + \log\frac{[NH_4^+]}{[NH_3]} \qquad (3)$$

where $[NH_4^+]$ is the equilibrium concentration of the conjugate acid (mol/L) and $[NH_3]$ is the concentration of the base (mol/L). Thus, the actual pH value depends on the ratio of the equilibrium concentrations $[NH_3]$ and $[NH_4^+]$, implying that the target pH can be achieved even when using economically preferable low ammonia concentrations.

To maintain a pH of 10.5 in a solution with a high total ammonia concentration (4.0 M), the addition of a significant amount of ammonium sulfate as a buffering agent is required. This leads to a drastic increase in the concentration of sulfate (SO_4^{2-}) and ammonium (NH_4^+) ions in the system.

Under these conditions, the solubility product of ammonium–metal double sulfates (Tutton salts) of the type $(NH_4)_2Me(SO_4)_2 \cdot 6H_2O$, where Me = Ni, Co, may be exceeded. The precipitation of these sparingly soluble salts, whether on particle surfaces or in the bulk solution, effectively removes the target metals from the liquid phase, which appears as a decrease in extraction efficiency.

Consequently, transitioning to a low-concentration system at the same pH helps avoid this "salt overload" effect, ensuring sufficient ligand concentration for complexation, maintaining high ionic mobility, and preventing secondary salt precipitation.

As illustrated in Figure 5b, increasing the concentration of $(NH_4)_2SO_4$ leads to a monotonic decrease in the system's pH, consistent with the theoretical shift in equilibrium towards the conjugate acid. However, the addition of the reducing agent (Na_2SO_3) results in a systematic increase in pH relative to the initial buffer solution, attributable to the alkaline hydrolysis of the sulfite ion ($SO_3^{2-} + H_2O \leftrightarrow HSO_3^- + OH^-$). This buffering behavior effectively stabilizes the medium, although the final operating pH is slightly higher than values predicted solely by the ammonia/ammonium ratio [35].

According to the experimental data presented in Figure 5a, the pH value of the buffer system decreases as the concentration of $(NH_4)_2SO_4$ in the solution increases, which is characteristic behavior for solutions containing salts formed from a strong acid and a weak base (eq. 3) [35]. This leads to a decrease in the fraction of free NH_3 and a reduction in the effective capacity of the medium to stabilize coordination-saturated $[Me(NH_3)_2]^{2+}$ complexes.

As demonstrated in Figure 5a, the three pH regions. In the "ligand deficiency zone" (the lower bound of the pH interval), a significant portion of ammonia is protonated; consequently, the conditional stability constants $\log\beta'_{Ni}$ and $\log\beta'_{Co}$ decrease, and the fraction of soluble ammonia drops, leading to reduced leaching efficiencies for Li, Co, and Ni [26, 36]. Under these conditions, a fraction of Mn(II), not being as strongly stabilized by ammonia, remains in ionic form and may be additionally incorporated into solid sulfite or oxide phases, which manifests as a relative increase in its leaching upon transitioning to more favorable pH values [37, 38]. In the optimal zone (around pH 10.5), the fraction of free NH_3 is close to unity, corresponding to the maximum of $\log\beta'_{Ni} = 2.83$ and $\log\beta'_{Co} = 6.60$ and ensuring the formation of stable $[Ni(NH_3)_4]^{2+}$ and $[Co(NH_3)_4]^{2+}$ complexes while the supersaturation threshold for $Me(OH)_2$ has not yet

