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RESEARCH ARTICLE

Development and Application of the Douglas-Xu Model for Rare Earth Element Recovery: A Case Study Using Saprolitic Ionic Adsorption Clay

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ABSTRACT - The extraction of rare earth elements is complex and resource-intensive that requires innovative approaches to optimize technical and economic outcomes. This study introduced the Douglas-Xu model, which integrates the Douglas design methodology with Xu's counter-current principle, for enhancing the economic evaluation and process optimization of rare earth element separation. The model comprises five hierarchical levels, namely input information, operation mode, input-output structure, recycling and separation/filtration, with each incorporating the economic potential analysis to ensure a cost-effective design. This study emphasizes on economic viability, process integration and environmental considerations when applying this model to a case study on extracting rare earth elements from Malaysian saprolitic ionic adsorption clay for a 10,000-ton production target. Findings indicate that the Douglas-Xu model can effectively balance process optimization with economic performance in order to offer a comprehensive approach that addresses the limitations of existing methods. This model shows promise for improving the sustainability and profitability of rare earth element extraction, particularly in regions outside China, where resource availability and market dynamics differ.

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1.0 INTRODUCTION

A conceptual design is vital for overcoming challenges and accelerating the development of any novel method for extracting rare earth elements (REEs). Process design is often viewed as an inventive approach that attempts to solve sophisticated design problems by identifying previous solutions, inferences, computing and experimenting with a new equipment arrangement that might work more effectively. The complexity of process design requires a preliminary conceptual design and it must comply with certain structure-based frameworks for ensuring its functionality. In the context of REE processing, no complete superstructure framework has been found for designing a comprehensive and exclusive separation of REEs. The structure-based framework can be a derivative product from hierarchical models. This hierarchical approach is a systematic top-down methodology that utilizes analysis and synthesis to develop a complete conceptual flowsheet for a chemical-like process. The major advantage of this approach is that the designer will have complete control of the analysis, sequence and results at the conceptual design stage [1]. Preliminary calculations can be carried out by employing a flow spreadsheet or computational software. The analysis and development of alternative routes require a more advanced thermodynamic database and dynamic modelling as well as innovative simulation code construction. Meanwhile, the original version may be lacking in terms of optimization attributes[2], where additional computational features are required.

REEs are widely known as essential components that are commonly utilized in various green technology applications, including super-magnet, energy storage, electrical vehicle, batteries and others. The scarcity of primary resources, complication of economic viability at the upstream phase, and also China's domination in terms of reserves and supply from a global perspective tend to drive a situation where these elements have become critical [3]. Hence, it is necessary to find an efficient method for extracting these elements from the primary source in any part of the world, especially outside China, which will create a balance and stable supply. In this light, a novel approach is crucial for developing and optimizing a separation technique, where the volume of deposits may be limited relative to China's resource capacity. Extraction limitations, such as high costs and difficulty in separation, extraction, and purification, as well as hazardous acids and alkalis culminating from the process are the drawbacks of extracting REE on an industrial scale [4]. The current extraction framework's missing link is the lack of consideration on the economic potential (EP) at the preliminary design stage, particularly during the initial processing stage. Economic potential analysis during the design stage will allow the primary producer to select the most efficient and economical extraction route that could potentially maximize the profit margin. Emphasis on the primary consideration should be on the selected critical REEs that provide higher economic returns with less processing complications, which this study strives to formulate.

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2.0 DEVELOPMENT OF THE DOUGLAS-XU MODEL

The proposed model synthesizes the Douglas hierarchical design approach and Xu's counter-current principle to guide the design of REE extraction process flowsheets. The Douglas approach was originally established specifically as a conventional petrochemical process design, hence, literal application of the Douglas approach for REE separation is not effective due to the fundamental differences between the two operation bases. This study mainly introduced the newly proposed Douglas-Xu model for enhancing the economic evaluation aspect of Xu's conventional counter-current principle for modelling the REE process, particularly highlighting design factors, such as alternative process pathways, process integration, cost analysis, environmental impact and economic potential analysis.

2.1 Level 1: Input Information

The first level of the procedure (see Figure 1) is input information preparation. Table 1 shows the complete proposed input information tasks that are required. Input information-associated tasks are divided into eight sub-tasks (tagged as T1 to T8). The economic potential (EP-1) was assumed to be zero in this particular level because the purpose was only to gather information regarding the extraction process.

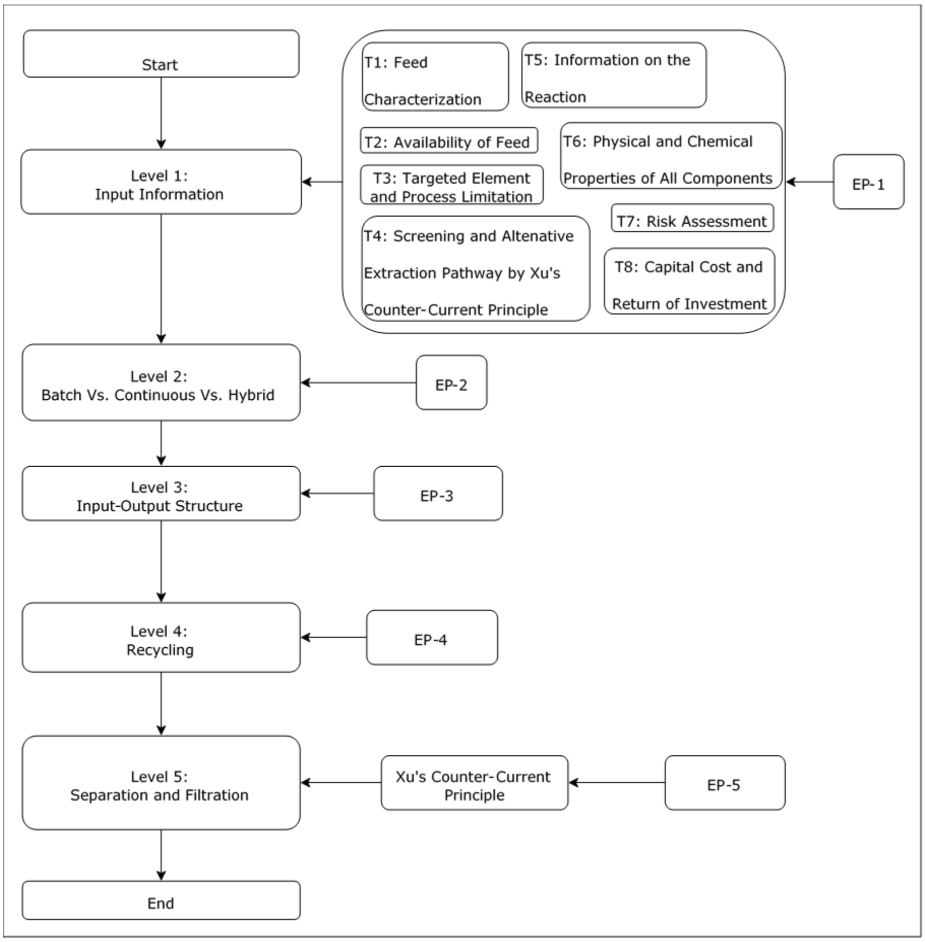

Figure 1. The newly integrated Douglas-Xu model for REE separation processing

Table 1. The proposed input information associated with Level 1 tasks

Task	Input information
T1	Input information
T2	Feed characterization
T3	Availability of feed
T4	Targeted element and process limitation
T5	Screening and alternative extraction pathways by Xu's counter-current principle
T6	Information on the reaction for extraction, scrubbing, and stripping
T7	Physical and chemical properties of all components
T8	Risk assessment

2.1.1 T1: Feed Characterization

The feedstock needs to be characterized to confirm the nature of the element's behaviours that is available. Different feedstocks might contain different types and amounts of REE as well as impurities, which should be considered at the preliminary design stage. It is crucial to determine basic information early on, such as REE profiles, concentration of impurities and the physical properties of the source material, so that the appropriate process technology, flow sequence and target output capacity can be properly designed.

