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Recovery Potential of Critical Rare Earth Elements from Coal Preparation Tailings: A Case Study of the Abayskaya Mine

Gulnara Katkeeva, Ilyas Oskembekov, Yerlan Zhunussov *, Zhamila Shaike *, Baurzhan Kozhabekov, Dilara Gizatullina, Karakat Turebekova and Sultan Kabylkanov

Chemical-Metallurgical Institute Named After Zh. Abishev, Karaganda 100030, Kazakhstan; katkeeva@mail.ru (G.K.); ilyasosk@yandex.kz (I.O.); bbk-78@mail.ru (B.K.); dilurin@mail.ru (D.G.); kakosh-94@mail.ru (K.T.); kabylkanov04@gmail.com (S.K.)

* Correspondence: xx_m9_xx@mail.ru (Y.Z.); zhamilya.shayke@mail.ru (Z.S.); Tel.: +7-707-541-20-90 (Z.S.)

Abstract

Coal preparation tailings from the K18 seam of the Abayskaya mine were evaluated as a potential secondary source of critical rare earth elements (REEs). The study showed that REEs are predominantly associated with the mineral fraction of coal; therefore, during beneficiation, approximately 70% of their total content is transferred to flotation tailings. The concentrations of valuable elements in the tailings are as follows (g/t): Li—65; Sc—16; Y—17; Yb—2.5; V—135; and Ti—2293. These values significantly exceed the Clarke values and are comparable to those of some low-grade primary ores, indicating the potential of coal preparation wastes as a technogenic raw material for critical elements. To extract REEs from the resistant aluminosilicate matrix, a fluorine–ammonium sulfate thermochemical activation method was proposed. Using a probabilistic–deterministic experimental design approach, a mathematical model of the process was developed and optimal parameters were determined (400 °C, 120 min, $(NH_4)_2SO_4$ consumption—140% relative to Al, NH_4HF_2 consumption—110% relative to Si), providing a feed liberation degree (by Al extraction) of up to 94%. Under optimal conditions, high leaching efficiencies of key elements were achieved: Sc (95%), Y (100%), Yb (100%), and Li (100%). The results demonstrate the significant potential of coal preparation tailings as a secondary resource of rare earth elements and confirm the efficiency of fluorine–ammonium sulfate technology for processing this type of technogenic waste.

Keywords: rare earth elements; coal preparation tailings; critical raw materials; secondary resources; resource recovery; coal beneficiation; mineral matter; critical elements

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1. Introduction

The rapid development of high-technology industries, the transition to low-carbon energy systems, and global requirements for reducing carbon emissions have led to a significant increase in demand for rare earth elements (REEs). These elements, recognized by the European Union, the United States, and international organizations as critical raw materials, play a key role in the production of permanent magnets, energy storage systems, high-strength alloys, electronic components, precision instruments, and nuclear technologies. The stability of their supply directly affects technological independence, economic resilience, and national security [1,2].

Kazakhstan possesses a unique mineral resource base and a well-developed mining and metallurgical infrastructure, positioning the country as a promising supplier of critical

raw materials in the Eurasian region. According to national geological surveys, numerous occurrences and deposits of rare earth elements have been identified, including both light and heavy lanthanides. In addition, Kazakhstan already maintains an established industrial base for the extraction and processing of several critical elements, including beryllium, tantalum, niobium, gallium, and rhenium, produced within major metallurgical clusters of Central and Eastern Kazakhstan [2]. However, further development of the industry increasingly depends on expanding deep processing technologies and involving technogenic mineral resources in the production cycle.

Technogenic deposits such as coal preparation tailings, combustion ash, sludge, and other coal-derived wastes have attracted increasing attention as potential secondary sources of REEs. International studies have demonstrated that these materials may contain concentrations comparable to low-grade primary ores [3–5]. Numerous investigations have confirmed that REEs are predominantly associated with the mineral fraction of coal and its processing products, including flotation tailings and ash residues [3–5]. This mineral association creates favorable conditions for the concentration of REEs in beneficiation waste streams and forms a basis for developing secondary resource recovery technologies.

In Kazakhstan, significant volumes of coal preparation tailings are accumulated at coal processing plants, particularly in the Karaganda coal basin. Despite their potential resource value, these technogenic materials are currently stored in tailing facilities and are rarely considered for the recovery of valuable elements. One of the main technological bottlenecks is the strong binding of rare earth elements within the aluminosilicate mineral matrix of coal, which significantly limits their extraction by conventional leaching methods. Therefore, the development of effective approaches for the destruction of this mineral matrix and the subsequent release of associated elements represents an important scientific and technological challenge for the metallurgical and coal-processing industries of Kazakhstan.

The Abayskaya coal mine (K18 seam), located in Central Kazakhstan, represents an important coal production facility with significant accumulated beneficiation tailings. Preliminary chemical, mineralogical, and petrographic data indicate that rare earth elements are primarily associated with the aluminosilicate mineral matrix of coal and may preferentially accumulate in flotation tailings [6–8]. The mineralogical characteristics of the aluminosilicate matrix suggest that the efficiency of REE recovery largely depends on the effectiveness of its structural destruction and the subsequent release of associated elements [9].

Recent international studies have demonstrated that acid leaching and combined thermochemical activation methods significantly enhance the extraction of rare earth elements from aluminosilicate matrices. Zhang and Noble (2023) showed that destruction of the silica matrix improves REE recovery during acid leaching [10], while Wang (2023) [3] and Akcil (2024) [4] reported that thermal activation increases extraction efficiency by 20–40%. Flotation and mineralogical studies have confirmed that REEs are predominantly associated with mineral matter, including clay minerals and aluminosilicate phases [11]. Furthermore, thermochemical activation using sulfate- and fluoride-based reagents has demonstrated high efficiency in aluminosilicate structures and improving metal recovery [4,12], whereas selective precipitation techniques provide effective separation and purification of critical elements [3,13]. These findings confirm the technological feasibility of involving coal preparation waste in the production cycle of critical raw materials.

Despite the growing body of international research, the resource potential and technological characteristics of coal preparation tailings from Kazakhstan deposits remain insufficiently studied. In particular, the distribution patterns, mineral associations, and extraction potential of REEs in coal beneficiation waste from the Abayskaya mine have not

been comprehensively evaluated. This creates a scientific and practical need for detailed investigation of coal preparation tailings as a potential secondary source of critical elements.

Therefore, the aim of this study is a comprehensive assessment of coal preparation tailings from the K18 seam of the Abayskaya mine as a potential secondary source of rare earth elements. The study includes granulometric, petrographic, X-ray diffraction, and chemical analyses, flotation separation, thermochemical activation using ammonium fluoride–sulfate reagents, and subsequent leaching of rare earth elements. The obtained results provide new insights into the distribution and mineral association of rare earth elements in coal beneficiation tailings and establish a scientific basis for developing effective recovery technologies. The scientific novelty of this work lies in the integrated evaluation of coal preparation tailings from the Abayskaya mine as a secondary resource of critical rare earth elements, identification of their mineral association and concentration patterns, and justification of thermochemical activation methods for improving extraction efficiency. These findings contribute to the development of sustainable resource utilization strategies and support the involvement of technogenic mineral resources in the circular economy of the mining and processing industry.

