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Changes in Major and Trace Element Concentrations in Low-Rank Coal after Hydrogen Peroxide Pre-treatment: A Screening Approach Based on Enrichment Index

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Abstract

Low-rank coal contains minerals and associated major and trace elements that may be mobilized during processing, particularly under pre-treatment and leaching conditions. This study aimed to characterize the major and trace elements in low-rank coal, evaluate their relative enrichment in solid residues following hydrogen peroxide (H_2O_2) pre-treatment, and assess the potential implications of mobile Fe and Mn for groundwater quality. Elemental concentrations before and after pre-treatment were determined using Inductively Coupled Plasma Mass Spectrometry (ICP-MS), while changes in elemental abundance were evaluated using an enrichment index (Δ%). The untreated coal contained a range of major and trace elements, including Fe, Mn, Yb, Er, Zn, Co, Ni, Mg, Al, Sc, Li, Na, Ga, and Ce. H_2O_2 pre-treatment altered the distribution of several elements in the solid residue, with Fe and Mn showing the most pronounced relative enrichment. These changes are likely associated with the oxidation and transformation of metal-bearing mineral phases under oxidative conditions, whereas other elements exhibited variable responses depending on their modes of occurrence and mineral associations. Leachate analysis by Atomic Absorption Spectroscopy (AAS) further confirmed the mobilization of Fe and Mn into the aqueous phase. Mn concentrations remained below the Indonesian mining wastewater standard (Permen LHK No. 5/2022), whereas Fe concentrations exceeded the regulatory limit in the 40- and 60-mesh samples. In addition, the leachates remained acidic, with pH values below 6. These findings indicate that oxidative pre-treatment can influence both elemental redistribution in coal residues and metal mobility into the aqueous phase, highlighting the importance of controlling pre-treatment conditions and neutralizing acidic leachates prior to discharge. Overall, the proposed screening approach provides a practical preliminary framework for assessing the geochemical mobility of elements in low-rank coal.

1. Introduction

Low-rank coal has abundant reserves in Indonesia, but its utilization faces significant economic constraints in the form of low selling prices in the global energy market [1]. The inherent characteristics of low-rank coal, such as high moisture content, low calorific value, high volatile matter content, complex macromolecular structure, and low chemical reactivity, result in its commercial value being far below that of high-rank coal such as anthracite and bituminous coal [1], [2].

One pre-treatment method that has been widely studied in recent years is oxidative pre-treatment using hydrogen peroxide (H_2O_2). Hydrogen peroxide was chosen because it has strong oxidizing power, is capable of working under mild temperature and pressure conditions, and produces relatively environmentally friendly by-products in the form of water and oxygen [3]. In the context of low-rank coal, oxidative pre-treatment with H_2O_2 is known to modify the organic matrix structure through the breaking of complex macromolecular bonds, the formation of oxygenated functional groups, and an increase in the fraction of more reactive low molecular weight compounds. These changes generally

have a positive impact on increasing coal reactivity and the efficiency of subsequent conversion processes, including in the production of biogenic methane and subsurface gasification.

However, oxidative pre-treatment not only affects the organic components of coal, but also has the potential to alter the behavior of the inorganic components contained therein, particularly major and trace elements. Low-rank coal generally contains various metallic elements, both those associated with inorganic minerals such as silicates, carbonates, and sulfides, and those complexed with the organic matrix [4]. Under natural conditions, most of these metals are in a relatively stable form and are not easily released. However, changes in chemical conditions due to oxidation, such as a decrease in pH, an increase in the oxidation of binding minerals, and changes in chemical speciation, can disrupt the stability of metal bonds and increase the potential for their release [5], [6], [7].

In the pre-treatment process using H_2O_2, the oxidation reaction that takes place can trigger the transformation of metal-bearing minerals, such as the oxidation of sulfide minerals or the weathering of clay minerals. Fragmentation of the organic matrix can release metals that were previously bound in complex forms, thereby increasing their mobility. This condition is important to note, given that the release of major and trace elements has the potential to cause environmental impacts, especially if pre-treatment is applied in underground coal utilization schemes that interact directly with groundwater systems [8], [9].