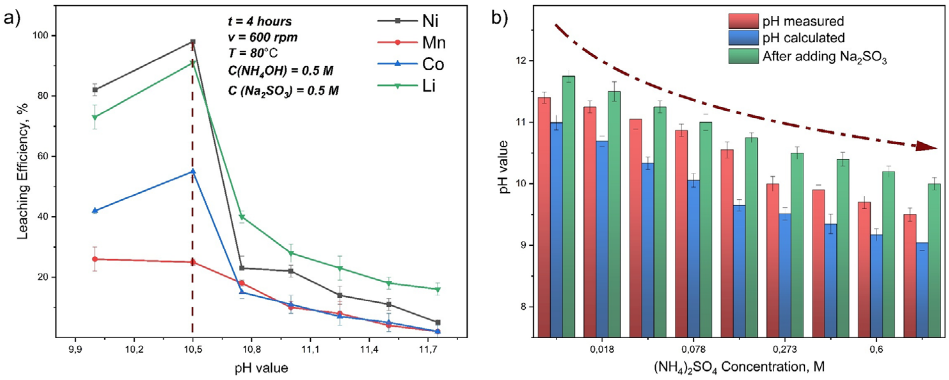

Figure 5 – a) Graph of the effect of $(NH_4)_2SO_4$ concentration on leaching efficiency; b) Graph of pH dependence on $(NH_4)_2SO_4$ concentration

been exceeded, due to the drastic reduction of free metal ion activity (α_{Me2+}) [36, 37]. Even though the concentration of OH^- ions is high at pH 10.5, the competitive coordination by NH_3 keeps the ion product $[Me^{2+}][OH^-]^2$ strictly below the Solubility Product constant (K_{sp}), effectively masking the metal cations from precipitation. Under these conditions, maximum leaching efficiencies for Ni, Co, and Li are achieved, whereas Mn is partially retained in the solid phase and/or precipitates as sulfite- and sulfate-containing compounds [26]. With a further increase in pH (>11.0), the rise in OH^- activity leads to the dominance of hydrolysis over complexation: the solubility products of $Ni(OH)_2$, $Co(OH)_2$, and $Mn(OH)_2$ hydroxides are exceeded, resulting in the formation of sparingly soluble hydroxide and oxide films on the particle surfaces.

Comparing two leaching regimes with different total ammonia concentrations at a fixed pH of 10.5 showed that decreasing NH_4OH from 4.0 M to 0.5 M, accompanied by a reduction in $(NH_4)_2SO_4$ from 0.75 M to 0.273 M, did not compromise the process; conversely, it substantially improved the recovery of all target metals (Figure 6a). Lithium recovery increased from 46.1% to 83.1%, nickel from 81.7% to 98.3%, cobalt from 17.8% to 57.6%, and manganese from 11.2% to 26.1%.

The observed increase in metal recovery upon reducing the ammonia concentration from 4.0 M to 0.5 M requires a precise mechanistic interpretation. The lower efficiency associated with the high-concentration medium (4.0 M NH_4OH + 0.75 M $(NH_4)_2SO_4$) is not attributable to any inhibitory effect of excess ligand (NH_3), but rather to the disruption of the acid-base equilibrium within the system [39].

As demonstrated in Figure 6a, at high base concentrations (NH_4OH), the amount of ammonium sulfate used (0.75 M) provides insufficient buffering capacity. According to the Henderson–Hasselbalch equation, this results in an uncontrolled rise in pH (>11.5), pushing the system outside the thermodynamic stability window of soluble ammonia complexes. At such elevated pH levels, the equilibrium shifts toward the formation of thermodynamically stable but insoluble hydroxides, specifically $Ni(OH)_2$ and $Co(OH)_2$. These hydroxide phases form passivating films on the surface of the electrode particles, hindering reagent diffusion and effectively blocking the dissolution process [36,38].

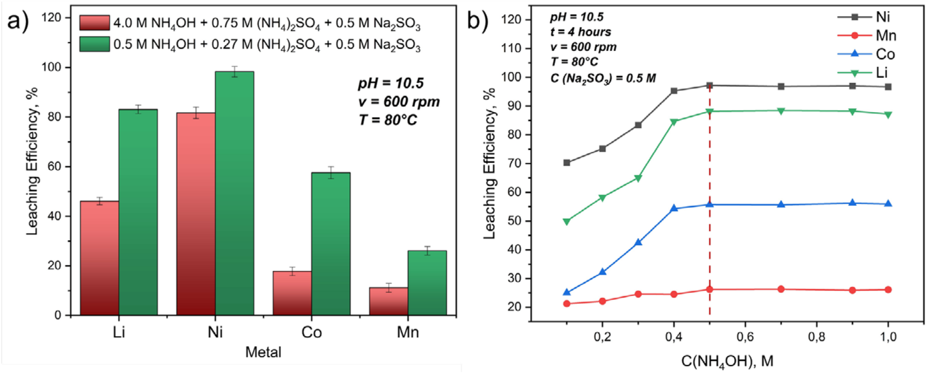

Figure 6 – a) Comparison of metal leaching efficiency at different equilibrium NH_3/NH_4^+ concentrations at pH 10.5; b) Dependence of metal leaching efficiency on NH_4OH concentration in the range of 0.1–1.0 M

