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Purification of lanthanum chloride solution through tertiary amine extraction: thermodynamic and graded assessment

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ABSTRACT

Purification of lanthanum chloride from high-load zinc contaminants remains a major challenge in producing grade 5N lanthanum oxides. This study investigates the process of matrix-driven solvent extraction using tertiary amine N235 to treat a 1.41 M rare earth oxides (REO) industrial lanthanum chloride feed containing 3000 mg/L zinc. Thermodynamic modelling with Medusa Hydra and Langmuir isotherms revealed that the high chloride activity (> 4 M) of the matrix induced significant changes in coordination towards the extractable $[ZnCl_4]^{2-}$ complex. This transition has a spontaneous Gibbs free energy of -14.68 kJ/mol. While the two-stage counter-current flow sheet meets the industry target of less than 50 mg/L zinc, the five-stage configuration achieves a four-log reduction to 0.23 mg/L, effectively achieving 99.999% purity. This reagent's lean approach, using water-induced stripping, offers a sustainable and mathematically validated framework for ultra-high purity rare earth finishes.

Keywords: lanthanum chloride, solvent extraction, zinc, N235, McCabe-Thiele.

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Introduction

Rare earth elements (REEs), from lanthanum (La) to lutetium (Lu), are essential in modern technologies such as communications, defence, medicine, and clean energy due to their magnetic, catalytic, and fluorescent properties. Global demand has soared with the shift to a high-tech, low-carbon economy, yet supply chains remain vulnerable, especially for ultra-high (5N, 99.999%) lanthanum oxide (La_2O_3) used in optical lenses, capacitors, and photocatalysts [1]. Impurities such as Zn severely degrade performance, disrupting dielectric properties or the lattice structure [[2], [3], [4]].

Purifying industrial lanthanum chloride ($LaCl_3$) solutions, often near saturation yet contaminated with thousands of ppm Zn, is a key bottleneck in hydrometallurgy [[5], [6]]. Conventional methods, such as sulphide precipitation, generate hazardous gases and fail to meet sub-ppm targets. Ion exchange suits only low-concentration, low-flow REE solution rates [[7], [8]]. Solvent extraction using organo-phosphonic acids, such as D2EHPA/PC-88A/Ionquest 801, incurs high cost [[9], [10], [11]. Tertiary amines such as N235 show promise for

Table 1 - A performance benchmark of the matrix-driven N235 system against literature-reported organophosphorus and solvating extractants for zinc removal

Extractant	Impurity	Extraction			Stripping		Ref
		Medium	D_{Zn}	Stages	Reagent	Stages	
DEHPA di-2-ethylhexyl phosphoric acid	Zn + Mn	Cl^- Zn-C battery leach liquor	9	1+3	6M HCl	1+3	[18]
Cyanex 923 trialkyl phosphine oxides	Zn + Fe	Steel pickle liquor Cl^-	5 - 100	3	0.8M HNO_3	1	[19]
D2EHPA + Cyanex 302 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester + bis(2,4,4-trimethylpentyl) monothiophosphinic acid	Zn $ZnSO_4[CS(NH_2)_2]$	Zn SO_4^{2-} solution	20 - 80	n/r	0.45M thiourea acid	2	[20]
N503 N, N-di(1-methylheptyl) acetamide	Fe/Zn $[CH3CONR2H]ZnCl_3$	Spent pickle solution Cl^-	278.92	4	0.4M HCl		[21]
N1953 primary amine	Zn RNH_3ZnCl_3	Spent pickle solution Cl^-		3	H_2SO_4 -> 5.39M Zn		[22]
Aliquat 336 quaternary ammonium salt	Zn From 17 g/L	Spent pickle solution Cl^-					[23]
TOA tri-n-octylamine	Zn	Spent pickle solution Cl^-		5	2M HNO_3		[24]
P507+P204 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester + di-2-ethylhexyl phosphoric acid	Zn	Spent acid Cl^-		84.7% E-Zn	H_2SO_4		[25]
Cyanex 272, bis(2,4,4-trimethylpentyl) phosphinic acid	Zn	Cobalt-Zn Cl^-		15	H_2SO_4		[26]

other metal separation, such as mini actinides and REE [12], molybdenum recovery from copper leach [13], but require a complexing agent such as tartaric acid to form extractable anionic species [13][14]. Despite advances in zinc recovery from secondary sources [[15], [16], [17] no reagent-free framework leverages high-salinity $LaCl_3$ matrices for deep purification in concentrated REE streams.