Most previous studies have focused on the effect of hydrogen peroxide pre-treatment on changes in the organic structure of coal, increased reactivity, and its implications for the efficiency of the energy conversion process [3]. Studies that specifically examine changes in the content and behavior of major and trace elements during the pre-treatment stage are still relatively limited. Recent studies have begun to address this gap from complementary angles. Demonstrated that the distribution of trace elements in low-rank coal is strongly governed by their mineral carrier phase, providing a basis for interpreting element-specific responses to oxidative treatment [4]. Meanwhile, Li et al. showed that transition metals such as Zn and Co are released into the liquid fraction of H2O2-pretreated lignite and can subsequently influence microbial activity, indicating that H2O2 pre-treatment does mobilize trace metals in coal systems, though prior work has emphasized their biological rather than environmental significance [10]. The present study extends this line of research by applying a relative enrichment index (Δ%) as a rapid, low-cost screening method to identify major and trace elements most sensitive to H2O2-induced oxidation in low-rank coal, prior to more resource-intensive leaching evaluation. The approaches used are generally descriptive and do not make much use of quantitative methods to screen for metals that are most sensitive to oxidative conditions. However, not all metals in coal will respond to pre-treatment in the same way, so an initial selection method is needed to identify metals that are potentially problematic from an environmental perspective [11], [12].

Analysis of metal enrichment using relative indices (Δ%) is an effective approach for evaluating changes in metal content before and after pre-treatment [13]. This index allows quantitative comparison between the initial and final concentrations of a metal, thereby enabling the identification of metals that have undergone relative enrichment as a result of the oxidation process. Metals with positive and significant Δ% values can be considered to have undergone relative enrichment, indicating a change in distribution or release from the solid phase to a more easily mobilized phase. Conversely, a negative Δ% value indicates a relative decrease in concentration, which may be caused by the release of metals into the dissolved phase or the transformation of metal-bearing minerals. This approach is very useful as an initial screening stage before further analysis, such as leaching tests, which require more time and resource [14], [15].

The use of analytical techniques such as ICP-MS provides advantages in terms of sensitivity and accuracy in detecting various major and trace elements at low concentrations. By combining ICP-MS data and Δ% enrichment analysis, a more comprehensive picture of the metals most affected by oxidative pre-treatment can be obtained. This information is an important basis for evaluating the potential environmental risks that may arise from changes in metal behavior during the pre-treatment process [16].

The advanced stage of evaluating the behavior of identified metals through the leaching process is crucial for assessing environmental implications more realistically. The leaching process simulates the conditions of metal release into the liquid environment, particularly groundwater, which has the potential to occur in field applications. Metals that show high enrichment levels but have low mobility may not pose a significant risk, while metals with moderate enrichment but high solubility can be a serious source of contamination. The integration of enrichment analysis and leaching tests provides a more comprehensive risk assessment framework [17].

Based on these considerations, this study aims to identify major and trace elements affected during the pre-treatment of low-rank coal using hydrogen peroxide based on ICP-MS analysis, evaluate metal enrichment behavior using the Δ% index, and assess the environmental implications of the identified metals through a leaching approach. This integrated approach is expected to bridge the gap between studies on increasing coal reactivity and environmental safety aspects, thereby providing a more comprehensive scientific contribution. The results of this study are not only relevant in the context of optimizing low-rank coal pre-treatment, but also important as a basis for decision-making in the application of sustainable and environmentally friendly coal utilization technologies.

2. Methodology

This research method was designed to systematically evaluate the effect of hydrogen peroxide pre-treatment on major and trace element behavior in low-rank coal and its implications for environmental mobility potential. Coal samples were collected from an active coal exploration site in Busang Subdistrict, East Kutai Regency, East Kalimantan Province. Representative samples (approximately 1 kg) were collected from the field, combined into a single composite, and transported to the laboratory in Yogyakarta for preparation. The site is located at coordinates 0°52'09.27" N and 116°34'16.24" E (WGS 84), recorded using a Garmin GPSMAP 78 GPS unit. Seam depth and the number of sampling increments were not recorded in the field documentation and remain a limitation of the present dataset (see Limitations). Samples were air-dried in an oven following ASTM D3172 (2013), crushed using a jaw crusher, ground using a pulverizer, and sieved using a sieve shaker into three particle size fractions (40, 60, and 100 mesh) before pre-treatment. Proximate analysis (moisture, ash, volatile matter, fixed carbon) was conducted on the raw and pretreated coal on a dry basis (DB) to characterize the physical response of the coal to oxidative treatment. In the initial stage, representative samples were analyzed using ICP-MS to determine the total content of major and trace metals. The results of this initial characterization were used as a baseline for evaluating changes in metal content due to pre-treatment.