Consequently, the transition to the 0.5 M NH_4OH regime, balanced with adequate buffering, maintains the pH within the optimal 'stability window' (10.0-10.5) (Figure 6b). This prevents the secondary precipitation of metals and facilitates the complete leaching of target components.

To quantitatively refine the boundaries of this optimum, the dependence of leaching efficiency on NH_4OH concentration was investigated in the range of 0.1-1.0 M at constant pH, temperature, and reducing agent concentration (Figure 6b). The obtained curves demonstrate that increasing concentration of NH_4OH to 0.5 M is accompanied by a significant rise in the recovery of Ni, Co, and Li, whereas a further increase in the base concentration has virtually no effect on the process efficiency, confirming the existence of a "plateau".

3.2.3 Effect of process temperature on leaching efficiency

The investigation of the temperature dependence was conducted in the range of 50-80°C at fixed pH and reagent concentrations, allowing the changes in leaching efficiency to be interpreted as a manifestation of kinetic limitations of the leaching process (Figure 7). For nickel and lithium, a nearly linear dependence of leaching efficiency on temperature was established: Ni recovery increases from 57.0% to 97.5%, and Li from 58.8% to 87.1%, indicating a significant reduction in the energy barrier for oxide lattice destruction and an acceleration of diffusion and complexation steps upon heating.

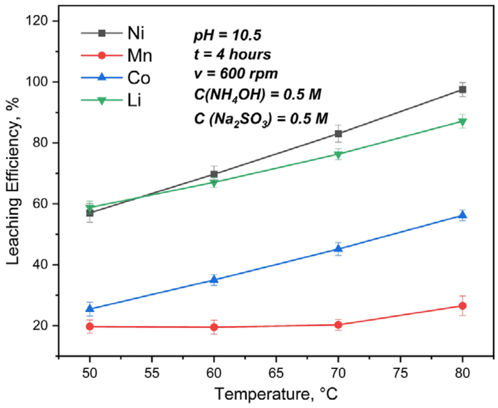

Figure 7 – Graph of leaching efficiency dependence on process temperature

Cobalt also exhibits a monotonic increase in leaching efficiency (from 25.5% to 56.2%); however, the absolute values remain substantially lower than those for nickel, confirming the more inert nature of Co(III)-containing phases and the higher energy requirements for their reductive dissolution in the ammonia–sulfite medium. Against this background, the behavior of manganese is fundamentally different: in the 50-70°C interval, its leaching rate remains practically unchanged (≈20%), and only at 80°C is a moderate increase to 26.6% observed.

The observed weak temperature dependence of Mn recovery indicates its unfavorable thermodynamic position in the Ni/Co/Li–Mn system: manganese ammonia complexes are less stable, and the corresponding solid phases (higher oxides) exhibit high solubility only under conditions outside the selected pH. Collectively, this suggests that increasing the temperature primarily intensifies the reductive dissolution of nickel and cobalt while maintaining the selective retention of manganese in the solid phase, which constitutes a significant advantage of the ammonia–sulfite system for processing cathode materials.

3.2.4 The role of the reducing agent in the leaching mechanism

The use of a reducing agent in the leaching of LIB electrode mass is a well-known and generally accepted practice, necessary for converting the transition metals of the cathode material into a more soluble form, thereby facilitating their transfer into solution and binding by the complexing agent. However, the electrode mass of batteries may also contain elements initially present in readily soluble forms. Thus, the efficiency of Li^+ recovery from the electrode mass should proceed without significant difficulties even in systems where a reducing agent is absent.