2. Materials and Methods

2.1. Materials

Coal preparation tailings obtained from the K18 seam of the Abayskaya coal mine were used as the study material. Representative samples were collected from the tailings storage facility and prepared by drying, homogenization, and quartering to ensure sample representativeness. The prepared samples were used for granulometric, mineralogical, petrographic, chemical, flotation, and thermochemical analyses.

2.2. Particle Size Analysis

The particle size distribution of the coal preparation tailings was determined using standard sieve analysis with laboratory sieves in the size range of 0.071–3.0 mm. Wet sieving and preliminary dispersion procedures were applied to improve accuracy and prevent particle agglomeration. This method is widely used for the characterization of dispersed coal materials and beneficiation products [14].

2.3. Methods Petrographic Analysis

Petrographic analysis of organic and mineral components was performed using a reflected light microscope in accordance with ICCP and ISO 7404 [15] standards. The analysis included determination of maceral composition, including vitrinite, inertinite, fusinite, and mineral inclusions. Special attention was given to identifying the mineral associations of rare earth elements. This approach is commonly applied in studies investigating REE distribution in coal and beneficiation products.

2.4. X-Ray Diffraction Analysis Method

The mineralogical composition of the samples was determined by X-ray diffraction (XRD) using a DRON-2 diffractometer (Bourevestnik, St. Petersburg, Russia) with CuKα radiation (λ = 1.5406 Å), operated at 30 kV and 20 mA. The measurements were carried out in the 2θ range of 5–80° with a step size of 0.02°. Powdered samples were ground and mounted on a flat sample holder. Phase identification was performed using the PDF-4+ database of the International Centre for Diffraction Data (ICDD) [16]. The analysis allowed identification of the main crystalline phases, including aluminosilicate minerals such as kaolinite, montmorillonite, and quartz.

2.5. Chemical and Spectroscopic Analysis

The concentrations of major components were determined using conventional chemical analysis methods. The contents of rare earth and associated elements (Li, Sc, Y, Yb, V, Ti, etc.) in solid samples (coal, concentrate, tailings, and residues), as well as in leach solutions, were determined using inductively coupled plasma optical emission spectrometry (ICP-OES). Certified reference materials were used to control analytical accuracy.

2.6. Flotation, Thermochemical Activation, and Leaching

Flotation experiments were conducted using a laboratory mechanical flotation machine with a cell volume of 1–2 L to separate the organic and mineral fractions of coal. The flotation scheme included rougher and scavenger stages. Prior to flotation, the coal sample was ground to a particle size of 95% passing −0.125 mm. Fuel oil was used as a collector at a dosage of 800–1400 g/t, while T-92 and KOBS were used as frothers at a dosage of 50 g/t. The conditioning time with reagents was 1 min. The pulp pH was not adjusted and remained in the range of 6.5–7.0. The operating parameters were optimized based on ash content, mineral matter recovery, and rare earth element (REE) distribution in the flotation products. This approach is consistent with internationally recognized methods for coal beneficiation and REE pre-concentration [10,17].

The flotation tailings, enriched in mineral matter, were subjected to thermochemical activation using ammonium fluoride–sulfate reagent mixtures to disrupt the aluminosilicate matrix and enhance REE accessibility. The samples were treated at temperatures ranging from 350 to 650 °C under controlled conditions with varying treatment durations and reagent ratios. Thermochemical activation was carried out in an electric muffle furnace in air atmosphere. This treatment promotes structural decomposition of mineral phases and facilitates the transformation of REEs into more soluble forms suitable for subsequent extraction [10].

Following thermochemical activation, water leaching was performed to dissolve the activated mineral components and transfer REEs into solution. The resulting sulfate solutions were analyzed to determine the concentrations of rare earth and associated elements after water leaching. Sequential precipitation of REEs may be applied in subsequent processing stages but was not investigated in the present study. This integrated flotation–thermochemical–hydrometallurgical approach is consistent with modern technologies for REE recovery from coal and coal-derived materials [17].

2.7. Mathematical Design of the Experiment

To establish a quantitative relationship between thermochemical activation parameters and the degree of liberation of the feed material, a probabilistic–deterministic method of mathematical experimental design was applied [18,19]. The independent variables were process temperature (X_1), treatment duration (X_2), ammonium sulfate consumption relative to aluminum content in the raw material (X_3), and ammonium bifluoride consumption relative to silicon content (X_4).

The response function (Y) was defined as the degree of liberation of the feed material, evaluated by the extraction of aluminum into solution during the water leaching of the sintered product (εAl, %). Aluminum was used as an indicator because it is the main component of the aluminosilicate matrix, whose destruction is necessary for the release of rare earth elements. Since rare earth elements in coal are mainly associated with the aluminosilicate mineral matrix, the degree of aluminum extraction was used as an indicator of matrix destruction and the potential release of REEs for subsequent leaching.

A schematic representation of the experimental design and the relationship between the process parameters and the response function is shown in Figure 1.

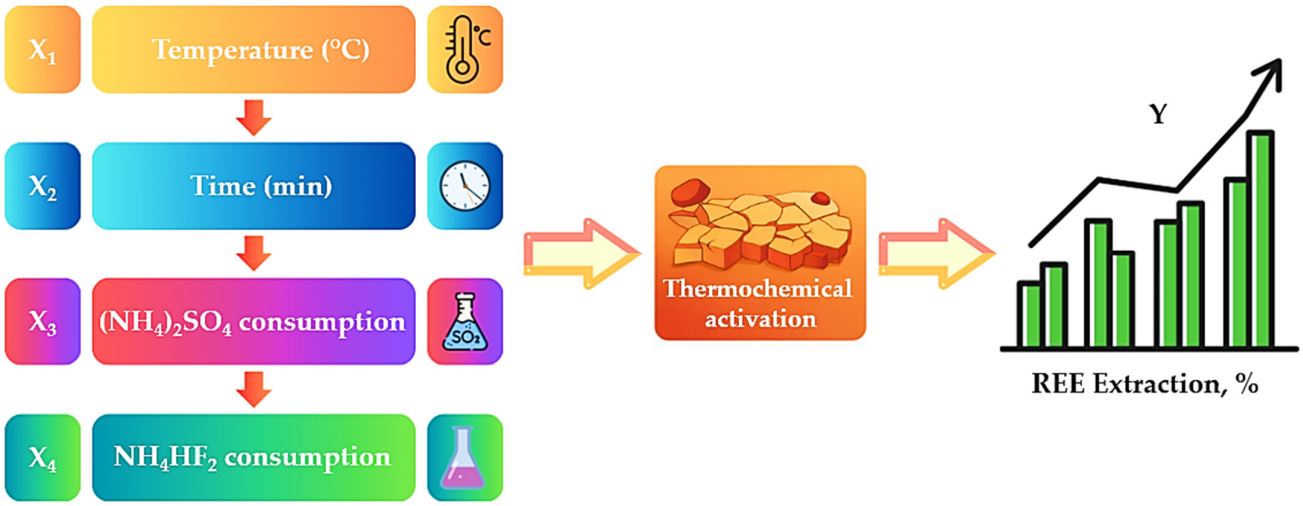

Figure 1. Schematic representation of the experimental design showing the influence of thermochemical activation parameters (temperature, time, and reagent consumption) on the degree of REE extraction.

3. Results and Discussion

3.1. Particle Size Distribution

To assess the particle size distribution of crushed run-of-mine coal from the K18 seam of the Abayskaya mine, a sieve analysis of the samples was carried out. A coal sample weighing 20 kg was taken to determine the content of rare earth elements (REE). The results of the sieve analysis are presented in Table 1.