Oxidative pre-treatment was carried out using hydrogen peroxide solution with a concentration of 0% as a control and 3% as a treatment, at room temperature for 10 days without the addition of a catalyst. The 3% H2O2 concentration was prepared on a w/w basis, while the 0% control used distilled water under otherwise identical conditions. Each treatment was applied to coal samples at a liquid-to-solid ratio of 1:10 (mL/g), using 20 g of coal per 200 mL of solution, in a closed reactor at ambient laboratory temperature (approximately 25-30 degrees Celsius), without agitation or light exclusion. Each particle-size and treatment combination was analyzed as a single sample without replication, which is acknowledged as a limitation (see Limitations). Solution pH, total dissolved solids (TDS), and residual H2O2 concentration were monitored daily throughout the 10-day treatment period to track the progress of the oxidation reaction. Coal samples were prepared in particle size variations of 40, 60, and 100 mesh to assess the effect of surface area on metal content changes during the oxidation process. Changes in metal content were analyzed using the relative enrichment index (Δ%), which allowed quantitative identification of metals that experienced an increase or decrease in concentration after pre-treatment. The enrichment index (Δ%) was calculated using the following equation:

$$\Delta\% = \frac{C_{\text{after}} - C_{\text{before}}}{C_{\text{before}}} \times 100\% \qquad \ldots. (1)$$

Where C_jinbefore and C_after are the element concentrations (in mg/kg, dry-mass basis) in the coal solid residue before and after pre-treatment, respectively. Because losses of organic matter and soluble mineral fractions during oxidation reduce the total mass of the solid residue, all Δ% values reported in

this study represent relative changes in concentration within the residue and do not by themselves indicate absolute mass loss or gain of an element from the coal-water system.

As a partial, independent check on this limitation, ash content from the proximate analysis was used as an internal tracer to estimate bulk solid mass recovery, based on the standard assumption that ash-forming mineral matter is approximately conserved relative to the organic fraction during oxidation. Ash content (dry basis) increased from 2.37% before treatment to 2.67% at 40 mesh with 3% H_2O_2, 3.80% at 60 mesh with 0% H_2O_2, 4.16% at 100 mesh with 0% H_2O_2, and 5.05% at 100 mesh with 3% H_2O_2, while it changed only slightly to 2.36% at 60 mesh with 3% H_2O_2 and decreased to 1.21% at 40 mesh with 0% H_2O_2. Solid mass recovery was estimated as (Ash%before / Ash%after) x 100, yielding approximate values of 88.8%, 62.4%, 100.4%, 57.0%, and 46.9% for the conditions above, respectively. The 40 mesh, 0% H_2O_2 condition could not be estimated this way because ash content decreased rather than increased, indicating that some mineral matter was likely released together with the organic fraction under that condition, which violates the conserved ash assumption. This bulk estimate is not a substitute for a full element specific mass balance, since that would additionally require leachate concentrations for every element, which were only measured for Fe and Mn in this study.

A positive Δ% value indicates relative enrichment of the element in the solid residue, while a negative value indicates relative depletion in the residue. A negative Δ% is not by itself evidence of dissolution into the aqueous phase; that conclusion is drawn only where the element is independently confirmed in the leachate. Interpretation of concentration changes is based on the following categories: $\Delta\% > +50\%$ (high increase), +10% to +50% (moderate increase), -10% to +10% (little change), -10% to -50% (moderate dissolution), and $< -50\%$ (significant dissolution).