Existing research, summarised in Table 1, mostly studies Zn removal from spent pickle solution of Cl^- basis and the stripping with acid, overlooking matrix-induced coordination shifts, limiting scalability from 99.9% industrial feed to 5N high-tech grades. This study harnesses chloride activity in $LaCl_3$ as a self-salting agent for Zn removal via N235-based solvent extraction, achieving <50 ppm and enabling 5N purity.

Experimental section

Chemicals and reagents

Aqueous feed is an industrial-grade solution of lanthanum chloride. The chemical properties are summarised in Table 2. This solution is characterised by a Total Rare Earth Oxide (TREO) concentration of 260 g/L (1.41 mol/L) and a base acidity of 0.012 mol/L (pH 1.92). A critical feature of this feed is a significantly high zinc concentration of 3000 mg/L, which represents the main impurity barrier to achieving high-purity-grade lanthanum.

To establish a thermodynamic basis for zinc removal, the stability of various zinc chloride complexes has been modelled using the Medusa Hydra software, as presented in Figure 1. The coordination sphere is evaluated as a function of chloride activity to confirm the self-salting potential of the matrix.

Table 2 - Characteristics of $LaCl_3$ industrial solution

Acidity	REO	La2O3 /REO	CeO2 /REO	Pr6Nd1 1 /REO	Nd2O 3 /REO	Sm2O 3 /REO	Eu2O 3 /REO	Tb4O 7 /REO	Tm2O 3 /REO	Y2O 3 /RE O	Yb2O 3 /REO	Fe	Zn
(mol/L)	(mol/L)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(ppm)	(ppm)
0.012	1.41	99.9	0.011	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1.44	3000

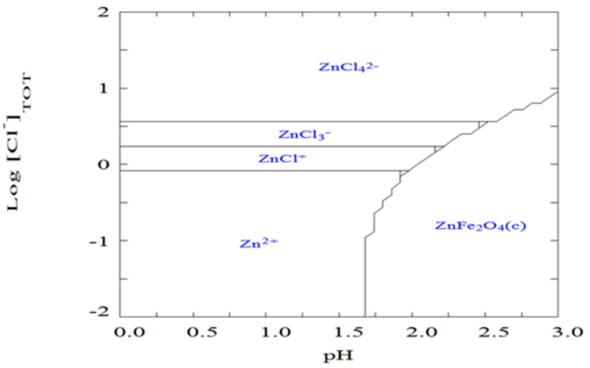

Figure 1 - Zinc species dominance diagram as a function of pH activity and chloride volume in the high Cl, high Zn $LaCl_3$ system

The dominance of the anionic species $[ZnCl_4]^{2-}$ at chloride levels above 4 M, naturally provided by a 1.41 M $LaCl_3$ matrix, supports a very high selectivity compared to conventional low-salinity environments.

At the industrial feed acidity (pH 1.9) and high chloride activity ($[Cl^-]$ 4.23M, or log $[Cl^-]$ 0.63), the system is in the predominance field of the anionic tetrachloride-zincate complex $[ZnCl_4]^{2-}$. The quantitative transformation of Zn^{2+} to the anionic tetrachloride-zincate complex $[ZnCl_4]^{2-}$, is represented by Equation 1.

$$Zn^{2+}(aq) + 4Cl^{-}(aq) = [ZnCl_4]^{2-}(aq) \quad (1)$$

The organic phase is prepared using tri-iso-octylamine (N235) (industrial grade, 98.5%) as the extractor, diluted in sulfonated kerosene (Escaid 110) (industrial grade, 99.8%). Isopropanol (IPA) (industrial grade, 99%) has been used as a polar modifier to stabilise mixtures. Although previous literature often used iso-butanol, this study strategically chose short-chain alcohol IPAs over iso-butanol to minimise overall viscosity and prioritise mass transfer kinetics.