2.1.2 T2: Feedstock Availability

The availability of feedstock data can be acquired either from an in-house study or outsourced from another organization. Feedstock availability is critical for ensuring production sustainability throughout the production year.

2.1.3 T3: Targeted Element and Process Limitation

Some elements are not economical to be extracted under various scenarios, such as when their concentrations are too low to be commercially viable, the process is very dangerous, technology is presently unavailable, unavailability of process components, low selling price that prevents the recuperation of production costs, or a combination of those factors [5], [6]. An economic viability analysis should be conducted to determine which REEs are feasible for extraction at a desired economic of scale prior to rigorous design commitment. The selection of elements to be extracted is also determined by the market size, which also corresponds to the supply and demand capability. As a new producer, it is critically important to understand the market gap to ensure that the market is not saturated and ready for a new entry. Another indicator that should be considered is the projection of market growth in relation to the compound annual growth rate (CAGR). The future projection of sales growth should be included when considering the design in order to avoid missing future opportunities.

2.1.4 T4: Screening and Alternative Extraction Pathways

Screening and evaluation of alternative REE extraction processes should be based on economic potential, technology readiness, complexity, safety and environmental impact. The best extraction process and technology is not always the best choice, as it should be accompanied by other attributes mentioned above to ensure that the process operates safely and remains viable at the intended economic scale. REE extraction is commonly performed by a solvent extraction (SX) system that generally comprises of a simultaneously and continuous operation of extraction, scrubbing and stripping phases. The REE feedstock usually co-exists with other elements that are considered impurities, such as silicon oxide (SiO_2), aluminium oxide (Al_2O_3), ferric oxide (Fe_2O_3), calcium oxide (CaO), thorium oxide (ThO_2), etc., which should be removed from the concentrated REE solutions. The removal of these impurities can be achieved by designing a dedicated standalone low-stage SX circuit to wash out the impurities from the REE solution. The common SX extractants used to remove these impurities are P507 and naphthenic acid [6], [7]. Each of these sub-processes needs to be incorporated into the conceptual design and evaluated at an early stage. Selection of alternative processes is determined based on the economic potential (EP-AL) and cost-revenue ratio (CRR), as shown in Equation (1)[8] and Equation (2) [9]. Douglas, (1985) defined economic potential (EP) as the ability of a chemical process to achieve the best possible economic performance. Meanwhile, Bragg (2012) described cost-revenue ratio as a financial metric to assess the relationship between cost incurred and revenue generated by a chemical process. This ratio helps to evaluate the economic performance of a process by comparing the total cost of production to the revenue it generates.

$$EP - AL = \{Total\ Revenue - Cost\ of\ Revenue\} \tag{1}$$

$$CRR = \frac{Cost\ of\ revenue}{Total\ revenue} \times 100 \tag{2}$$

2.1.5 T5: Information on the Reaction for Extraction, Scrubbing, and Stripping

Once the extraction pathway was decided, detailed information on the reaction for impurity removal, extraction, scrubbing, and stripping were then collected. This information is intended to provide data used for material balance, thermodynamic analysis and risk assessment.

2.1.6 T6 to T8

Steps T6 to T8 include the physical and chemical properties of all the components, risk assessment, capital cost summary and return on investment analysis, which are not discussed since they fall outside the scope of this study.

2.2 Level 2: Batch Versus Continuous Versus Hybrid

At this level, the REE separation's operation mode was decided based on various factors, such as process complexity, production rate, market demand and scale-up problem. The production plant with a capacity of more than 4500 tons/year is usually continuous [10]. The REE extraction plant is usually designed for large scale operations in a continuous mode because the extraction process is naturally arduous and tedious, thus, it is only possible with the introduction of the SX operation [5]. Nevertheless, there is also a possibility of introducing a hybrid model application, whereby an integrated separation process comprising batch and continuous methods are employed.

2.3 Level 3: Input-Output Structure

The input-output structure for the flowsheet was formulated at this level. The separation system was assessed before the feed was allocated to the system and the complete mass balance for the separation process was also carried out. It is easier to determine material balance for conventional chemical processes by resolving the production rate, stoichiometry and distribution. However, REE extraction is sophisticated due to the formation of various complexes, a large number of separation stages as well as insufficient stoichiometry information. In general, REE processing needs to go through four processes, namely the removal, extraction, scrubbing and stripping of impurities. The economic potential at this level was determined by adapting the original Douglas approach and using Equation (3) [8].

$$EP-3=\{Product\ value\}+\{By-product\ value\}-\{Raw\ material\ costs\}-\{Waste\ treatment\ cost\} \tag{3}$$

Once the separation system was decided, the number of separation stages required for extracting the desired elements was determined, either mathematically or modelled by using commercial software. The separation stages in this model were determined mathematically based on Xu’s counter-current principle [7]. Data on the number of separation stages was crucial for helping determine the number of separator/extractor equipment that was required, as it reflects the initial investment cost.

2.4 Level 4: Recycling

The heavy usage of water, solvents and extractants is vital for leveraging the opportunity for recycling. The Douglas approach separates the recycling into gaseous and liquid materials. Recycling gaseous materials is usually expensive due to the need to convert the gaseous waste to liquid form using compression. The chemical plant usually consumes a large amount of gaseous stream; however, in the case of the REE extraction plant, the recycling tends to focus more on the recovery of extractants, scrubbing agents, diluents and stripping agents. The waste can be recycled but it depends on the economic prospect of the deposits, because under certain circumstances, it would be more economical to dispose the waste rather than recycle it. The EP factor at this level follows the original Douglas approach [1], as indicated by Equation (4) [8], [10].

$$EP-4=\{EP-3\}+\{Reaction\ system\ costs\}-\{Recycle\ costs\} \tag{4}$$

2.5 Level 5: Separation and Filtration

The process designer should create a specification design for the separation and filtration process in order to obtain the desired product’s purity as well as capacity. It is crucial to determine the type of separator used for separating REEs from each other individually as well as removing the bulk of impurities, such as iron, zinc and aluminium. There are various types of separators (or extractors), such as mixer-settler, stage-type extractors, column-type extractors and centrifugal extractors. Criteria for an appropriate separator is that it must have good phase separation, fast mass transfer, high production rate, simplicity and low cost (operation and maintenance) [5]–[7]. Whereas, from the operation perspective, the separator should be flexible, reliable, operable and easy to maintain. Nevertheless, the irony is that there is no such separator available with all these criteria. A number of factors should be considered when setting up the separator operation, such as the extraction system, extraction capacity, number of stages, critical constraints and economic viability [7]. Economic viability is the most influential parameter at this level that should be of critical concern relative to others. The best equipment and technology do not always yield the best economic potential; hence, this study will help the process designer to carefully choose the most suitable equipment and technology. The ultimate purpose of the Douglas-Xu approach is to determine the best alternative process that suits the requirements for achieving the study’s goal. Economic potential at this level is determined by the Douglas approach [1] according to Equation (5) [10].

$$EP-5=\{EP-4\}-\{Separation\ costs\} \tag{5}$$

3.0 CASE STUDY

The model in this study was evaluated based on the case study designed for extracting REEs from Malaysian saprolitic ionic adsorption clay (SIAC). The extraction of REEs by a particular SX system was examined based on feed phase, feed ratio, product purity, product recovery, product throughput, reflux ratio, maximum extraction and scrubbing. The mass balance table was constructed to summarize all process parameters and gain insight into the optimization process, as part of overall performance evaluation. The model's performance was ultimately assessed through an overall evaluation, supported by a case study to validate the separation approach. The case study was designed to produce 10,000 tons of rare earth elements (REE) from Malaysian SIAC using a fractional cascade SX method. The targeted REEs included light rare earth elements (LREE), which consist of lanthanum (La), cerium (Ce), praseodymium (Pr), and neodymium (Nd). The middle rare earth elements (MREE) include samarium (Sm), europium (Eu), and gadolinium (Gd), while the heavy rare earth elements (HREE) include terbium (Tb), dysprosium (Dy), holmium (Ho), erbium (Er), and yttrium (Y).) In this case study the mixer to settler ratio (*r*) was 1.4, but the size of the mixer and settler was upscaled to 30x larger in order to cater for the production of 10,000 tons of REEs. Hence, the following discussion exemplifies the evaluation of a proposed superstructure process design for REE processing, which particularly highlights the elements of process synthesis and integration, economic potential analysis, environmental impact as well as process hazards.