Elements identified as most sensitive to pre-treatment, particularly Fe and Mn, were further evaluated through a batch leaching test to assess their mobility into the aqueous phase. The coal residue from each pre-treatment condition was leached using 400 mL of distilled water per sample. Distilled water was added incrementally in 50 mL steps to a cumulative volume of 400 mL per sample, without mechanical agitation, at ambient laboratory temperature. Based on the initial 20 g coal mass used in pre-treatment, this corresponds to a nominal liquid-to-solid ratio of approximately 20:1 (mL/g), although the ratio relative to the actual post-pre-treatment residue mass was not separately verified. Leachate aliquots of 20 mL were withdrawn at cumulative volumes of 100, 200, 300, and 400 mL and filtered through Whatman No. 42 filter paper prior to analysis. Leaching contact time was not fixed but varied with particle size and H_2O_2 concentration, ranging from approximately 2 to 3.5 minutes at 40 mesh under 0% H_2O_2 to approximately 8 to 60 minutes at 40 mesh under 3% H_2O_2, based on the time required to complete each incremental addition. Eh was not measured, and no procedural blanks or replicate leaching runs were conducted; both are acknowledged as limitations. The resulting leachate was analyzed for pH, TDS, residual H_2O_2, and dissolved Fe and Mn concentrations using Atomic Absorption Spectrophotometry (AAS), following the standardized batch leaching principles described by Gao et al. [13]. Leachate results were compared against the Indonesian coal mining wastewater quality standard [18], with TDS additionally compared against Government Regulation No. 22 of 2021 [19].

For ICP-MS analysis, a 2 g coal sample was used per treatment condition, analyzed at the Integrated Laboratory of Universitas Pembangunan Nasional Veteran Yogyakarta. For AAS analysis of dissolved Fe and Mn in the leachate, samples were acidified to $pH < 2$ using HNO_3 to prevent precipitation and analyzed by flame AAS (acetylene-air flame) at the Integrated Laboratory of Universitas Islam Indonesia. Detailed digestion protocol, instrument calibration standards, procedural blanks, certified reference materials, and detection/quantification limits were not documented in the underlying study and are acknowledged as a limitation (see Limitations). Similar validation frameworks for multi-element ICP-MS analysis in aqueous and solid environmental matrices have been described by Kilic [20].

3. Results and Discussion

3.1 Identification of Major and Trace Elements During Pre-treatment

Identifying the composition of inorganic elements in low-rank coal is a fundamental step in understanding the potential for changes in geochemical behavior during the oxidative pre-treatment

process. This initial characterization provides information about the profile of major and trace elements contained in the coal matrix, which is then used as a reference in evaluating the extent to which oxidative treatment changes the distribution and mobility of these elements. The results of analysis using ICP-MS show that coal from the Busang area, East Kalimantan, contains various metal elements with varying concentrations.

The concentration of elements before pre-treatment is presented in Table 1, which shows that Fe is the dominant element with a concentration of more than 2,700 mg/kg, followed by Mg (469 mg/kg), Al (1,152 mg/kg), Na (146 mg/kg), and Ca (133 mg/kg). Transition metal elements such as Mn (44.9 mg/kg), Zn (46.3 mg/kg), Ni (17.2 mg/kg), Cu (3.0 mg/kg), and Co (4.6 mg/kg) were also detected in significant concentrations. The presence of rare earth elements (REE) such as Ce (0.76 mg/kg), La (0.28 mg/kg), Nd (0.30 mg/kg), Y (0.28 mg/kg), as well as other trace elements such as Sc (0.20 mg/kg), Li (0.25 mg/kg), Sr (10.3 mg/kg), and Cr (3.3 mg/kg) indicate the complexity of the mineral composition of low-rank coal.

Table 1. Concentration of Coal Elements Before Pre-treatment

No.	Element	Coal Before Treatment (mg/kg)	No.	Element	Coal Before Treatment (mg/kg)
1	Cd	0.133	21	Lu	0.004
2	Pb	1.781	22	Tm	0.004
3	Tl	0.016	23	Ho	0.011
4	Bi	0.071	24	Pr	0.072
5	Ag	0.034	25	Eu	0.044
6	Fe	2,782.566	26	Na	146.070
7	Mn	44.856	27	Mg	469.021
8	Cu	3.021	28	K	86.885
9	Zn	46.254	29	Ca	132.535
10	Co	4.603	30	B	17.477
11	Ni	17.216	31	Li	0.246
12	La	0.279	32	Al	1,152.301
13	Ce	0.759	33	Sc	0.202
14	Nd	0.297	34	Cr	3.348
15	Sm	0.070	35	Ga	0.300
16	Gd	0.096	36	Sr	10.320
17	Y	0.276	37	In	0.053
18	Dy	0.061	38	Ba	45.479
19	Er	0.036	39	Tb	0.012
20	Yb	0.027			