The organic mixture has been pre-treated with an alkaline wash using an 8 wt.% sodium carbonate solution to remove impurities. This is followed by protonation with 4.5 M hydrochloric acid to form a substituted quaternary ammonium cation, as shown in Equation 2

$$R_3N(org) + H(^{+}aq) + Cl(^{-}aq) \rightleftharpoons (R_3NH^{+}Cl^{-})(org) \quad (2)$$

where R represents the octyl chain.

Extraction occurs when the anionic complex $[ZnCl_4]^{2-}$ has a strong affinity for the protonated amine carrier R_3NH^+Cl-. This causes the target species to be separated into organic phases through the formation of stable ion pairs as described in Equation 3.

$$2(R_3NH^{+}Cl^{-})(org) + [ZnCl_4]^{2-}(aq) \rightleftharpoons ([R_3NH]_2[ZnCl_4])(org) + 2Cl(^{-}aq) \quad (3)$$

This is unlike the extracted zinc with primary amine N1953 as RNH_3ZnCl_3 and tri-n-octylamine (TOA) as $R_3NHZnCl_3$[24].

Extraction and Analysis Procedures

Batch extraction tests were conducted in a 250 mL borosilicate glass beaker using an IKA RW20 digital overhead mixer at 700 RPM at an ambient temperature of 25 ± 2°C. For isotherm extraction studies, the aqueous-to-organic (A/O) ratio ranges from 1:5 to 5:1. The sample is equilibrated for 15 minutes to ensure thermodynamic equilibrium [18].

After phase discharge, aqueous fines were analysed for zinc using Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES). The concentration of metals in the organic phase is determined by mass balance. The organic phase is then stripped by contacting it with 0.1 M hydrochloric acid (HCl) and deionized water to assess the stripping efficiency. After separation, the aqueous phase was analysed for zinc, lanthanum, and total rare earth oxides (TREO). Zinc is measured using atomic absorption spectroscopy (AAS) while REO and lanthanum are determined by ICP-OES. The concentration of metals in the organic phase (C_{org}) is determined by the mass equilibrium as in Equation 4.

$$C_{org} = \frac{(C_{init} - C_{equil}) \times V_{aq}}{V_{org}} \qquad (4)$$

Where C_{init} and C_{equil} are the initial aqueous and equilibrium concentrations, and V_{aq} and V_{org} are the aqueous and organic phase volumes, respectively. The refining purity target has been set at a zinc concentration of <50 ppm to meet stringent industry specifications.

The distribution ratio, D_{Zn}, which measures the zinc equilibrium distribution between the organic and aqueous phases, has been calculated using Equation 5.

$$D_{Zn} = [Zn]_{organic}/[Zn]_{aqueous} \qquad (5)$$

To assess the loading capacity and equilibrium behaviour, the initial Zn concentration was varied from 10 to 2000 mg/L. The resulting data were fitted to the Langmuir adsorption isotherm model as Equation 6

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \qquad (6)$$

where q_m (mg/g) is the amount of Zn extracted per unit of extractor mass, C_e (mg/L) is the equilibrium concentration in the aqueous phase, q_m is the maximum load capacity, and KL is the Langmuir constant.

The spontaneity of the extraction process was evaluated by calculating the standard Gibbs free energy (ΔG°) from the equilibrium constant (K_c) derived from the Langmuir model, as given in Equation 7.

$$\Delta G^{\circ} = -RTln(K_C) \qquad (7)$$

This calculation provides a rigorous thermodynamic assessment of coordination shifts in the $LaCl_3$ matrix.

From the isotherm, the McCabe-Thiele construction method will be used to determine the number of stages required to achieve 5N purity.

As in any continuous solvent extraction system, the loaded organics must be efficiently stripped to recover the extracted product. The barren organic matter is then regenerated and recycled back to the beginning of the system, repeating the process. In REE recovery through a continuous solvent extraction system, strong acids such as HCl are used to remove the extracted elements. The water is used to wash away the waste acids, produce a barren organic backing, and is then treated, ready for extraction. In this study, 0.1 M HCl and water were compared for their ability to strip the zinc loaded at N235 at an A/O of 0.5-10.