Table 1. Particle size distribution of coal.

Size Class, mm	Fraction Yield	
	m, g	γ, %
−2.0 + 1.0	15.75	15.95
−1.0 + 0.5	25.38	25.70
−0.5 + 0.25	19.65	19.90
−0.25 + 0.125	12.54	12.70
−0.125 + 0.071	8.54	8.65
−0.071 + 0.063	0.94	0.95
−0.063 + 0.045	1.83	1.85
−0.045	14.12	14.3
total	98.75	100

The results of the sieve analysis of the coal sample are presented in Table 1. The particle size distribution shows that the dominant size fraction is −1.0 + 0.5 mm, accounting for 25.70% of the total mass. Significant proportions are also observed in the −0.5 + 0.25 mm (19.90%) and −2.0 + 1.0 mm (15.95%) fractions. Finer fractions such as −0.125 + 0.071 mm and −0.071 + 0.063 mm is present in smaller amounts, representing 8.65% and 0.95%, respectively. The finest fraction (−0.045 mm) accounts for 14.3% of the sample. Overall, the results indicate a predominance of medium-sized particles in the studied coal sample.

3.2. Proximate Analysis

The results of the proximate analysis of raw coal from the K18 seam of the Abayskaya mine are presented in Table 2. The ash content (A^c) is 33.47%, indicating a high mineral matter content. The volatile matter yield (V^{daf}) is 19.67%, corresponding to a moderate

level of volatile components. The moisture content (W^a) is low, at 1.25%, indicating minimal influence of moisture. These characteristics classify the coal as high-ash with moderate volatile matter and low moisture content, which is important for evaluating its beneficiation and thermochemical processing behavior. The obtained data also provide a basis for assessing the suitability of the flotation tailings material for further processing and the recovery of rare earth elements (REE).

Table 2. Proximate analysis of raw coal from the K18 seam of the Abayskaya mine.

Material	Technical Composition, %		
	A^c	V^{daf}	W^a
Run-of-mine coal	33.47	19.67	1.25

3.3. X-Ray Diffraction Analysis Results

The mineralogical composition of the host rock associated with coal from the K18 seam of the Abayskaya mine was determined using X-ray diffraction analysis. The results are presented in Table 3. The analysis showed that the mineral fraction is predominantly composed of clay minerals, quartz, feldspar, and carbonate phases, indicating a complex mineral structure of the host rock.

Table 3. Mineral phase composition of the host rock from the K18 seam of the Abayskaya mine.

Mineral (Phase)	Content, %
Montmorillonite ($Al_2(OH)_2[Si4O_{10}]\cdot H_2O$)	25
Kaolinite ($Al_2Si_2O_5(OH)_4$)	20
Quartz (SiO_2)	20
Feldspar [K, Na, Ca][Al, Si, O]	15
Siderite ($FeCO_3$)	10
Dolomite, limestone (Ca, Mg)CO_3	10

Montmorillonite is the dominant mineral phase, accounting for 25% of the total mineral composition. Kaolinite and quartz are present in significant amounts (20% each), followed by feldspar (15%) and carbonate minerals, including siderite, dolomite, and calcite (10%). The high proportion of clay minerals, particularly montmorillonite and kaolinite, indicates that the mineral matter is mainly composed of aluminosilicate phases. Quartz and feldspar contribute to the silicate matrix, while carbonate minerals confirm the presence of carbonate components. The identified mineral composition provides a basis for understanding the mineral structure and evaluating the distribution of rare earth elements in the mineral fraction.

3.4. Results Petrographic Analysis

Petrographic analysis of the organic matter in raw coal and coal concentrates from the Abayskaya mine (K18 seam) was carried out. The study included raw coal as well as coal concentrates of fine and coarse fractions obtained during the beneficiation process. The macrostructure of raw coal and the presence of mineral inclusions, including phlogopite, are shown in Figure 2.

The microstructure of the maceral composition was examined using reflected light microscopy at magnifications ranging from $\times 100$ to $\times 600$. The analysis was performed in accordance with standard petrographic methods for coal characterization.

The identified maceral groups were classified according to accepted petrographic nomenclature. The following symbols were used to designate maceral components: Vt—vitrinite; If—fusinite; Isf—semiquinone; A—argillite; and K—kaolinite.

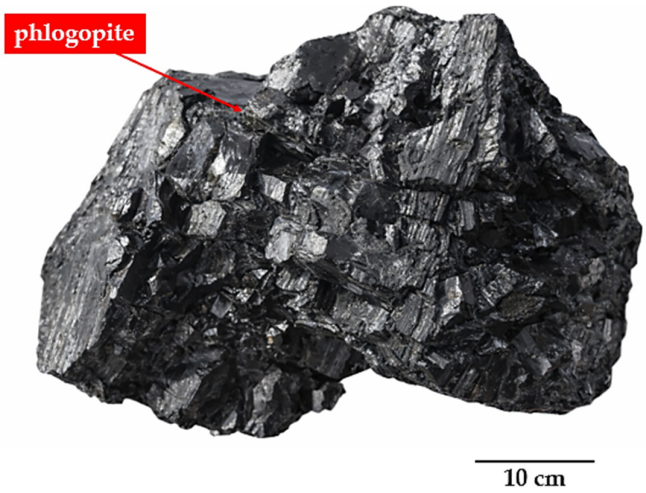

Figure 2. Macrostructure of raw coal from the Abayskaya mine (K18 seam), with phlogopite inclusions.

The petrographic composition of raw coal from the Abayskaya mine (K18 seam) is mainly represented by macerals of two major groups, namely vitrinite (approximately 73%) and inertinite (predominantly fusinite), as well as microinclusions of minerals such as feldspar and kaolinite. The coal lump sample is penetrated by phlogopite mica layers with a thickness of 1–3 mm. Small particles of pyrite, argillite, and clay minerals were locally identified within the fusinite structure.

In reflected light (polished lump section, Figure 3a), the main mass of vitrinite appears homogeneous and structureless, indicating the complete gelification of plant tissues during coal metamorphism. Vitrinite is light gray in color and contains distinct vertical shrinkage cracks filled with clay minerals. The presence of these cracks is associated with the combined effects of metamorphic and thermobaric processes.