To verify the aforementioned hypothesis, an experiment was conducted using two solutions − with and without the addition of a reducing agent. 0.5 M Na_2SO_3 was used as the reducing agent. The solutions employed had the following composition: 0.5 M NH_4OH + 0.273 M $(NH_4)_2SO_4$; 0.5 M NH_4OH + 0.273 M $(NH_4)_2SO_4$ + 0.5M Na_2SO_3.

The results (Figure 8a) clearly demonstrate that in the absence of a reducing agent, the process is virtually blocked: the leaching efficiencies of nickel and cobalt are close to zero. The exception is lithium, which partially transfers into solution via ion exchange; however, its leaching remains low due to the integrity of the oxide matrix, which hinders ion diffusion from the particle bulk.

The introduction of Na_2SO_3 fundamentally changes the process kinetics. The sulfite anion, containing sulfur in an intermediate oxidation state (S^{+4}), acts as an effective reducing agent, facilitating heterogeneous electron transfer at the phase interface (eq. 4):

$$2Me^{3+}_{(S)} + SO_3^{2-} + H_2O \rightarrow 2Me^{2+}_{(aq)} + SO_4^{2-} + 2H^+ \qquad (4)$$

The resulting Co^{2+} and Ni^{2+} cations exhibit a high affinity for ammonia and are instantly bound into stable, soluble ammonia complexes of the type $[Me(NH_3)_n]^{2+}$ (where n=4-6), which shifts the reaction equilibrium towards the complete dissolution of the solid phase.

To minimize reagent costs, a series of experiments was conducted to determine the critically necessary concentration of the reducing agent. The concentration of Na_2SO_3 was varied in the range of 0.1-1.0 M under otherwise identical conditions. Analysis of the dependence of leaching efficiency on the concentration of the reducing agent (Figure 8b) allows for the

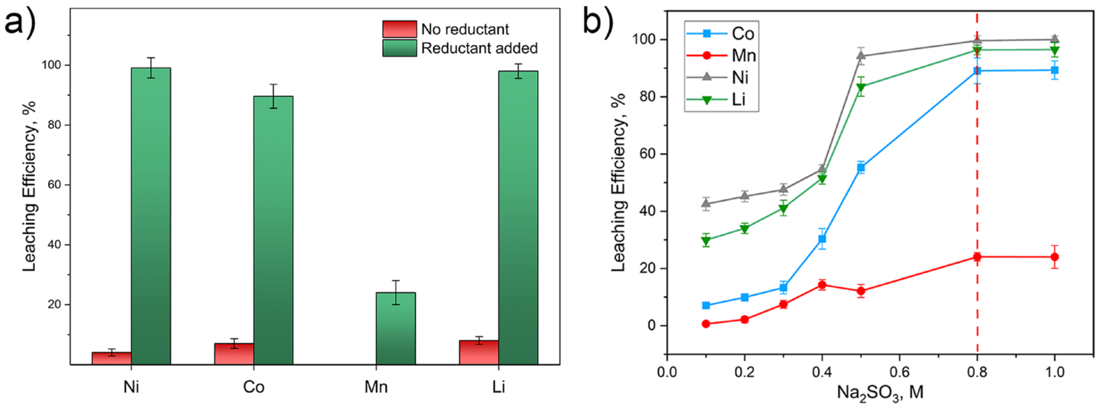

Figure 8 – a) Comparative leaching diagram: with and without reducing agent,
b) Graph of leaching efficiency dependence on Na_2SO_3 concentration

identification of two characteristic regions: 1) Deficiency Region (< 0.5 M): a sharp decline in process efficiency is observed. Insufficient reducing agent results in incomplete reduction of Co^{3+}, leaving a portion of the material undissolved. 2) Saturation Region (≥ 0.5 M): at a concentration of 0.8 M, the maximum leaching of the target components is achieved. A further increase in concentration to 1.0 M does not lead to a statistically significant increase (only Co efficiency is increased) in efficiency (a "plateau").