Results and Discussions

Distribution Coefficient: Extraction Rate

The distribution ratio (D_{Zn}) in this $LaCl_3$ matrix exceeded 150 at low A/O, significantly surpassing the DEHPA benchmark (D_{Zn}=45 in Cl^- leach). This demonstrates N235's superior affinity for $[ZnCl_4]^{2-}$ at low A/O ratios, as shown in Figure 2 (a). D_{Zn} drops dramatically from over 20 to under 5 when the A/O increases from 0.25 to 1.0 with 7% v/v N235. Higher concentrations (40% to 99% extraction at A/O=2) further exacerbate this effect. Interestingly, the D_{Zn} values for 15% and 30% N235 are identical across the higher A/O range (1.5 to 5.0). This indicates that beyond a 15% concentration, the extraction is no longer limited by extractant availability but is instead governed by the aqueous speciation of the $[ZnCl_4]^{2-}$ complex. This supports the "matrix-driven" hypothesis, where the 1.41 M $LaCl_3$ environment dictates the maximum possible formation of extractable anionic species, as illustrated in Figure 2 (b).

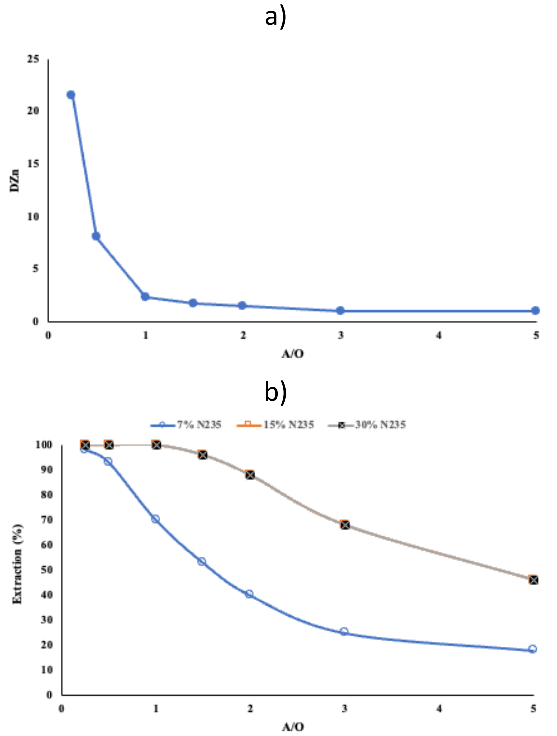

Figure 2 – Zn extraction from La chloride, a) the effect of A/O on the distribution ratio, and b) the effect of N235 concentration and A/O on the extraction efficiency

Table 3 summarises D_{Zn} values across N235 concentrations (7-30% v/v) and A/O ratios (0.25-2.0), confirming peak extraction efficiency (>150) under optimal, low A/O conditions and highlighting the system's robustness across industrial operating windows. These data validate 7% v/v N235 as the cost-effective choice for continuous modelling, balancing high D_{Zn} with minimal reagent use.

Table 3 - Distribution coefficients (D_{Zn}) for N235 extraction from $LaCl_3$ matrix

N235 (v/v%)	A/O 0.25	A/O 0.5	A/O 1.0	A/O 2.0	Extraction % (A/O=2)
7%	>150	85	18	5	40%
15%	220	140	45	22	90%
30%	280	195	75	45	90%

The higher polarity of isopropanol effectively dissolves the large ion pair complex $(R_3NH^+)_2ZnCl_4^{2-}$, preventing third phase formation and maintaining a sharp interface even at maximum zinc loading.

The distribution ratio (D_{Zn}) in this REE matrix exceeds 150. This D_{Zn} >150 in concentrated $LaCl_3$ exceeds DEHPA benchmarks (D_{Zn}=45) and Cyanex 923 (3 stages), due to $[ZnCl_4]^{2-}$ stability vs cation exchange limits of phosphonic at high salinity [27].

Equilibrium Modelling and Thermodynamic Evaluation

Extraction data have been analysed to fit the Langmuir isothermal model. The linearised Hanes-Wool shape was used as Equation 8.

$$\frac{x}{y} = \frac{1}{q_m}x + \frac{1}{q_m K_L} \qquad (8)$$

The extraction balance has been carefully modelled to assess the process efficiency for handling a 3000 ppm zinc load. The data show a strong correlation with Langmuir Isotherms, as illustrated in Figure 3.