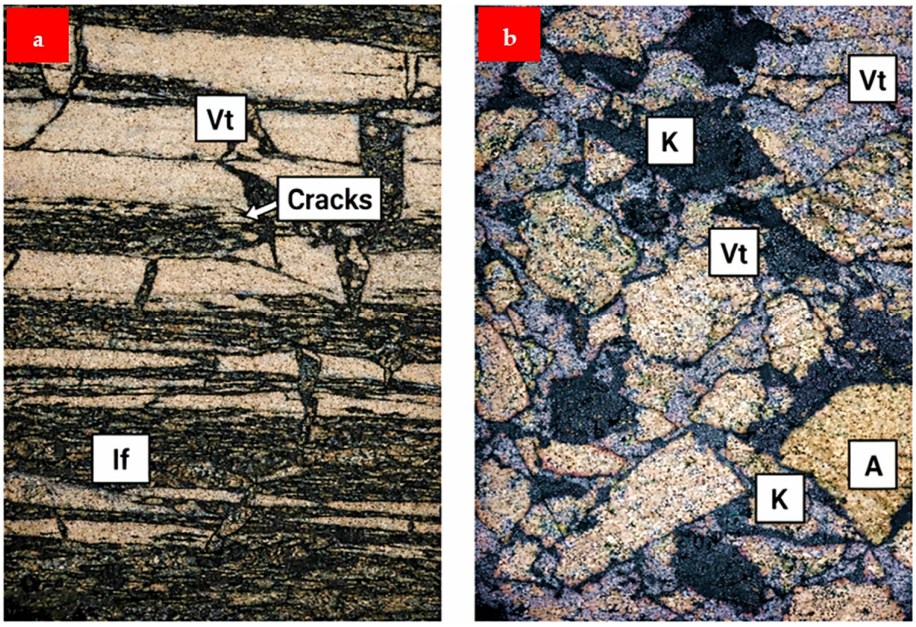

Figure 3. Petrographic microstructure of raw coal from the Abayskaya mine (K18 seam): (**a**) polished lump section showing vitrinite (Vt), fusinite (If), and shrinkage cracks; (**b**) polished briquette showing vitrinite (Vt), kaolinite (K), and argillite (A).

Standard petrographic analysis of polished briquettes of coal concentrate from the K18 seam, including both fine and coarse fractions (Figure 3b), showed that these fractions

have similar maceral compositions. The main mass of vitrinite is characterized by short, differently oriented streaks and fine granular structures. Mineral inclusions are represented by kaolinite, as well as microinclusions of clay and siliceous minerals.

Standard petrographic examination of polished briquettes of coal concentrate from the Abayskaya mine (K18 seam), including both fine and coarse fractions, showed that these fractions exhibit similar maceral compositions. The predominant maceral component is vitrinite, which appears in the form of short, irregularly oriented streaks as well as fine granular structures. These features indicate a uniform distribution of vitrinite within the concentrate.

Mineral inclusions are mainly represented by dark gray kaolinite, along with minor micro inclusions of clay and siliceous minerals. These mineral components occur as dispersed particles within the organic matrix and are associated with the mineral fraction of the coal concentrate.

The preliminary quantitative results of maceral and mineral component distribution, determined by standard reflected light petrographic analysis, are presented in Table 4.

Table 4. Petrographic composition of macerals and mineral components in coal from the Abayskaya mine (K18 seam).

Group	Vitrinit. V	Semivitrinitis. Sv	Inertinite. I		Mineral Inclusions. M		Sum of Points. N	Sum of Points N + M
Micro-Component	Vitrinit. Vt	Semivitrinitis. S_{vt}	Semifuzinitis I_{sf}	Fusinite. I_f	Sulfides. Fe	Carbonates		
Quantity	69.0	2.0	7.0	20.0	9.0	6.0	98.0	113.0
Share N.%	70.4	2.0	7.1	20.4	0.0	0.0	100.0	
Share M.%	61.1	1.8	6.2	17.7	8.0	5.3		100.0

Thus, coal from the K18 seam of the Abayskaya mine is characterized by a banded and structurally heterogeneous texture. During crushing and preparation of polished briquettes, such banding may result in the selective exposure of individual macerals on the polished surface, which can lead to misinterpretation of their actual proportions if not properly considered. To minimize this effect, additional petrographic examination was conducted on the brightest clarain layers of the coal lump in order to identify macerals belonging to the liptinite group.

Figure 4 shows selected areas of the coal lump where vitrinite occurs as light gray, slightly curved, and well-oriented layers without preserved plant cellular structures. Fusinite locally retains rounded cellular features; however, in some areas, the pore and cell structures appear blurred, resembling the texture of bark, cuticles, and plant stem or leaf tissues.

As shown in the reflected light micrographs of layers (a) and (b) in Figure 4, the bulk of the vitrinite in the polished coal specimen is characterized by a light gray color and occurs as elongated, slightly curved, and well-oriented layers, without preservation of the original plant tissue structure. The vitrinite layers have undergone complete stages of gelification and catagenesis.

Fusinite in some areas of the coal specimen is represented by clearly preserved rounded cellular structures of plant tissue. However, in other areas, the cellular cavities and pores in fusinite appear blurred and resemble the pores of bark (cork), stem cuticles, and leaves rather than the typical cellular structure characteristic of fusinite.

Further microstructural analysis of the polished coal specimen under reflected light microscopy at magnifications of $\times 40$ and $\times 100$ revealed macerals belonging to the liptinite group, including resinite (Lr) and cutinite (Lkt), as shown in Figure 5. In addition, detailed examination identified sporinite (Lsp) and resinite (Lr) macerals, demonstrating their

morphological characteristics and distribution within the coal structure, as presented in Figure 6.

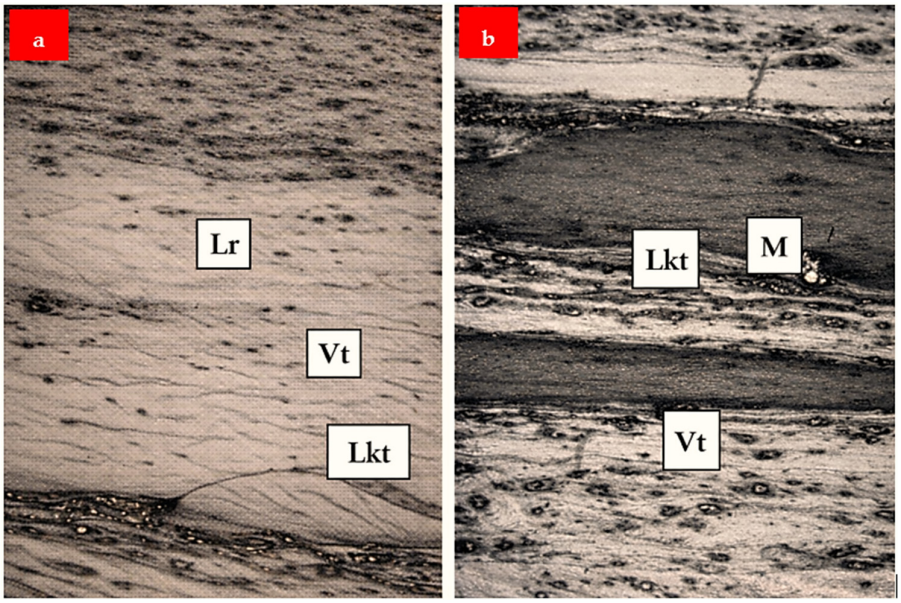

Figure 4. Microstructure of coal from the Abayskaya mine (seam K18) (polished specimen, reflected light microscopy, magnification ×100): (**a**) vitrinite (Vt), resinite (Lr) and liptinite (Lkt); (**b**) liptinite (Lkt), vitrinite (Vt), and mineral inclusions (M).