3.1 Level 1 Outcomes

In general, Level 1 outcomes emphasize data preparation, process evaluation and economic pre-assessment. The main aim is to determine the most promising process route for the core process base prior to technical design specifications. However, the focus of this case study was restricted to T1 to T4.

3.1.1 Feed Characterization, Feedstock Availability and Targeted Production Element (T1-T3)

The input data on REEs used in this study were acquired from Tohar & Yunus, (2020), as summarized in Table 2.The major constituents of this SIAC are SiO_2 and Al_2O_3, with both constituting 94.250 wt% of the mineral. Small fractions of other impurities constituted 5.516516 wt% and 0.234 wt% of the REEs, respectively, bringing the total composition of impurities to 99.766 wt%. In the separation processing section, the feed was presumed to be approximately 98-99% pure, in the form of rare earth chloride or carbonate that was used as feed for the SX process, whereby most of the impurities (>95%) were removed by the leaching process (pre-treatment before the separation processing). This assumption aligns with the findings of Peelman et al., (2018).

Table 2. The chemical composition of Malaysian saprolite ionic clay based on XRF analytical testing

Impurities		Rare earth element	
Composition	Content (wt%)	Composition	Content (wt%)
Al_2O_3	24.50	La_2O_3	0.0655
SiO_2	69.75	CeO_2	0.0285
P_2O_5	0.020	Pr_2O_3	0.0142
K_2O	2.720	Nd_2O_3	0.0517
Na_2O	0.170	Sm_2O_3	0.0100
CaO	0.060	Eu_2O_3	0.0008
TiO_2	0.160	GdO_2	0.0084
MgO	0.120	TbO_8	0.0014
Fe_2O_3	2.200	Dy_2O_3	0.0061
MnO	0.034034	Ho_2O_3	0.0014
BaO	0.032032	Y_2O_3	0.0388
		Er_2O_3	0.0035
		Tm_2O_3	0.0007
		Yb_2O_3	0.0025
		Lu_2O_3	0.0005

Table 3 shows the economic analysis of the REE spectrum derived from the proportion of elements available in the saprolite adsorption ionic clay stockpile. Several setting criteria were considered when determining the commercial viability, including potential revenue, market size and CAGR. Potential revenue is calculated from the direct product, based on the percentage of elements and its corresponding selling price. The most economically viable element to be extracted was Nd, with a potential annual revenue of $228.09M USD. Besides, its by-product, Pr, can also generate an additional amount of $65.32M USD in economic returns. Meanwhile, Eu was identified as the element with the least attractive profit totalling merely $0.98M USD, alongside Sm, which yielded a total of $5.38M USD in potential revenue.

The CAGR were used to project the future market size for the next five to fifteen years of operations. This study chose a reasonable 10-year projection given the sufficient time required for various decision-making stages including [13], [14]:

Table 3. Economic viability analysis and market projection

REE	Price 2021 ($/kg)	Element fraction in feed (%)	Recovery (Ton)	Potential Revenue ($) (million)	Market Size in 2021 (Ton)	CAGR (%)	Market Size projection in 2031 (Ton)
La	3.64	0.0655	2,816.50	10.25	192,060	10.0	498,155
Ce	3.86	0.0285	1,225.50	4.73	67,306	3.8	97,729
Pr	106.97	0.0142	610.6	65.32	26,465	8.6	60,392
Nd	102.6	0.0517	2,223.10	228.09	20,175	15.0	81,621
Sm	12.52	0.01	430	5.38	42,652	3.1	57,879
Eu	28.38	0.0008	34.4	0.98	8,742	5.0	14,240
Gd	40.38	0.0084	361.2	14.59	136,206	5.3	228,286
Tb	1,797.30	0.0014	60.2	108.20	37,278	6.8	71,973
Dy	389.29	0.0061	262.3	102.11	12,844	5.2	21,323
Ho	88.05	0.0014	60.2	5.30	60	6.6	114
Y	34.2	0.0388	1,668.40	57.06	2,424	4.0	3,588
Er	37.47	0.0035	150.5	5.64	2,877	4.8	4,598
Tm	1,500	0.0007	30.1	45.15	64	5.5	110
Yb	13.83	0.0025	107.5	1.49	284	5.2	463
Lu	851.35	0.0005	21.5	18.30	102	8.2	225
LREE	Nil	0.16	6,875.7	308.39	5,859.9	9.35	737,897
MREE	Nil	0.02	825.6	20.9595	6,282.1	4.5	300,405
HREE	Nil	0.05	2,360.7	343.2525	72,663.7	5.8	102,394
Total REE	Nil	0.23	10,062	672.5959	84,805.7	6.5	1,140,696

Table 4. Decision-making stages

Aspect	Duration
Preliminary feasibility study	Two to six months
Detailed feasibility study	Six to eighteen months
Investment decision-making	One to three months
Plant construction and commissioning	Two to Three years

Based on the CAGR data, Nd has the highest CAGR value of 15% and the market was expected to grow from 20,175 tons in 2021 to 81,621 tons in market size by 2031. Meanwhile, Sm experienced the least market growth with a relative 3.1% annually, however, its market capacity is about twice in size compared to Nd in 2021 alone. Even so, the prospect of economic returns for Sm is still relatively low ($5.38M USD annually) due to its small proportion in the SIAC profile. The ultimate requirement for any single REE to be viably extracted is that it must demonstrate a significant trading outlook in terms of mineral quality as well as market share. According to Gupta and Krishnamurthy, (2005), elements such as Tm, Yb and Lu generally have very limited commercial application and a small niche market demand, making them commercially less attractive. Referring to the data in Table 3, the market size for Tm, Tb, and Lu is notably small, with annual sizes of merely 64, 284, and 102 tons, respectively, in 2021. In general, Table 3 also reveals that the most attractive REEs with a high profit generating potential are Nd, Tb, Dy, Pr, Y, and Gd. However, elements such as La, and Ho also have a promising future prospect as their CAGR is approximately 10.0% and 6.6%, respectively. In addition, elements such as Ce, and Er could be also commercially processed as secondary value-added deposits as they are the by-products of La and Ho extractions, respectively.

3.1.2 Selection of the SX system

A suitable extraction system must be carefully selected because the extractant might form a very stable complex with a REE, which prevents the elements from being stripped off from the extractant itself. Several considerations must be seriously and systematically assessed when selecting a suitable extraction system. Critical factors that indicate effective extraction are the targeted elements' extractability rate, selectivity of extractant for extracting the element, tendency to form emulsions, loading capacity, stripping difficulty, cost of extractant and toxicity level. Six common extractants were used for extracting REEs, namely Di(2-ethylhexyl) phosphoric acid (P204), 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester (P507), Di(1-methyl-heptyl) methyl phosphonate (P350), Bis(2,4,4-trimethylpentyl) phosphinic acid (Cyanex 272), a mixture of trialkyl phosphine oxides (Cyanex 923), and naphthenic acid. Figure 2 shows the chemical structure of the extractants. Figure 3 shows the relative strengths and weaknesses of these extractants. The attributes were measured in arbitrary units. All data used for analysing and constructing the diagram were sourced from previous literature. A multi-extraction system (MES) consisting of P204, P507 and C272 was selected to demonstrate the Douglas Xu model in this case study.