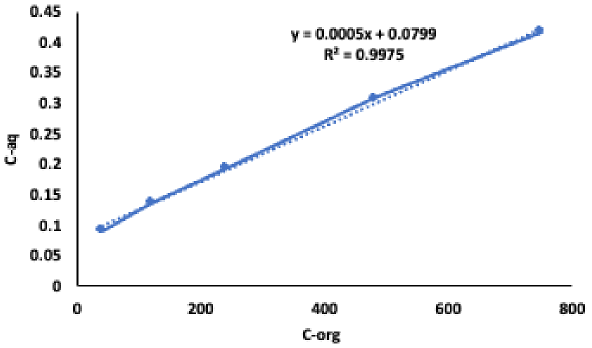

Figure 3 - Plot of the Hanes-Woolf of the linearised Langmuir fit

The linear regression analysis yields an R^2 value of 0.9975, indicating a good fit. The maximum loading capacity (q_m) has been determined to be 2222 mg/L, indicating that the N235 system is well-suited for high-impurity industrial flows. Furthermore, a standard Gibbs free energy (ΔG) of -14.68 kJ/mol confirms that the extraction is thermodynamically spontaneous. This is in line with the extraction of Zn using DEHPA in the Zn-C battery chloride leach solution, where ΔH was -245.59 kJ/mol and 100% extraction in one stage.

Multi-Stage Simulation for 5N Purity

The McCabe-Thiele diagram for the industrial feed containing 3000 ppm Zn is shown in Figure 4(a). The concentration profile is shown in Figure 4(b).

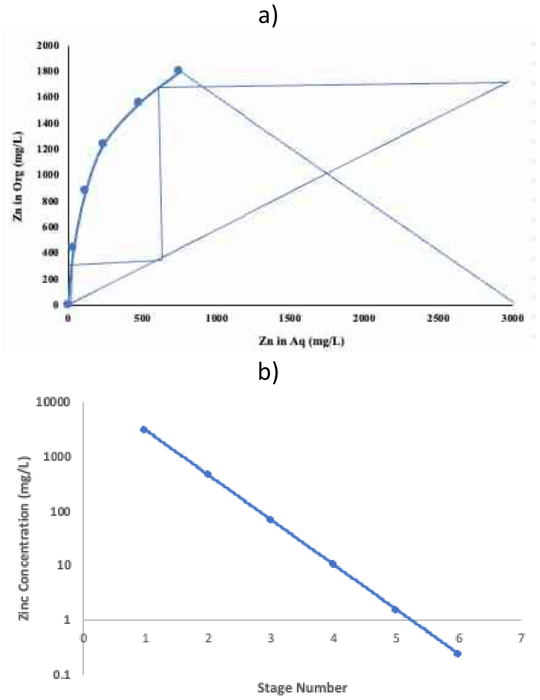

Figure 4 – $LaCl_3$ Zn extraction with 15% N235 at A/O 1.25 a) McCabe-Thiele construction, and b) stage concentration profile

The $LaCl_3$ purification circuit's main goal is to reduce zinc pollution from 3000 mg/L to <50 mg/L. The McCabe-Thiele construction shows that a 2-stage counter-current extraction with an A/O ratio of 1:25 is enough to meet this commercial threshold. This 2-stage configuration is highly efficient and reagent-lean, unlike other systems that need 3 stages, such as Cyanex 923.

The concentration profile provides a deeper scientific insight into the system's ultimate limits of purification. Although two stages are sufficient for bulk removal, linear developments on the logarithmic scale indicate that the N235 carrier does not experience loading inhibition at the trace level. As seen in the profile, the zinc concentration decreases exponentially across 5 stages. By the final stage, the concentration reached < 0.5 ppm, indicating that the matrix-driven self-salting effect was sufficient to bridge the gap from the 99.9% industrial grade to the 99.999% high purity threshold required for advanced optical and electronics applications. By extending the circuit to 5 stages, the system can achieve a 4-log reduction, reaching 0.23 mg/L Zn. This confirms that the same matrix-driven self-salting mechanism used for bulk recovery can be scaled to produce 5N (99.999) grade lanthanum, offering a versatile flow sheet that can be adjusted to meet the purity requirements of the final application.