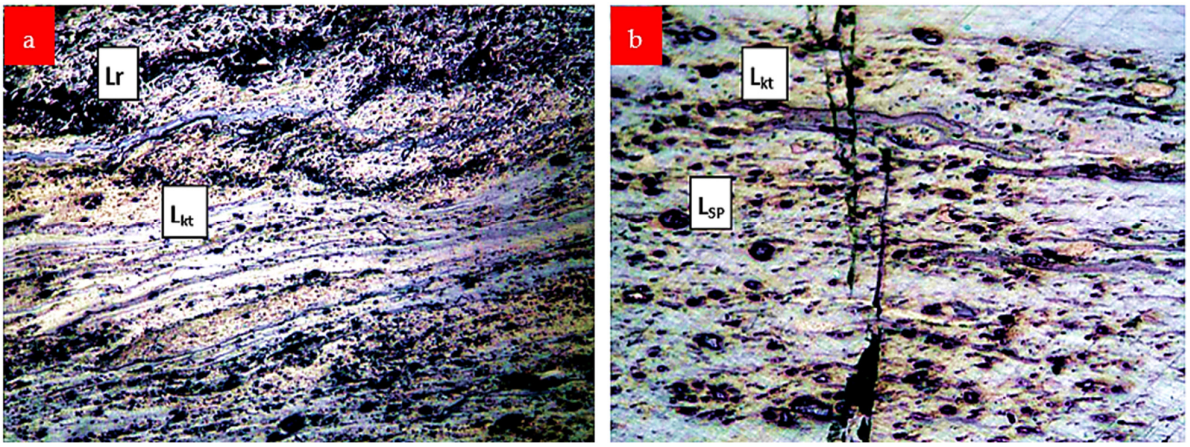

Figure 5. Liptinite group macerals in a polished coal specimen under reflected light microscopy: (**a**) magnification ×40, showing resinite (Lr) and cutinite (Lkt); (**b**) magnification ×100, showing cutinite (Lkt) and sporinite (Lsp).

Sporinite is observed in the form of flattened rings of macro- and microspores composed of wax-like material. Resinite occurs as resin inclusions represented by various rounded and oval bodies with irregular shapes.

Considering the fluorescent properties of liptinite, additional investigations were performed using fluorescence microscopy. Figure 7 shows paired images of the same areas under reflected and fluorescent light (λ = 365 nm).

In the ultraviolet spectrum, vitrinite appears black with clearly defined grain boundaries. Interlayers within its fractures, exhibiting intense dark blue and violet fluorescence, are interpreted as liptinite matter formed from gelified cutinite residues of stems, leaves, and bark. The presence of cuticles is confirmed by the characteristic serrated and clotted outlines of several fluorescent regions. Clay mineral particles in the ultraviolet spectrum

appear as bright red and purplish-pink wedge-shaped inclusions filling transverse fractures that intersect the organic matter layers.

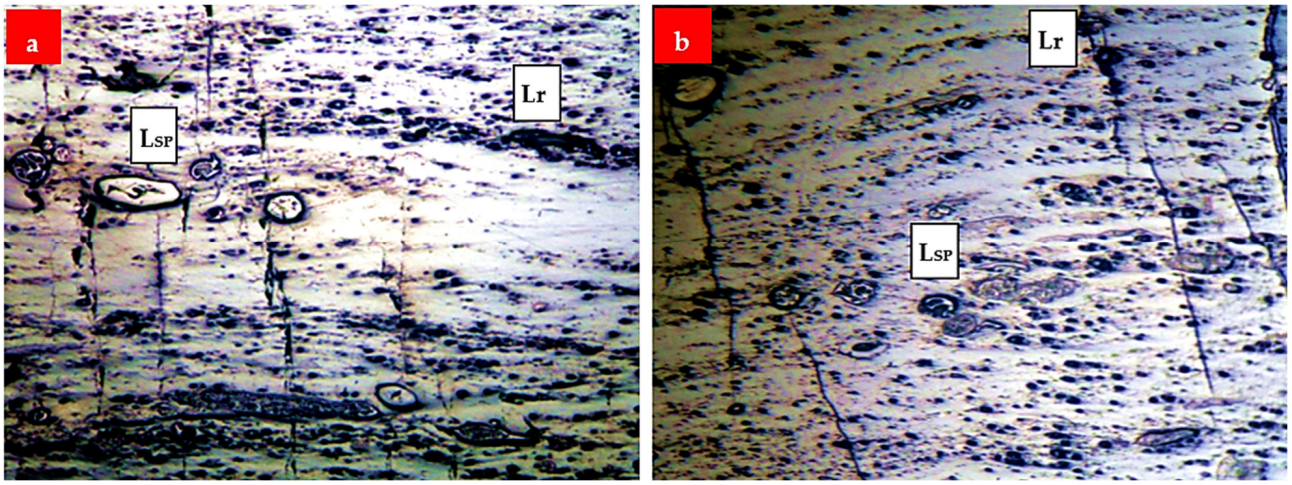

Figure 6. Liptinite group macerals in a polished coal specimen under reflected light microscopy at ×100 magnification: (**a**) sporinite (Lsp) and resinite (Lr); (**b**) sporinite (Lsp) and resinite (Lr).

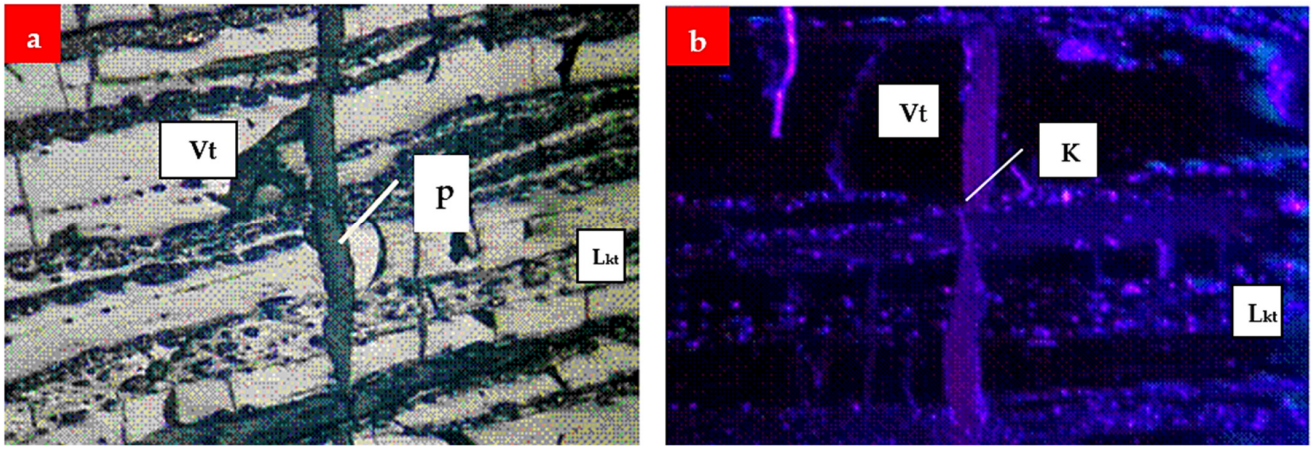

Figure 7. Microstructure of coal from the Abayskaya mine (seam K18) (polished specimen, ×100 magnification): (**a**) reflected light microscopy; (**b**) fluorescence microscopy (λ = 365 nm).

Therefore, the fluorescence study confirms the occurrence of liptinite macerals in coal from seam K18, which may be incorrectly interpreted as vitrinite or fusinite under reflected light alone. The observed fluorescence characteristics indicate the presence of hydrogen-rich macerals associated with plant-derived organic precursors. These results emphasize the necessity of combining reflected light and fluorescence microscopy to ensure accurate petrographic identification and reliable assessment of the coal maceral composition and its genetic features.