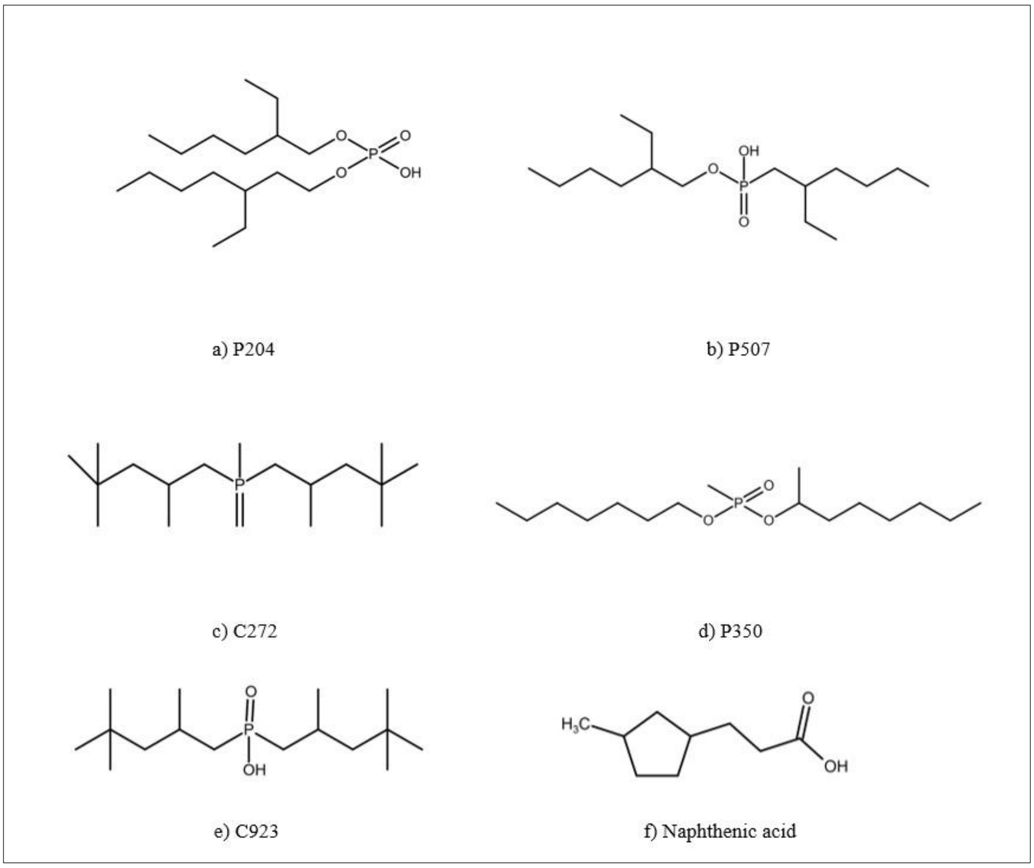
a) P204
b) P507
c) C272
d) P350
e) C923
f) Naphthenic acid

Figure 2. Extractant chemical structures

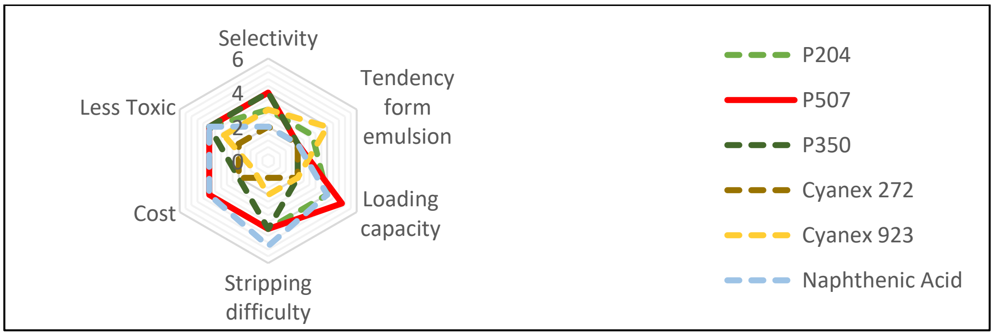

Figure 3. Attribute analysis of SX systems

3.1.3 Screening Alternative Pathways (T4)

In this section, the economic potential (EP) of each alternative pathway was measured based on the size of the mixer settler single train and the number of operating days. The basis of production was generally set as a single train over 292 days of operations, which accounts for 80% (η=0.8) of the plant's operating schedule. Cost estimation was based on the REE's material balance, capacity of the extractant, diluent and scrubbing agents, as well as the throughput plant data. The optimum daily processing of REEs, Q_{REE} (depending on their extractability A or B) was determined by Equation (6) and Equation (7). Here, V, t, R, $[B_{(1a)}]$, $[A_{(n+m)}]$, and M denote the total extraction volume, extraction time, phase ratio, concentration of B at the aqueous outlet, concentration of A at the organic outlet and molar mass, respectively. Prior to determining the optimal production of A and B, it is necessary to determine the phase ratio (R) as well as the outlet concentrations of A ($[A_{(n+m)}]$) and B ($[B_{(1a)}]$) in the organic and aqueous phases. The phase ratio was determined using Equation (8), where V_O is the organic flow rate, V_W is the scrubbing flow rate and V_F is the feed flow rate. Economic potential and cost-revenue ratio formed the foundation for analysing the economic viability of the alternative pathways.

$$Q_B = 1.44 \frac{V}{t} \frac{[B_{1(a)}]}{(1+R)} \tag{6}$$

$$Q_{\mathrm{A}} = 1.44 \frac{V}{t} \frac{[A_{(n+m)}]}{(1+R)} \tag{7}$$

$$R = \frac{V_o}{V_W + V_F} \tag{8}$$

3.1.4 Solvent Extraction Primary Pathway Extraction: P507, P204 and C272

As discussed earlier, this particular MES system was identified as the most ideal choice with respect to the technical operation evaluation, where the REEs were separated by using integrated multi extractant applications, as in P507, P204, and C272. Table 5 highlights the separation hierarchy that involved P507, P204 and C272.

Table 5. Extraction steps by P507, P204 and C272

Hierarchy	Steps	SX system
1	La-Ce/Sm-Y	P507-Kerosene-HCl
1(a)	LaCe/PrNd	P204-Kerosene-HCl
1(b)	La/Ce	P204-Kerosene-HCl
1(c)	Pr/Nd	P204-Kerosene-HCl
2	Sm-Gd/Tb-Y	P507-Kerosene-HCl
2(a)	SmEu/Gd	P204-Kerosene-HCl
2(b)	Sm/Eu	P204-Kerosene-HCl
3	Tb-Er/Tm-Y	P507-Kerosene-HCl
3(a)	TbDy/HoEr	P507-Kerosene-HCl
3(b)	Tb/Dy	P507-Kerosene-HCl
3(c)	Ho/Er	C272-Kerosene-HCl
3(d)	Tm-Lu/Y	C272-Kerosene-HCl

The REEs were stripped from P507-Kerosene-HCl, P204- Kerosene-HCl and C272-Kerosene-HCl by employing selective multi-type acids at various concentrations depending on the elements to be stripped. The economic potential of this particular system is shown in Table 6. The positive and negative values reflect the system's revenue and cost aspects, respectively. Extractants, diluents and scrubbing agents, such as P507, P204, C272, HCl and kerosene, have negative values as they are consumables used to extract REEs. Meanwhile, there were twelve (12) potential REEs (La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, and Y) that indicated positive values as they are income generating products. The intermediate products, such as LaCe, PrNd, MREEs, HREEs and others, represent zero values as they are not the real commodities involved in the sales. Figure 4 shows the comparison between annual throughput and revenue of REEs produced. The main elements that generate high amounts of revenues are Nd, Tb, and Ho. Although high throughput elements, such as La and Ce, are produced in larger quantities, they contribute less in profits compared to the overall revenue. For example, La is produced at approximately twice the amount of Nd but contributes 64 times less income compared to Nd. This magnitude of discrepancy signifies that a high throughput does not always correlate to substantial economic revenue due to various factors, such as processing costs and market prices. The net EP value provides a comprehensive indicator of the entire economic strength of the selected extractant system. In this study, the EP of MES, obtained by using P507, P204, and C272 pathways, was determined to be approximately $19.3M USD, while the cost-revenue ratio was approximately 11.1%.