Extractor Stripping and Regeneration

The stripping study evaluated the comparative efficiency of deionised water and 0.1 M HCl across varying A/O ratios (Figure 5a) and stripping stages (Figure 5b), using the McCabe-Thiele construction.

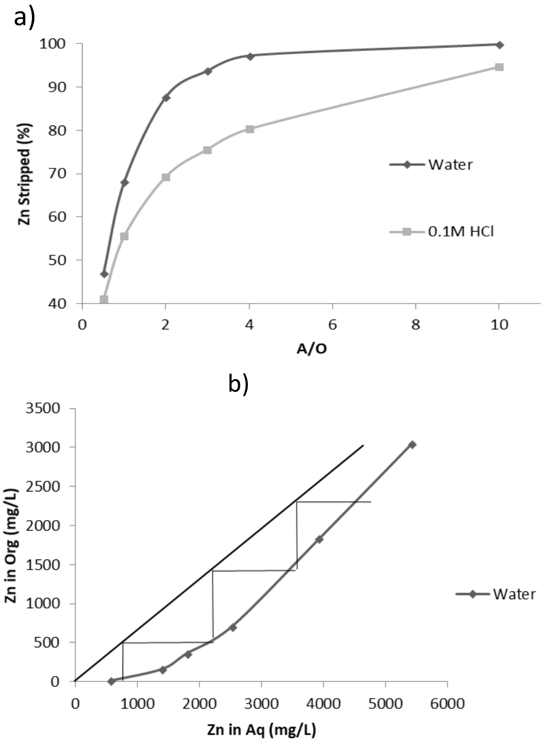

Figure 5 - Zn stripping with water a) efficiency at different A/O, and b) McCabe Thiele diagram at A/O 1.3

The results show that water is a superior stripping agent, achieving almost quantitative efficiency (about 100%) at 10 A/O. This significantly outperforms the 92% efficiency observed with 0.1 M HCl. Water stripping (100% at A/O 10) surpasses HCl (92%) and thiourea systems, disrupting $[ZnCl_4]^{2-}$ without complexing. This high efficiency is attributed to the water-induced separation mechanism. When the concentration and acidity of chloride decrease during contact with pure water, the complex balance of ion pairs shifts back towards the aqueous phase.

Although recent studies have successfully used thiourea in hydrochloric acid media to remove zinc, such a system relies on the formation of a strong and stable complex to attract the metal into the aqueous phase.

The McCabe-Thiele construction shows that a three-stage counter-current stripping process at an A/O ratio of 1:3 is sufficient to completely strip the zinc from the organic phase. The absence of a high chloride background destabilizes the $[ZnCl_4]^{2-}$ complex, causing it to decompose into Zn^{2+} cations, which are insoluble in the organic phase.

While previous studies reported a two-stage stripping process, the three-stage stripping process with water in this study resulted in a more concentrated zinc strip liquor with a higher O/A ratio and more favorable stripping chemistry.

Figure 6 summarises the complete extraction and stripping mechanism. It depicts the transition from the aqueous matrix to the organic phase, followed by the next stage of green stripping using deionised water. This water-induced separation is the main sustainable feature of the proposed flow sheet.

Flowsheet

The process flow sheet is depicted in Figure 7. The successful integration of extraction and stripping circuits demonstrates that the continuous counter-current solvent extraction process is technically superior and environmentally friendly [[28], [27][29]]. It meets the 5N purity requirements of the high-purity lanthanum application.

Conclusion

The study successfully demonstrated a high-efficiency solvent extraction flow sheet for deep purification of industrial-grade lanthanum chloride solutions, specifically addressing continuous 3000 ppm zinc jamming. By investigating the chemical mechanisms, it was established that the high chloride activity ($[Cl^-]$ about 4.23 M) of the 1.41 M $LaCl_3$ matrix drives the displacement of quantitative coordination. This transforms the hydrated zinc cation into an anionic tetrachloride-zincate complex ($[ZnCl_4]^{2-}$-), which is then selectively partitioned into the organic phase N235 via ionic pairing.