The dominance of Fe in the elemental composition of low-rank coal is a common characteristic associated with the presence of iron oxide and hydroxide minerals, as well as sulfide minerals such as pyrite (FeS_2) that are often associated with coal. These mineral-phase assignments are consistent with findings that different mineral carriers in low-rank coal host distinct groups of trace elements; for

instance, [21]. Reported that pyrite in Chinese low-rank coals preferentially hosts Cu, Zn, Tl, As, Cd, Sn, Ni, Sb, and Pb, while barite hosts Gd, Sr, Ba, Eu, and Bi, and Fe-bearing carbonates host Cr and Mo [4]. In the absence of direct mineralogical characterization (XRD or SEM-EDS) in the present study, these associations are presented as working hypotheses to guide interpretation of the elemental enrichment patterns observed. High concentrations of alkali and alkaline earth elements such as Mg, Na, Ca, and K indicate the contribution of clay and carbonate minerals in the coal matrix. Meanwhile, the presence of transition metals such as Mn, Zn, Cu, Ni, and Co may be related to isomorphous substitution in the mineral structure or complex bonding with the organic matrix of coal [22], [23].

The detected REE element profiles show a distribution pattern characteristic of low-rank coal, with a predominance of light rare earth elements (LREE) such as Ce, La, and Nd compared to heavy rare earth elements (HREE) such as Yb, Er, and Lu. This pattern is consistent with the geochemical characteristics of coal formed in a sedimentary environment with the influence of groundwater rich in dissolved elements. The presence of trace elements such as Sc, Li, Ga, and Cr also indicates the influence of clastic material sources and diagenesis processes during coal formation. This initial characterization is an important basis for understanding how oxidative pre-treatment changes the distribution and behavior of these elements. Not all detected elements will respond to pre-treatment in the same way, so identifying initial concentrations is crucial for evaluating changes caused by H_2O_2 exposure [3].

3.2 Major and Trace Element Enrichment Behavior Due to Pre-treatment

The behavior of inorganic elements during pre-treatment was evaluated by analyzing concentration changes using the relative enrichment index (Δ%). This approach enabled quantitative identification of elements that experienced concentration increases (enrichment) or decreases (depletion) due to the oxidative process. Changes in element concentrations for each variation in particle size (40, 60, and 100 mesh) and H_2O_2 concentration (0% and 3%) showed different patterns, reflecting the sensitivity of elements to oxidative conditions and the influence of particle surface area. The Δ% calculation results show that not all elements undergo changes in the same direction. Some elements show positive Δ% values, indicating relative enrichment in the solid residue, while other elements show negative Δ% values, indicating release into the dissolved phase. Based on the concentration change patterns, the elements can be classified into several behavior groups, as presented in Table 2.

Table 2. Classification of Elements After Pre-treatment (Reclassified)

No.	Group	Element Name	Description
1	Consistently mobile (negative Δ% in most/all conditions)	Fe, Mg, Al, Sc, Ga, Li, Na, Ce, In	These elements show negative Δ% in at least 5 of 6 tested conditions, indicating consistent release from the solid residue regardless of H2O2 concentration or particle size.
2	Conditionally mobile (positive Δ% at 0% H2O2, negative Δ% at 3% H2O2)	Mn, Co, Ni, Zn, Yb, Er, Nd, Gd, Sm, Dy, Tm, Ho, Tb, B, Ca, Pr, Y, Lu	These elements accumulate in the residue under the control condition and generally shift toward dissolution as H2O2 concentration increases from 0% to 3%, most consistently at 40 mesh; the pattern is only partially reproduced at 60 and 100 mesh for several elements in this group, so the 0%-to-3% shift should be read as a dominant tendency rather than a uniform response across all particle sizes.
3	Consistently retained (positive Δ% in most/all conditions)	Cd, Tl, Bi, Ag, Cu, Eu, K, Sr, Ba, Cr, La	These elements show positive Δ% in at least 4 of 6 tested conditions, indicating consistent accumulation in the solid residue.