Table 6. Economic potential of P507, P204 and C272 pathways

Element	Extractability	Daily processing Capacity, (Kg/Day)	Cost ($)	Annual Throughput/consumption (Kg/Year)	Cost/Revenue ($)
LREE	*A*	853.0	0.00	249,066.3	0.0
MREE+HREE	*B*	3,189.0	0.00	931,173.8	0.0
LaCe	*A*	254.4	0.00	74,289.6	0.0
PrNd	*B*	210.4	0.00	61,447.3	0.0
La	*B*	165.4	0.98	48,306.0	47,448.6
Ce	*A*	35.0	1.00	10,215.0	10,259.9
Pr	*B*	69.1	139.58	20,183.4	2,817,244.4
Nd	*A*	88.9	116.69	25,954.3	3,028,555.3
MREE	*A*	70.7	0.00	20,639.6	0.0
HREE	*B*	1131.7	0.00	330,468.3	0.0
SmEu	*A*	30.7	0.00	8974.5	0.0
Gd	*B*	31.8	65.73	9,271.1	609,384.6
Eu	*A*	1.0	28.80	304.4	8,766.0
Sm	*B*	27.2	2.22	7,946.1	17,605.3
Tb-Er	*A*	13.4	0.00	3,920.3	0.0
Tm-Y	*B*	99.3	0.00	28,995.8	0.0
TbDy	*A*	44.7	0.00	13,059.2	0.0
HoEr	*B*	80.9	0.00	23,612.2	0.0
Tb	*B*	12.9	2,053.12	3,752.3	7,703,930.8
Dy	*A*	20.1	361.88	5,856.3	2,119,280.4
Ho	*B*	116.6	138.11	34,035.2	4,700,444.9
Er	*A*	87.9	43.57	25,674.3	1,118,712.4
Tm-Lu	*B*	499.0	0.00	145,709.7	0.0
Y	*A*	484.3	7.83	141,426.1	1,107,142.8
P507	n.a	1,001.9	1.40	877,625.1	-1,228,675.21
P204	n.a	410.1	2.50	359,213.4	-898033.5
C272	n.a	572.3	4.60	100,260.2	-461,196.94
Kerosene	n.a	992.1	0.74	494,726.5	-494,726.5
HCl	n.a	5,134.2	0.18	1,499,191.7	-883,312.0
Cost Revenue ratio					11.1%
Economic Potential					$19,322,826.4

3.2 Level 2: Batch Versus Continuous Versus Hybrid

In the context of REE extraction, the continuous operation mode was preferred and selected because it can generate higher throughput compared to batch processing. However, a hybrid operation mode that comprises a batch and continuous operating bases might be implemented if necessary. The REE separation process is arduous and tedious, while the separation stages may be in the hundreds or even thousands, hence, the necessity for employing the continuous mode. The REE's concentration might also be varied in the feedstock, thus aggravating the difficulty in controlling certain process parameters. At this stage the economic potential for Level 2 (EP-2) was set at zero since this phase solely focuses on collecting information for the design work at the initial stage.

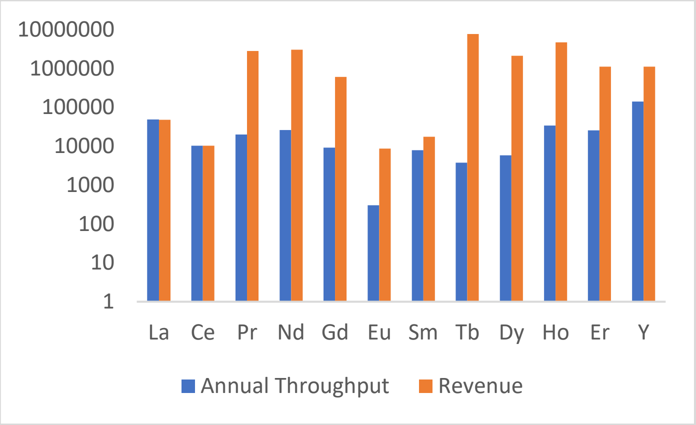

Figure 4. The annual throughput and revenue of REEs extracted using P507-P204-C272

3.3 *Level 3: Input-Output Structure*

The presence of various impurities has a detrimental effect on the separation of the REE extraction circuit, where Si, Al, and Fe could form emulsions during solvent extraction [15]. This small fraction of impurities was removed by a dedicated SX battery. In this study, the P507-HCl, P204-HCl and C272-HCl were presumed to be diluted in sulfonated kerosene for the purpose of REE extraction. The ratio of extractants (P507, P204, and C272) to diluent (sulfonated kerosene) was typically in the range of 30% to 50% [16]. It is not possible for a single extraction system to extract all REEs due to the nature of the bonding complexity with REE ions. There are numerous separation systems readily available, but the integration of P507, P204 and C272 was chosen mainly due to the economic potential factor and attributes of the extractant. Table 7 shows all the input structures for the whole extraction of REEs, covering the impurity's removal, extraction, scrubbing and stripping.

Once the separation system was decided, the number of separation stages required for extracting the desired elements must be determined. In this case study, the separation stage was mathematically determined based on Xu's counter-current principle [7]. Data on the number of separation stages are crucial for determining the number of separator/extractor equipment that is required, which reflects the initial investment cost. Table 8 shows the output information for extraction in terms of the products and by-products as well as the corresponding source and destination. The EP at this level was calculated by deducting the revenue obtained from selling products from the total raw materials, waste disposal costs and EP-2. As previously mentioned, EP-2 was assigned a value of zero because this stage exclusively concentrated on gathering information for the initial design process. Table 9 presents the economic potential for Level 3, which targets an approximate production of 10,000 tons of REEs. In contrast, the economic potential of the alternative pathway (Table 6) was evaluated based on an annual production of 300 tons, with the primary aim of gathering data and identifying the most effective alternative pathway. The cost for the saprolite ionic clay and waste disposal were assumed to be fixed at $1 USD per ton respectively (the cost might vary depending on the local governing authority). The price of REEs was acquired from *SMM - China Metal Market*, (2022).