The petrographic observations also provide important information for interpreting the distribution of rare earth elements in the studied coal. The dominance of vitrinite together with the presence of mineral inclusions such as clay minerals, feldspars, and aluminosilicates confirms that a significant portion of REEs is associated with the mineral fraction rather than the organic macerals. This observation supports the effectiveness of flotation as a preliminary step for separating organic matter and concentrating REE-bearing mineral phases in the flotation tailings, which are subsequently subjected to thermochemical processing.

3.5. Flotation

Flotation experiments were conducted to separate the organic and mineral components of coal and to determine the distribution of rare earth elements (REEs) among the beneficiation products. The initial coal sample was dispersed in water at a solid-to-liquid ratio (S:L) of 1:1 to obtain a homogeneous pulp. The resulting mixture was loaded into a laboratory ball mill and ground for a controlled period sufficient to liberate mineral inclusions without excessive overgrinding of the organic matter.

After grinding, the pulp was diluted with water to a working S:L ratio of 1:4, ensuring optimal viscosity and hydrodynamic conditions for the separation of particles with different surface properties. The prepared pulp was then transferred to the flotation chamber of a laboratory mechanical flotation machine. The froth layer was formed by adding collector reagents and controlled amounts of frother. The reagents were dosed according to predetermined consumption rates and conditioned with the pulp for 1 min to ensure adequate adsorption on the carbonaceous phase surface.

Flotation was carried out according to the scheme shown in Figure 8, including primary and scavenger stages. This scheme enables more efficient removal of the organic phase and improves the selectivity of separation based on differences in particle hydrophobicity.

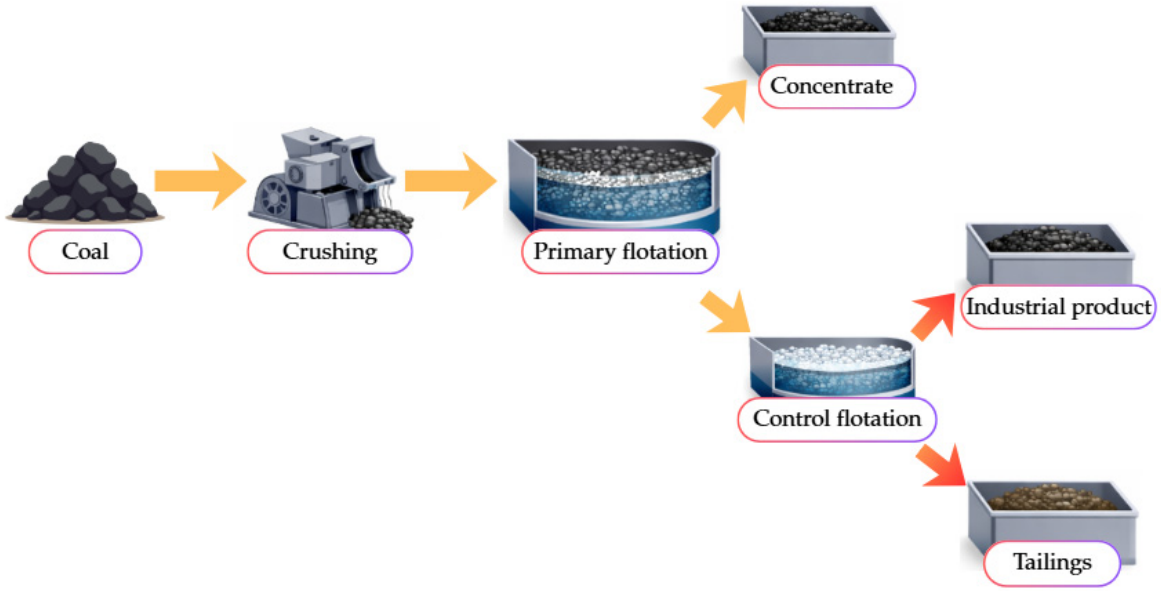

Figure 8. Coal flotation flowsheet including primary and control flotation stages.

The results of chemical and spectroscopic analysis of the flotation products—concentrate and tailings—indicate that rare earth elements (REEs) are predominantly associated with the mineral fraction of coal and are therefore enriched in the flotation tailings (Tables 5 and 6). As shown in Table 6, approximately 70–75% of most elements are transferred to the flotation tailings, confirming their preferential association with mineral matter.

Table 5. Chemical composition of flotation products.

Product	Product Yield, %	Content of Major Components, %			
		Organic Matter	SiO_2	Al_2O_3	Fe
Feed coal	100.0	65.52	20.77	6.86	1.72
Concentrate	69.0	86.32	8.16	2.72	0.73
Tailings	31.0	20.95	47.17	15.80	4.04

Table 6. Concentration and distribution of rare earth and associated elements in flotation products.

Element	Feed Coal	Concentrate	Tailings	Distribution in Tailings, %
Li	28	11.9	65	~72
Sc	7	2.9	16	~71
Y	7	3.0	17	~75
Yb	1.1	0.4	2.5	~70
V	59	24.6	135	~71
Ti	998	416.8	2293	~71
Be	0.7	0.3	1.5	~66
Ga	7	3.1	17	~75
La	9	3.9	21	~72
Ce	21	9.0	49	~72
Zr	30	12.5	69	~71

Note: Calculated based on the tailings yield (31%) and the element contents.

This observation is consistent with previous studies reporting that REEs in coal and coal beneficiation products are mainly linked to clay minerals, aluminosilicate matrices, carbonates, and fine-grained sulfide phases rather than organic matter [20,21].

Similar trends have been reported for coal flotation products from Canadian and Australian coal basins, where REEs were found to be concentrated in the mineral residue, and their distribution between concentrate and tailings correlated with ash content and mineral phases [11,22].

Thus, the experimental results obtained for coal from seam K18 confirm the general trend that flotation concentrate is enriched in organic matter and characterized by lower REE contents, whereas flotation tailings represent a mineral-rich fraction that serves as the main carrier of REEs.

From a technological perspective, flotation acts as an effective preliminary step for concentrating REEs in the mineral fraction, thereby facilitating further thermochemical and hydrometallurgical processing.

As shown in Table 5, the majority of mineral components are concentrated in the flotation tailings. A similar distribution pattern is observed for rare earth elements (Table 6), confirming their preferential association with the mineral fraction.

The data presented in Table 5 confirm that approximately 70% of rare earth and other rare elements contained in the feed coal are associated with the mineral fraction and are transferred to the flotation tailings. The concentrations of lithium (65 g/t), scandium (16 g/t), yttrium (17 g/t), ytterbium (2.5 g/t), and vanadium (135 g/t) in the tailings reach levels that may be of potential interest for industrial recovery as by-products, confirming the potential of these wastes as a secondary raw material.

3.6. Results of Mathematical Modeling

The degree of aluminosilicate matrix decomposition was evaluated based on aluminum extraction into solution during the water leaching of the calcined product obtained after thermochemical treatment with ammonium bifluoride and ammonium sulfate. Aluminum recovery was used as a quantitative indicator of the effectiveness of thermochemical activation and the extent of mineral structure destruction. Leaching was performed at a temperature of 90 °C for 2 h with a solid-to-liquid ratio of 1:10. The experimental conditions and results of the matrix experiments used for mathematical modeling are presented in Table 7.

Considering the degree of raw material decomposition as the response function, the experimental data were grouped according to the factor levels, and the mean experimental

values of the response were determined. The experimental values of the partial response functions and their mean values are presented in Table 8.