Note: Pb does not fit consistently into any of the three groups above. Its Δ% is positive at 40 mesh and 100 mesh but negative at 60 mesh, under both H2O2 concentrations, indicating a particle-size-driven rather than oxidant-driven response. Ba shows one exception at 40 mesh under the control

condition (Δ% = -99.85%, in contrast to positive values at all other five conditions), which may reflect an isolated measurement artifact rather than a systematic pattern and is reported as observed.

This reclassification is based on the condition-specific Δ% values reported for all three particle sizes and both H2O2 concentrations (see Supplementary Table S1), and resolves the overlap present in the original five-group scheme. Elements in Group 1 have the highest and most consistent mobility potential and are the primary candidates for groundwater risk assessment. Group 2 elements are conditionally mobile and become relevant primarily under higher oxidant concentrations, which has direct implications for controlling H2O2 dosing in field-scale applications. Group 3 elements are more relevant to solid residue management and potential slag formation in downstream gasification, rather than to groundwater quality [14].

3.2.1 Elements Showing Relative Depletion in the Solid Residue

The group of elements showing relative depletion in the solid residue consists of two main categories: elements that are consistently soluble under all conditions, and elements whose solubility is enhanced by the presence of H_2O_2. The first category includes Mg, Al, Sc, Li, Na, Ga, and Ce, which show negative Δ% values in almost all treatment variations. Magnesium shows the most extreme solubility with Δ% values reaching -94.24% to -96.03%, indicating that almost all Mg in coal transfers to the dissolved phase during pre-treatment. Aluminum also shows significant dissolution with Δ% ranging from -34.16% to -85.06%, depending on the H_2O_2 concentration and particle size [8]. The extensive dissolution of alkali and alkaline earth elements such as Mg, Na, and Li is related to the transformation of their carrier minerals during oxidation. Carbonate and clay minerals, which are the main carrier phases of these elements, are susceptible to oxidative conditions and pH changes induced by H_2O_2. Mineral structure fragmentation and chemical weathering facilitate the release of these elements into the dissolved phase, thereby increasing their concentration in the leaching solution.

The second category includes transition metals such as Fe, Mn, Zn, Co, and Ni, which show high sensitivity to H_2O_2 concentrations. Iron shows a very clear pattern of change, where at 0% H_2O_2 conditions, the Δ% value ranges from -23.65% to -39.18%, but at 3% H_2O_2 conditions, solubility increases dramatically to -51.24% to -77.06%. A similar pattern is also shown by Mn, which under some 0% H_2O_2 conditions still shows positive enrichment (Δ% +41.71% to +57.91%), but turns negative under 3% H_2O_2 conditions with Δ% values reaching -29.19% [5]. The increase in Fe and Mn solubility at higher H_2O_2 concentrations can be explained through the redox oxidation mechanism. Hydrogen peroxide acts as an oxidizer that converts Fe(II) into Fe(III); however, Fe(III) does not necessarily remain in solution, as it commonly hydrolyzes and precipitates as iron hydroxide depending on solution pH and the availability of complexing ligands [24]. Under the acidic conditions observed during pre-treatment (pH 3.3-4.2 at 3% H2O2, monitored daily during the 10-day pre-treatment), Fe(III) hydrolysis is expected to be limited, favoring the retention of dissolved iron in solution rather than immediate precipitation. In addition, Fe and Mn can act as catalysts in the decomposition of H2O2 into hydroxyl radicals (•OH) through Fenton-type reactions, which is consistent with the acid-generating oxidation mechanisms described for pyrite and other sulfide minerals in acid mine drainage systems [25], further accelerating oxidative reactions and the release of metals from the coal matrix [26].