Table 7. Input information for the extraction at Level 3

Input	**Detail**
Solvent Extraction (SX)	Requirement: Dedicated SX to remove impurities Multi-extraction system (Integration of multiple extractants) Extractant: P507 (0.20 mol/L, pH 3.0), P204 (0.30 ml/L, pH 2.78), and C272(0.120 mol/L, pH 2.80) Diluent: Sulfonated kerosene Scrubbing: HCl Operating condition: T=30 °C
Impurities removal	A dedicated circuit to remove the impurities P507 diluted in sulfonated kerosene

Table 7. Continued

Input	**Detail**
Extraction	The extractant was selected according to the targeted elements P507 diluted in sulfonated kerosene P204 diluted in sulfonated kerosene C272 diluted in sulfonated kerosene
Scrubbing	The scrubbing agent was depended on the economic potential and extractant HCl
Stripping	Stripping reagent was selected according to the individual REE Sulfuric acid Hydrochloric acid Nitric acid
Input	Detail
General reaction	SX for impurity removal P507-Kerosene-HCl $Al^{3+}_{(a)} + 3(HA)_{2(o)} = Al(HA_2)_{3(o)} + 3H^+_{(a)}$ $Fe^{3+}_{(a)} + 3(HA)_{2(o)} = Fe(HA_2)_{3(o)} + 3H^+_{(a)}$
	Extraction Extractant-diluent: P507-Kerosene $RE^{3+}_{(a)} + 3(HA)_{2(o)} = RE(HA_2)_{3(o)} + 3H^+_{(a)}$ Extractant-diluent: P204-Kerosene $RE^{3+}_{(a)} + 3(HL)_{2(o)} = RE(HL_2)_{3(o)} + 3H^+_{(a)}$ Extractant-diluent: C272 Kerosene $5RE^{3+}_{(a)} + 3(HL)_{2(o)} = 5REL.2HL_{(o)} + H^+_{(a)}$
	Scrubbing Scrubbing agent: HCl $Re^{3+}+9HCl=3RECl_3+9H^+$
	Stripping From P507 $RE(HA_2)_{3(o)} + 3H^+_{(a)} = RE^{3+}_{(a)} + 3(HA)_{2(o)}$ From P204 $RE(HL_2)_{3(o)} + 3H^+_{(a)} = RE^{3+}_{(a)} + 3(HL)_{2(o)}$ From C272 $5REL.2HL_{(o)} + H^+_{(a)} = 5RE^{3+}_{(a)} + 3(HL)_{2(o)}$

Table 8. Output information for Level 3 extraction

Product	Source	Destination	Product	Source	Destination
La	SX-4	Product	Er	SX-12	Product
Ce	SX-4	Product	Y	SX-13	Product
Pr	SX-5	Product	Impurities	SX-1	By-product/Waste residue
Nd	SX-5	Product	Tm-Lu	SX-13	By product/ Waste
Sm	SX-8	Product	Extractant (P507-HCl-Kerosene)	SX-1, SX-2, SX-6, SX-9, SX-10, and SX-11	Raffinate back to the SX batteries
Eu	SX-8	Product	Extractant (P204-HCl-Kerosene)	SX-3, SX-4, SX-5, SX-7, and SX-8	Raffinate back to the SX batteries
Gd	SX-7	Product	Extractant (C272-HCl-Kerosene)	SX-12, and SX-13	Raffinate back to the SX batteries
Tb	SX-11	Product	HCl	Stripping	Complexing with product
Dy	SX-11	Product	HNO_3	Stripping	Complexing with product
Ho	SX-12	Product	H_2SO_4	Stripping	Complexing with product

Table 9. Economic potential for Level 3 based on material balance

Product and by-product	Cost ($/ton)	Annual consumption (ton)	Annual production (ton)	Cost/Revenue ($/ton)
Lanthanum	982.25	-	2,816.50	2,766,507.1
Cerium	1,004.40	-	1,225.5	1230892.2
Praseodymium	139,582.29	-	610.6	85,228,946.3
Neodymium	116,687.84	-	2,223.1	259,408,737.1
Samarium	2,215.59	-	430	952,703.7
Gadolinium	65,729.23	-	361.2	23,741,397.9
Europium	28,800	-	34.4	990,720
Terbium	2,053,120	-	60.2	123,597,824
Dysprosium	361,880	-	262.3	94,921,124
Holmium	138,105.23	-	60.2	8,313,934.8
Erbium	43,573.31	-	150.5	6,557,783.2
Yttrium	7,828.42	-	1668.4	13,060,935.9
Saprolite	1	4,300,000	-	-4,300,000
Hydrochloric acid	180	92,411.0721	-	-16633992.9
Nitric acid	220	786.9	-	-173,118
Kerosene	740	19,061.5	-	-14,105,510
P507	1,400	26,457.9	-	-37,041,060
P204	2,500	23,968.2	-	-59,920,500
C272	4,600	1,091.3	-	-5,019,980
EP-3				483,577,345.2

3.4 Level 4: Recycling

Separation processes generally use a huge volume of solvents and extractants, whereby these solutions can be recycled back to the mixer settler batteries via raffinate streams. The economic potential at this level (EP-4) was neglected due to the cost of recycling the extractants, which is primarily related to the operation of pumps that return the extractant to the mixer-settler, which was minimal. In conventional chemical processes, recycling costs are often driven by the energy-intensive compression of gases into liquids. However, no phase change was involved in the REE extraction, which would require high energy consumption. Therefore, the economic potential at EP-4 is comparable to that at EP-3.

3.5 Level 5: Separation and Filtration

In this study, the separation mechanism was performed via fractional cascade SX by using a multi-extraction-based system, P507-HCl-Kerosene, P204-HCl-Kerosene, and C272-HCl-Kerosene. Filtration is not discussed in this study as it falls outside the scope of the investigation Even though cascade SX is the most efficient method available, the separation process is lengthy and tedious when aiming to acquire the targeted production capacity. The separation was carried out using multi-stages of mixer-settler batteries, where the elements were separated into aqueous and organic phases and stripped from the organic phase by applying stripping agents.