Following the reductive leaching process in the optimized low-concentration medium (0.5 M NH_4OH + 0.273 M $(NH_4)_2SO_4$ + 0.8 M Na_2SO_3), the diffractogram of the solid residue (Figure 9) demonstrated a near-complete disappearance of reflections associated with the nickel-rich phases, confirming the effective transfer of nickel into the solution. Crucially, the manganese-bearing phase, identified as the spinel $LiMn_2O_4$, remained intact in the residue. This crystallographic evidence confirms that under the established conditions (pH 10.5), manganese does not form stable soluble ammonia complexes and is selectively retained in the filter cake, validating the in-situ separation capability of the process.

Furthermore, the diffraction pattern of the leached residue revealed the persistence of characteristic peaks attributed to the $LiCoO_2$ phase. Despite the high cobalt leaching rate (89.1%), the presence of this residual phase indicates that the highly crystalline core of lithium cobalt oxide possesses greater kinetic resistance to reductive dissolution compared to the mixed oxide phases. Consequently, the refractory fraction of cobalt remains in the solid phase alongside graphite and manganese compounds, explaining the difference in leaching efficiency between nickel and cobalt.

3.3 Comparison of leaching efficiency with other systems

To assess the competitiveness of the optimized reagent regime, a comparative analysis was conducted to evaluate the efficiency of the developed system against traditional inorganic and organic leaching agents, as well as high-concentration

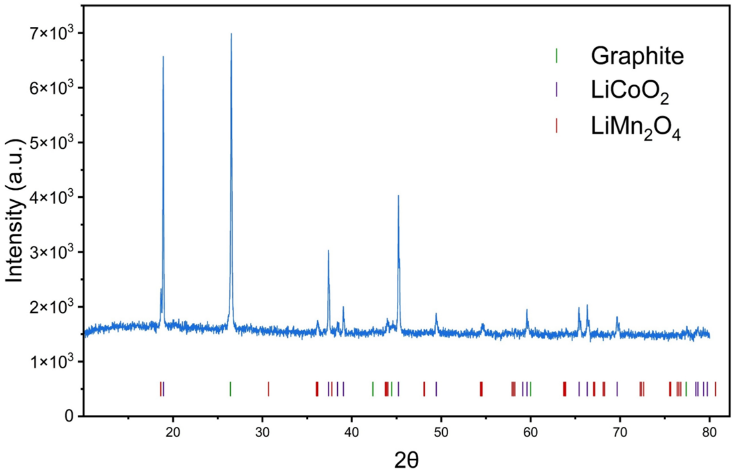

Figure 9 – X-ray diffractograms of the studied black mass: a) before and b) after leaching at optimal conditions