Table 7. Factors and their variation levels used in the study of thermochemical activation of coal flotation tailings.

Factor	Level				
	1	**2**	**3**	**4**	**5**
X_1, temperature, °C	350	375	400	425	450
X_2, time, min	30	60	90	120	180
X_3, ammonium sulfate consumption, %	50	75	100	125	150
X_4, ammonium hydro fluoride consumption, %	50	75	100	125	150

Table 8. Influence of sintering parameters on the degree of thermochemical activation of coal preparation flotation tailings.

Experiment No	X_1, °C	X_2, min	X_3, %	X_4, %	Degree of Liberation of the Feed Material	
					Experimental, ε_e, %	Calculated, ε_p, %
1	2	3	4	5	6	7
1	350	30	50	50	49.95	64.18
2	350	90	100	125	86.57	87.51
3	350	60	75	75	85.89	75.53
4	350	180	150	150	95.27	97.25
5	350	120	125	100	89.68	87.00
6	400	30	100	75	82.61	78.72
7	400	90	75	150	91.50	92.03
8	400	60	150	100	88.48	89.73
9	400	180	125	50	82.42	80.60
10	400	120	50	125	85.22	86.51
11	375	30	75	100	79.58	80.00
12	375	90	150	50	78.65	78.52
13	375	60	125	125	91.59	90.90
14	375	180	50	75	82.03	79.04
15	375	120	100	150	95.27	95.01
16	450	30	150	125	91.00	85.98
17	450	90	125	75	80.68	80.83
18	450	60	50	150	82.10	82.26
19	450	180	100	100	84.65	86.46
20	450	120	75	50	71.86	71.47
21	425	30	125	150	86.86	90.60
22	425	90	50	100	90.05	80.81
23	425	60	100	50	75.07	73.87
24	425	180	75	125	83.96	90.87
25	425	120	150	75	82.42	86.58
Average value					83.73	83.69

The data used for constructing the partial response functions (Table 9) were obtained by grouping the experimental results from Table 2 according to the levels of each factor (X_1–X_4). The mean decomposition degree was calculated for each group. This approach allowed the determination of the averaged partial functions ε_1–ε_4, which represent the individual effect of each factor while statistically averaging the influence of the remaining variables.

Using the data presented in Table 9, point plots illustrating the partial relationships between the decomposition degree of the raw material and the investigated factors were constructed. The resulting plots are presented in Figure 9.

Table 9. Experimental values of the partial liberation functions of the feed material.

Function	Levels					Average Value
	1	2	3	4	5	
ε_1	81.47	85.42	86.05	83.67	82.06	83.73
ε_2	78.00	84.63	85.49	84.89	85.67	83.73
ε_3	77.87	82.56	84.83	86.25	87.16	83.73
ε_4	71.59	82.73	86.49	87.67	90.20	83.73

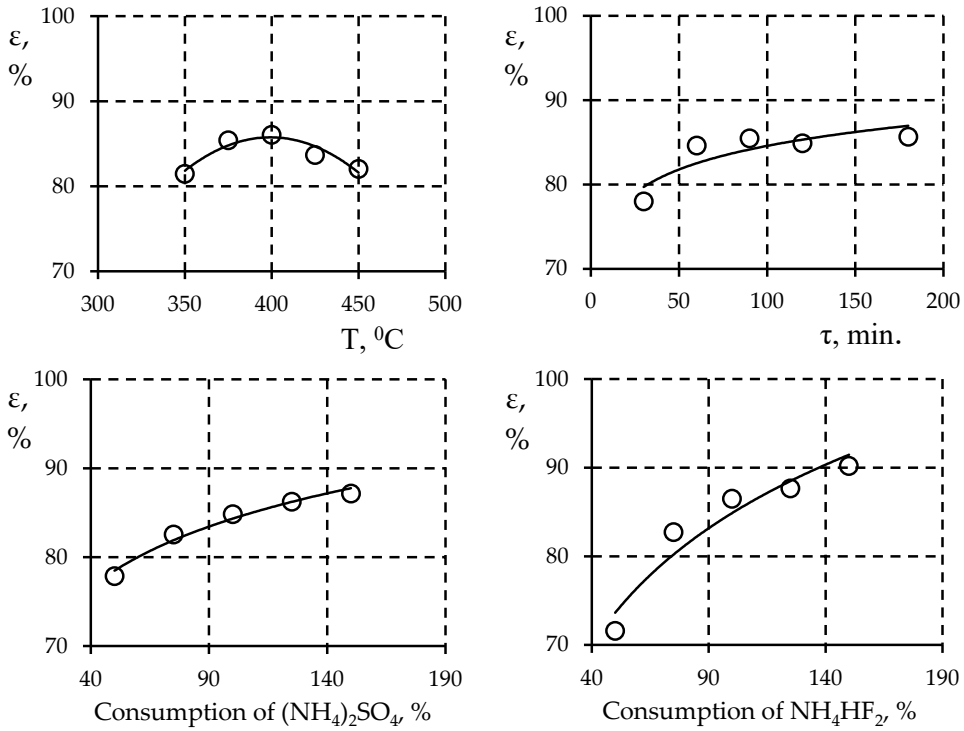

Figure 9. Dependences of the degree of opening of flotation tailings of coal enrichment waste on the studied factors.

The plots shown in Figure 9 illustrate the influence of each of the four investigated factors on the degree of thermochemical decomposition of coal flotation tailings. The analysis demonstrated that ammonium bifluoride consumption had the most significant effect on the decomposition degree. Specifically, the decomposition degree increased by 19% with an increase in ammonium bifluoride consumption from 50 to 125%. Moreover, the increase in decomposition was observed throughout the entire studied range, approaching a limiting value.

The next factor influencing the decomposition degree was ammonium sulfate consumption. Within the investigated range, the decomposition degree increased by approximately 10% with an increase in ammonium sulfate consumption from 50 to 150%.

The temperature dependence exhibited a maximum at 400 °C. The decomposition degree increased as the temperature rose from 350 °C to 400 °C, reaching its maximum value, and then decreased with further temperature increase, indicating the presence of an optimal temperature range for the thermochemical activation process.

The influence of sintering time (within the range of 30–180 min) on the decomposition degree was found to be relatively insignificant and showed only a weak positive effect. The decomposition degree gradually increased with increasing time; however, the difference between the minimum and maximum levels did not exceed 8%, confirming the secondary role of this factor.

Overall, the obtained plots demonstrate the different nature and magnitude of factor effects and allow the identification of the key process parameters required for the optimization of ammonium fluoride–sulfate thermochemical activation technology.

To quantitatively describe the established partial relationships between the decomposition degree and each investigated factor, approximating functions were fitted to the experimental data presented in Table 7. The shape of the curves shown in Figure 9 determined the selection of different types of approximation equations. A quadratic function was used to describe the temperature dependence (X_1), reflecting the presence of an optimum, whereas logarithmic functions were applied to represent the dependencies on sintering time (X_2), ammonium sulfate consumption (X_3), and ammonium bifluoride consumption (X_4), corresponding to the gradual decrease in the rate of decomposition increase at higher factor values.