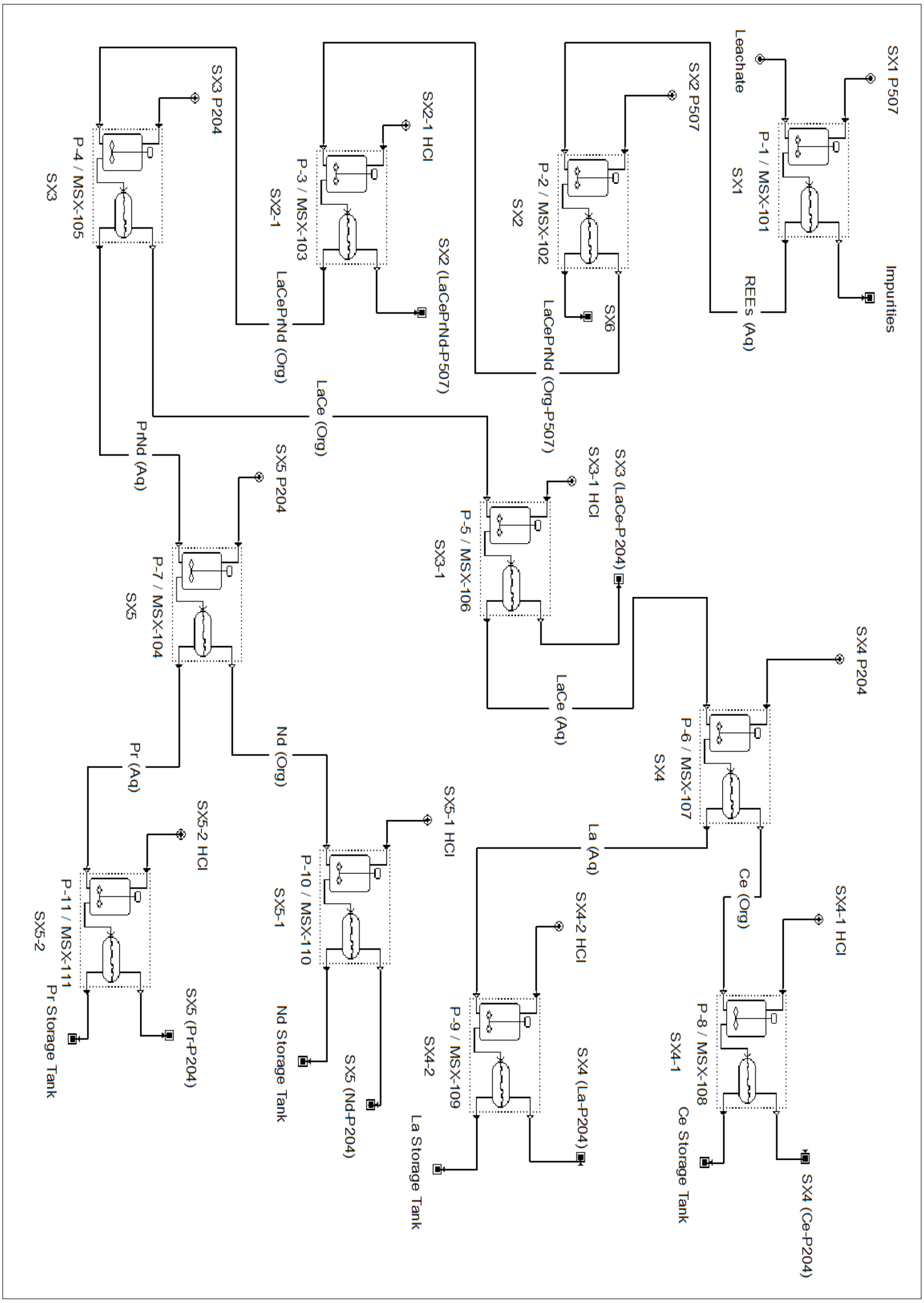

Figure 5. Section 1 - Removal of impurities and recovery of LREEs

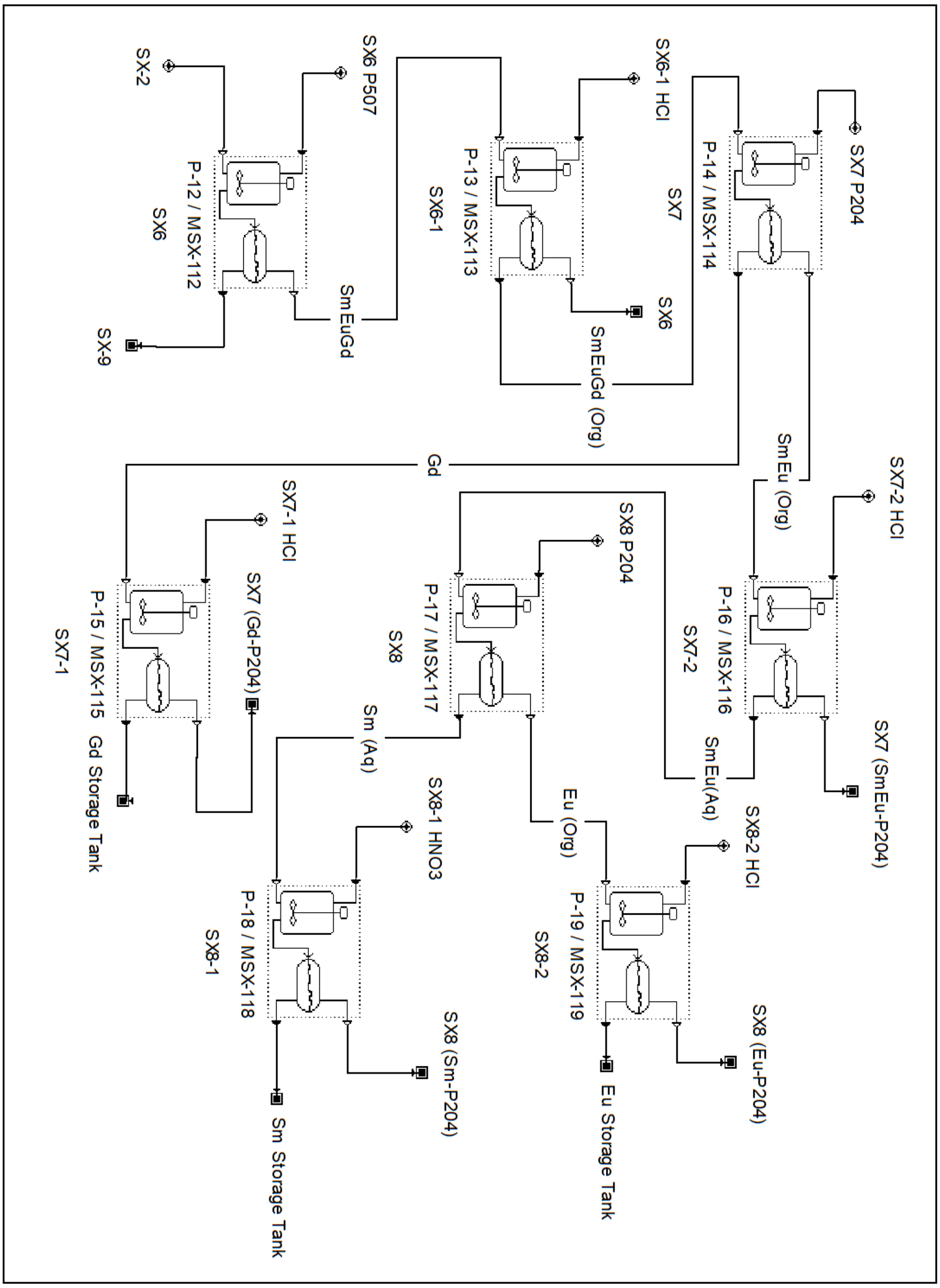

Figure 6. Section 2 - Recovery of MREEs, HREEs, Gd, Sm, and Eu

In order to recover the specified REEs (La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er and Y), including the impurities, the whole operation required thirteen (13) sets of SX-batteries. The batteries were divided into three separate sections to simplify the massive circuit structure, namely Section 1: Impurities removal and recovery of LREEs, Section 2: Recovery of MREEs, and Section 3: Recovery of HREEs. The impurities were extracted from REEs in the SX-1 battery at the beginning of the operation. As discussed earlier, it is important to dedicate a circuit specifically for impurity removal, especially for preventing the formation of gel-like emulsion. The REE concentration had achieved 99.0% purity [18], [19] once it left the SX-1 circuit. Whereas in the SX-2 battery, the LREE was initially separated from the MREE in separate groups, namely into La/Ce and Pr/Nd groups (SX-3). SX-4 and SX-5 batteries were designed specifically for recovering the individual La, Ce, Pr and Nd.

Meanwhile in Section 2, the circuits were solely dedicated for extracting REEs in both mediums, namely as groups as well as individually. At first, the SX-6 battery operation involved separating MREEs from HREEs in bulk. The SX-7 battery was then used to extract Sm from Gd and Eu. Lastly, the SX-8 battery performed the Eu separation from Gd. Finally, Section 3 focused on HREE processing that primarily comprised SX-9 to SX-13 batteries and involved the purification of Tb, Dy, Ho, Er and Y. Since the whole SX process was in a continuous mode, thus, all the products were kept in storage tanks before precipitating them into rare earth oxalate or carbonate. Figures 5, 6 and 7 show the flow diagram for the complete process involving all corresponding SX batteries (Sections 1, 2 and 3), starting from the leached liquid until the acquired REE chlorides in their respective tanks.