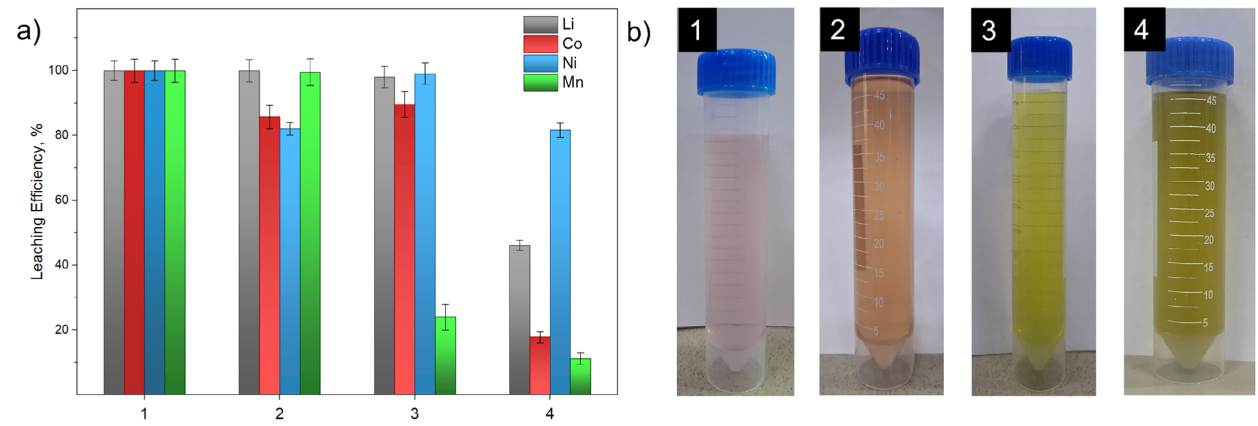

Figure 10 – (a) comparative diagram of metal leaching efficiency; (b) comparative photographs of leached liquor for different systems: (1) 2.0 M H_2SO_4 + 5 v/v % H_2O_2, T = 70°C; (2) 1.25 M H_3Cit + 1 v/v % H_2O_2; T = 90°C; (3) 0.5 M NH_4OH + 0.273 M $(NH_4)_2SO_4$ + 0.8 M Na_2SO_3; (4) 4.0 M NH_4OH + 0.75 M $(NH_4)_2SO_4$ + 0.5 M Na_2SO_3

ammonia media. Optimization studies established that the low-concentration system (0.5 M NH_4OH, 0.273 M $(NH_4)_2SO_4$, and 0.8 M Na_2SO_3), under conditions of constant pH maintenance at 10.5 and a temperature of 80°C, yielded the highest recovery rates for target metals within the studied reagent composition: Ni – 99.6%, Li – 96.4%, and Co – 89.1%. A distinct feature of this process is its high selectivity towards manganese, with a leaching efficiency of only 24.1%, confirming its predominant retention in the solid phase.

Analysis of the experimental data presented in Figure 10 reveals significant disparities in the behavior of the systems investigated. While the use of sulfuric acid (Figure 10, System 1) results in the nearly complete dissolution of all electrode mass components (close to 100%), this method is characterized by extremely low selectivity. The co-dissolution of impurities (Mn, Fe, Al) alongside target metals, combined with the generation of toxic acidic effluents, significantly complicates downstream purification stages and increases the environmental burden. Although the application of organic acids, specifically citric acid (Figure 10, System 2), represents a more environmentally sustainable alternative, it is frequently associated with surface passivation phenomena induced by a local pH increase within the reaction zone, ultimately leading to reduced overall leaching efficiency compared to mineral acids [40].

In contrast to acidic methods and traditional high-concentration ammoniacal leaching (4-6 M NH_4OH, Figure 10, System 4), the proposed low-concentration approach (Figure 10, System 3) achieves comparable leaching efficiencies for nickel and lithium while significantly reducing reagent consumption. The transition to ammonia concentrations at the level of 0.5 M ensures an eightfold reduction in ammonia consumption compared to classical schemes. This not only decreases direct operating costs but also lowers the carbon footprint of the process, considering the energy intensity of ammonia production (2.5 kg CO_2-eq/kg NH_3) [41], thereby enhancing the economic and environmental feasibility of the proposed method.

4. Conclusion

This study successfully demonstrates the feasibility of a sustainable, low-concentration ammoniacal leaching process of critical metals from black mass of spent NMC/LCO lithium-ion batteries. Through the optimization of thermodynamic and kinetic parameters, a highly efficient reagent regime was established, utilizing 0.5 M NH_4OH, 0.273 M~ $(NH_4)_2SO_4$, and 0.8 M Na_2SO_3 at a temperature of 80°C and pH 10.5. Under these conditions, the system achieved leaching efficiencies of 99.6% for nickel, 96.4% for lithium, and 89.1% for cobalt, effectively competing with traditional high-concentration methods while requiring significantly lower ammonia consumption.

From an industrial perspective, this method offers a compelling alternative to traditional routes. An 8-fold reduction in ammonia concentration lowers environmental risks associated with volatility and substantially decreases the carbon footprint of the recycling process. The obtained results create a solid scientific foundation for the development of "greener" and economically efficient closed-loop recycling technologies suitable for the growing stream of battery waste.

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CRediT authorship contribution statement

Artur Grigoryev: writing – original draft, methodology, investigation. *Saken Abdimomyn:* writing – review & editing, writing – original draft, investigation, conceptualization. *Mikhail Simonov:* original draft, methodology, investigation. *Fyodor Malchik:* writing – review & editing, supervision, conceptualization, project administration, funding acquisition.

Conflicts of 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.

Data availability

Data will be made available on request.

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