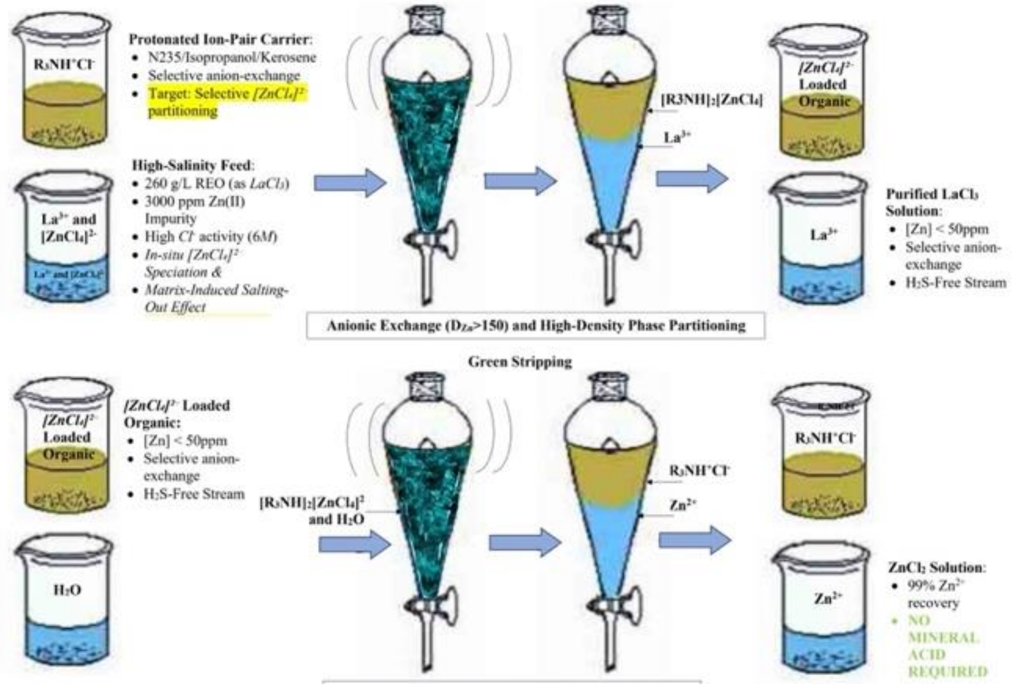

Figure 6 – Schematic diagram for Zn partition from concentrated $LaCl_3$ solution through N235 solvent extraction and water stripping

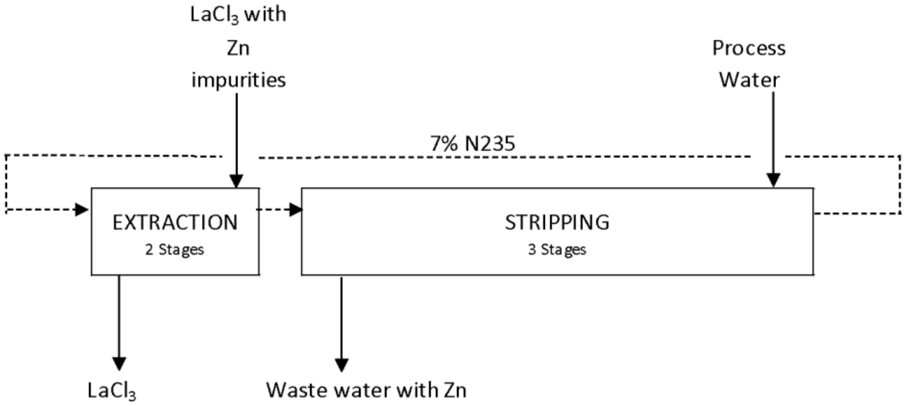

Figure 7 - Flow sheet for continuous counter-current zinc extraction with N235 in $LaCl_3$ and stripping with water

Thermodynamic evaluations using Langmuir isotherms confirmed that the process was very spontaneous (ΔG = -14.68 kJ/mol). The system's robustness under high-load industrial flows is confirmed by a maximum loading capacity of 2222 mg/L. Furthermore, a five-stage counter-current simulation shows that the self-salting effect of this matrix is sufficient to reduce the zinc concentration to < 0.5 ppm. This bridges the gap from 99.9% purity to the 99.999% (5N) threshold required for advanced optical and electronic applications.