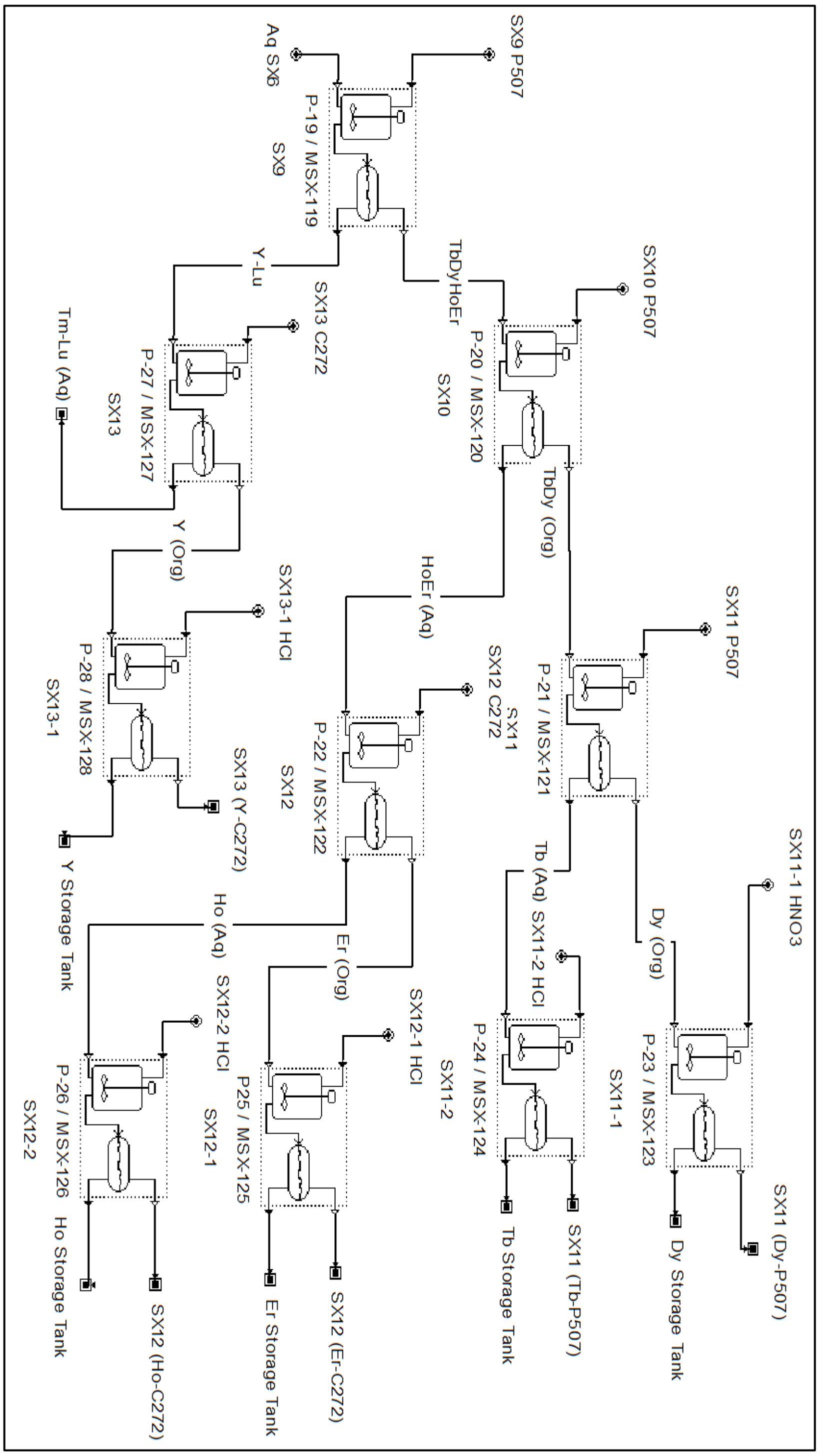

Figure 7. Section 3 - Recovery of Tb, Dy, Ho, Er, and Y

The economic potential of Level 5 (EP-5) was calculated by deducting the economic potential of Level 4 (EP-4) with the overall cost for separation operations. Table 10 shows that EP-5 is $234,911,245.23. Equipment purchase (CapEx) and separation (OpEx) costs were determined by the SuperPro designer software.

Table 10. Economic Potential for Level 5

Economic potential for Level 5 (EP-5)			
Mixer settler	Separation Circuit	Stages	Cost ($)
SX1	Impurities removal	3	-510,000
SX2	LREEs/MREEs+HREEs	19	-3,240,000
SX2-1	LaCePrNd Stripping	3	-510,000
SX3	LaCe/PrNd	31	-5,280,000
SX3-1	LaCe Stripping	3	-510,000
SX4	La/Ce	31	-5,460,000
SX4-1	La Stripping	3	-510,000
SX4-2	Ce Stripping	3	-510,000
SX5	Pr/Nd	32	-5,610,000
SX 5-1	Pr Stripping	1	-165,000
SX 5-2	Nd Stripping	1	-165,000
SX6	MREEs/HREEs	34	-597,000
SX6-1	SmEuGd Striping	3	-510,000
SX7	SmEu/Gd	97	-16,530,000
SX7-1	Gd Stripping	4	-690,000
SX7-2	SmEu Stripping	3	-510,000
SX8	Sm/Eu Extraction	68	-11,580,000
SX8-1	Sm Stripping	4	-690,000
SX8-2	Eu Stripping	3	-510,000
SX9	Tb-Er/Tm-Y Extraction	76	-12,930,000
SX10	TbDy/HoErExtraction	94	-16,020,000
SX11	Tb/Dy Extraction	91	-15,510,000
SX11-1	Dy Stripping	5	-840,000
SX11-2	Tb Stripping	5	-840,000
SX12	Ho/Er Extraction	34	-5,820,000
SX12-1	Er Stripping	4	-690,000
SX12-2	Ho Stripping	4	-690,000
SX13	Y/Tm-Lu Extraction	10	-1,710,000
SX13-1	Y stripping	4	-690,000
Total installation cost			-54,913,500
Annualized Separation cost			-83,925,600
EP-4			483,577,345.23
EP-5			234,911,245.23

6.0 CONCLUSION

The Douglas-Xu model provides a novel structured process design for the extraction of REEs by taking into consideration the process optimization and cost analysis for every layer of the process design procedure. Xu's counter-current principle generally lacks the cost analysis and alternative pathway screening aspects, and exclusively focuses on acquiring an optimized process using a particular SX system of interest. However, adopting the Douglas approach alone cannot correctly justify the intended product target parameters, such as purity, recovery, throughput and optimization factors. Integrating Xu's counter-current principles into the Douglas approach helps to complement each other in designing a complete and validated operation for the separation of REEs.

5.0 NOMENCLATURES

$[M_{(a)}]$	The total concentration of rare earth in the aqueous phase, mol/dm^3
$[M_o]$	The total concentration of rare earth in the organic phase, mol/dm^3
A	Solute(s) easily extractable
a	The concentrating factor of a
$A_{(n+m)}$	Concentration of A in organic outlet
b	The concentrating factor of B
B	Solute(s) difficult to extract
$B_{1(a)}$	Concentration of B in aqueous outlet
m	Number of scrubbing stages excluding the feeding stage
$M_{(a)}$	The mass flow rate of an aqueous phase, mol/min
$M_{(o)}$	The mass flow rate of the organic phase, mol/min
$M_{n+m(o)}$	The mass flow rate of A and B in the organic outlet
n	Number of extraction stages including the feeding stage
Q_A	optimum throughputs of A at the organic outlet
Q_B	optimum throughputs of B at the aqueous outlet
R	Phase ratio
t	Time, min
T	Total stage number of extraction stage and scrubbing
V_F	Feed flow rate, cm^3/min
V_O	Organic flow rate, cm^3/min
V_w	Scrubbing flow rate, cm^3/min
η	Plant efficiency, %

5.0 ABBREVIATIONS

HREE	Heavy Rare Earth Element
LREE	Light Rare Earth Element
MREE	Middle Rare Earth Element
OPE	Overall Process Evaluation
REE	Rare Earth Elements
SX	Solvent Extraction

6.0 CONFLICT OF INTEREST

The authors declare that they have no known competing financial interests or personal relationships that can appear to influence the work reported in this article.

7.0 AUTHORS CONTRIBUTION

F.Ahmat (Writing, Data, Curation, Conceptualization; Formal analysis; Visualization, Methodology)

M.Y.M. Yunus (Formal analysis; Methodology; Project Administration; Supervision)

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