The obtained regression equations adequately describe the experimental data, as evidenced by the following results:

$$\varepsilon_1 = -0.00162x_1^2 + 1.289x_1 - 171.66; \quad (1)$$

$$\varepsilon_2 = 4.048\ln x_2 + 65.94; \quad (2)$$

$$\varepsilon_3 = 8.443\ln x_3 + 45.45; \quad (3)$$

$$\varepsilon_4 = 16.22\ln x_4 + 10.18. \quad (4)$$

Using Equations (1)–(4), the theoretical values of the partial response functions were calculated for all factor levels. The calculated results are presented in Table 10.

Table 10. Calculated values of private functions for raw material opening.

Function	Levels					Average Value
	1	2	3	4	5	
ε_1	81.79	84.76	85.70	84.63	81.53	83.68
ε_2	79.71	82.51	84.16	85.32	86.96	83.73
ε_3	78.48	81.90	84.33	86.22	87.76	83.74
ε_4	73.63	80.21	84.88	88.50	91.45	83.73

The comparison between the calculated average values (83.68–83.74%) and the overall experimental mean value (83.73%) showed negligible deviations (<0.05%), indicating the high accuracy of the approximation and the strong agreement between the developed mathematical models and the experimental data.

To quantitatively assess the adequacy of the models, the nonlinear multiple correlation coefficients (R) and their statistical significance (t_R) were determined. The corresponding results are summarized in Table 11.

The correlation coefficients (R) fall within the range of 0.80–0.98, confirming a strong relationship between the investigated factors and the degree of thermochemical decomposition. The highest correlation values were observed for ε_3 (R = 0.98) and ε_4 (R = 0.95), highlighting their dominant influence on the ammonium fluoride–sulfate activation process.

The calculated t_R values considerably exceed the critical tabulated values, demonstrating the statistical significance of all partial functions and confirming the reliability and applicability of the developed multifactor model.

Table 11. Correlation coefficient and its significance for particular functions for the opening of flotation tailings of coal enrichment waste.

Function	R	t_R	Significance of the Function
y_1	0.88	6.72	Significant
y_2	0.8	3.81	Significant
y_3	0.98	49.2	Significant
y_4	0.95	16.74	Significant

Based on the statistically significant partial dependencies identified through probabilistic–deterministic analysis, a generalized multifactor mathematical equation was established to quantitatively describe the influence of key process parameters on the degree of thermochemical decomposition of the raw material:

$$\varepsilon = (-0.0016T^2 + 1.29T - 171.7)(4.05 \ln \tau + 65.9)(8.44 \ln Pc + 45.5)(16.2 \ln Pd - 10.2) \times 83.73^{-2} \quad (5)$$

The obtained expression represents a comprehensive mathematical model of the ammonium fluoride–sulfate thermochemical activation process of coal preparation flotation tailings and accounts for the simultaneous influence of four factors: temperature and sintering time, as well as ammonium sulfate and ammonium bifluoride consumption. The adequacy of the model is confirmed by the high degree of agreement between the calculated values and the experimental data (Table 2). The correlation coefficient was R = 0.84, and the statistical significance criterion t_R = 12.09 indicates the reliability and reproducibility of the developed model.

Based on Equation (5), the optimal thermochemical activation conditions were determined. The most effective combination of parameters corresponds to a sintering temperature of 400 °C, a process duration of 120 min, ammonium sulfate consumption of 140% relative to the aluminum content in the raw material, and ammonium bifluoride consumption of 110% relative to the silicon content. Under these conditions, the calculated aluminum decomposition degree reaches 96.54%, demonstrating the high efficiency of the proposed technology.

From a chemical perspective, during the sintering process, the mineral components of the raw material (except silica) react with ammonium sulfates and fluorides, forming predominantly water-soluble sulfate compounds. As a result, the calcined product becomes suitable for subsequent water leaching, enabling the selective transfer of aluminum and associated elements into solution.

To confirm the effectiveness of the proposed method, thermochemical activation of flotation tailings was carried out under the optimal conditions (400 °C, 120 min, $(NH_4)_2SO_4$ consumption—140%, NH_4HF_2 consumption—110%). After the water leaching of the sintered product, both the obtained solution and the solid residue were analyzed. The extraction efficiencies of key elements are presented in Table 12.

As shown in Table 12, the high degree of decomposition of the aluminosilicate matrix (93.8% based on Al) correlates with the almost complete extraction into solution of valuable elements such as yttrium, ytterbium, lithium, and titanium, as well as the high extraction of scandium and vanadium. This confirms that the proposed method effectively destroys the mineral matrix, making rare earth elements accessible for leaching. The lower extraction of lanthanum (55%) may be associated with its occurrence in more resistant mineral phases.

It should be noted that, in addition to chemical activation methods, physical approaches for enhancing the permeability and fragmentation of coal matrices have been investigated in recent studies. For example, high-voltage electrical pulse treatment has been shown to intensify structural destruction of coal and improve permeability. In contrast to such physical methods, the ammonium fluoride–sulfate thermochemical activation applied in this work directly decomposes the aluminosilicate mineral matrix hosting rare earth elements, thereby facilitating their transfer into solution during subsequent leaching.

Table 12. Extraction of rare earth and associated elements under optimal thermochemical activation conditions.

Element	Extraction Into Solution, %
Aluminum (Al) *	93.8
Scandium (Sc)	95
Yttrium (Y)	100
Ytterbium (Yb)	100
Lithium (Li)	100
Titanium (Ti)	100
Vanadium (V)	95
Beryllium (Be)	91
Lanthanum (La)	55

* Note: Degree of feed decomposition calculated based on aluminum extraction.

4. Conclusions

As a result of the comprehensive study, flotation tailings of coal from the K18 seam of the Abayskaya mine were evaluated as a potential secondary source of critical metals. For the first time for this deposit, quantitative data confirming the resource potential of these technogenic materials have been obtained. The following conclusions were reached:

1. It was established that rare earth elements (La, Ce, Y, etc.), as well as Li, Sc, V, and Ti in the feed coal, are predominantly associated with the mineral fraction (approximately 70% of their total content). As a result, during flotation beneficiation, they concentrate in the tailings, reaching the following concentrations (g/t): Li—65; Sc—16; Y—17; Yb—2.5; V—135; and Ti—2293.
2. A method for the fluorine–ammonium sulfate thermochemical activation of the aluminosilicate matrix of flotation tailings was proposed and optimized. Using mathematical modeling, the optimal process parameters were determined (400 °C, 120 min, $(NH_4)_2SO_4$ consumption—140%, NH_4HF_2 consumption—110%), providing a feed decomposition degree (based on Al extraction) of up to 94%.
3. It was experimentally demonstrated that the high degree of matrix decomposition leads to the efficient extraction of target elements into solution: Sc—95%; Y—100%; Yb—100%; and Li—100%.
4. The obtained results demonstrate that the proposed technology enables the transfer of key rare earth elements from technogenic raw materials into solution, creating the basis for their subsequent recovery as concentrates by sorption, extraction, or precipitation methods, which will be the focus of future research.

Thus, using coal from the Abayskaya mine as an example, the feasibility and high efficiency of involving coal preparation waste in processing for the recovery of a wide range of critical elements has been demonstrated. This approach corresponds to the principles of rational resource utilization and the circular economy in the mining and metallurgical industries. The thermochemical activation method applied in this work represents an effective approach for the disintegration of refractory mineral matrices, while alternative

physical activation methods, such as electro-pulse treatment, may also be considered at the stage of preliminary material preparation.

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