Finally, this research provides a sustainable, lean reagent alternative to traditional purification methods, complementing the cycle of recovery-to-purification recently emphasised in this journal by offering a high-purity aqueous finishing stage that operates at ambient temperature. Future work would focus on the organic stability and coextraction of Fe.

Conflict of interest. On behalf of all authors, the corresponding author states that there is no conflict of interest.

CRediT author's statement: **N. Zulkifli:** Conceptualization, Methodology, Formal analysis, Writing – Original Draft; **N. Shoparwe**: Supervision, Writing – Review & Editing; **A.H. Yusoff**: Supervision, Validation; **A.Z. Abdullah**: Supervision, Methodology support; **M.N. Ahmad**: Supervision, Review & Editing.

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Лантан хлориді ерітінділерін үшінші деңгейлі амин экстракциясы арқылы тазарту: термодинамикалық және кезеңдік бағалау

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ТҮЙІНДЕМЕ

Лантан хлоридін мырыш құрамы жоғары мырыш қоспаларынан тазарту 5N класты лантан оксидтерін өндіруде басты мәселе болып қала береді Бұл зерттеу құрамында 3000 мг/л мырыш бар 1,41 М сирек кездесетін жер оксидтері (СЖО) концентрациясы бар өндірістік лантан хлоридінің шикізатын өңдеу үшін N235 үшіншілік аминін пайдаланып, матрицалық еріткішті экстракциялау процесін зерттейді. Medusa Hydra және Langmuir изотермаларын қолдана отырып, термодинамикалық модельдеу матрицаның жоғары хлоридті белсенділігі (> 4 М) экстракцияланатын $[ZnCl_4]^{2-}$ кешеніне қарай координацияда айтарлықтай өзгерістер тудыратынын көрсетті. Бұл ауысудың өздігінен пайда болатын Гиббстің бос энергиясы -14,68 кДж/моль құрайды. Екі сатылы қарсы ток ағыны схемасы 50 мг/л-ден төмен мырыштың өндірістік мақсатына сай болса, бес сатылы конфигурация төрт логарифмдік төмендетуді 0,23 мг/л-ге дейін қамтамасыз етеді, бұл тиімді түрде 99,999% тазалыққа қол жеткізеді. Бұл реагенттің үнемді тәсілі, су арқылы алынған стриппингті пайдаланып, өте жоғары тазалықты сирек кездесетін жер элементтерін өңдеу үшін тұрақты және математикалық тұрғыдан расталған негіз ұсынады.

Түйін сөздер: Ерітінді экстракция, мырыш, лантан хлориді, N235, McCabe-Thiele.

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Очистка растворов хлорида посредством третичной аминной экстракции: термодинамическая и этапная оценка

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АННОТАЦИЯ
Очистка лантана от загрязнителей с высокой нагрузкой цинка остаётся одной из основных задач при производстве оксидов лантана 5N класса. В данном исследовании изучается процесс экстракции растворителя с помощью матричного растворителя с использованием третичного амина N235 для обработки промышленной подачи оксидов редкоземельных элементов (REO) с содержанием 3000 мг/л цинка. Термодинамическое моделирование с помощью изотерм Медузы Гидры и Лангмюра показало, что высокая хлоридная активность (> 4 M) матрицы вызывала значительные изменения координации в направлении экстрируемого комплекса $[ZnCl_4]^{2-}$. Этот переход имеет спонтанную свободную энергию Гиббса -14,68 кДж/моль. В то время как двухступенчатый противотоковой расходный лист достигает отраслевой цели — менее 50 мг/л цинка, пятиступенчатая конфигурация достигает четырёхлогадичного сокращения до 0,23 мг/л, фактически достигая чистоты 99,999%. Бережливый подход этого реагента, использующий водяное удаление, предлагает устойчивую и математически валидированную основу для покрытия из редкоземельных материалов сверхвысокой чистоты.

Ключевые слова: Экстракция растворителя, цинк, хлорид лантана, N235, McCabe-Thiele.

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