Zinc, cobalt, and nickel also showed a trend consistent with increased mobility under stronger oxidative conditions, based on solid-phase Δ%; unlike Fe and Mn, this trend was not independently confirmed by leachate analysis for these three elements. Zn, which showed minimal change (Δ% -12.60% to +8.14%) under 0% H_2O_2 conditions, experienced more significant dissolution at 3% H_2O_2 with a Δ% of -28.99% at 60 mesh, although at 100 mesh Zn showed a positive Δ% of +28.53% under 3% H_2O_2, indicating that the mobilization response is not uniform across particle sizes. Cobalt and nickel showed a similar pattern, where dissolution increased with increasing H_2O_2 concentration. This behavior indicates that transition metal elements are bound in a relatively stable mineral phase under normal conditions but are susceptible to further oxidation induced by H_2O_2 [10]. The high mobility of these elements is an important concern from an environmental perspective. Elements such as Fe and Mn, although essential, can cause water quality problems when dissolved in high concentrations, including changes in color, taste, and disruption of water distribution systems. Meanwhile, trace elements such as Zn, Co, and Ni

have the potential for toxicity at certain concentrations and can disrupt aquatic ecosystems when accumulated in groundwater systems [11].

Based on Table 1, coal before pre-treatment contained Fe at 2,782.6 mg/kg and Mn at 44.9 mg/kg. Among all the elements analyzed, iron (Fe) and manganese (Mn) showed the most significant response to oxidative pre-treatment using hydrogen peroxide. The magnitude of these Δ% responses, which predominantly reflect relative depletion rather than retention in the solid matrix, confirms that Fe and Mn are highly sensitive to chemical changes during oxidative pre-treatment.

3.2.2 Behavior of Elements that did not undergo Significant Mobilization

Unlike the group of elements that are easily mobilized, several elements tend to remain in the solid phase or even increase in relative concentration in the residue. This group includes Ag, Bi, Tl, K, Ba, Sr, Cu, Eu, Cd, and several REE elements such as La and Nd. Silver shows extreme enrichment with a Δ% value of +301,141.64% under conditions of 40 mesh with 0% H_2O_2, indicating a very significant accumulation in the solid residue. Bismuth also shows high enrichment with Δ% reaching +3,496.15%, while Tl reaches +973.60%. These extreme percentage values should be interpreted with caution, as elements such as Ag, Bi, and Tl were present at low absolute concentrations before treatment (0.034, 0.071, and 0.016 mg/kg, respectively), so small analytical fluctuations near the detection limit can translate into very large relative changes. In the absence of procedural blank data and certified reference material recovery for this dataset, these values are reported as observed but should not be over-interpreted mechanistically until confirmed by repeat analysis. This extreme enrichment does not reflect the absolute addition of elements to the system, but is a phenomenon of relative enrichment that occurs due to a reduction in the total mass of the residue. During pre-treatment, organic and easily soluble mineral components undergo degradation and release, thereby reducing the total mass of solids. Relatively stable and insoluble elements become more concentrated in the remaining residue, resulting in high positive Δ% values. This interpretation is supported by an ash-tracer estimate of bulk solid mass recovery (see Methodology), which indicates that the solid residue retained roughly 47% to 100% of its original mass across most treatment conditions. A residue mass loss in this range is sufficient to account for much of the extreme positive Δ% observed for low-concentration elements such as Ag, Bi, and Tl through simple concentration in a smaller remaining mass, without requiring absolute accumulation of these elements in the system.

Potassium showed a consistent enrichment pattern across all treatment variations, with Δ% values ranging from +166.76% to +562.81%. The increase in K concentration in the residue is related to the transformation of feldspar and mica minerals, which are the main K-bearing phases in coal. Although some K can be released during pre-treatment, the dissolution rate of K-bearing minerals is lower than that of other alkali-bearing minerals, so K tends to accumulate in the residue. REE elements such as La, Nd, Sm, Eu, and some HREE exhibit mixed behavior depending on the pre-treatment conditions. Under 0% H_2O_2 conditions, most REE show positive enrichment or minimal change, but under 3% H_2O_2 conditions, some REE undergo more significant dissolution. Europium is an exception, consistently showing positive enrichment under almost all conditions with Δ% ranging from +32.74% to +85.99%. Eu's unique behavior is related to its ability to form stable complexes with the organic matrix of coal and its resistance to mild oxidation [14].

From an environmental perspective, elements that accumulate in residues pose a low risk of direct mobilization to groundwater quality. However, the presence of elements such as Tl, Cd, and Ag in high concentrations in solid residues still needs to be considered in the context of solid waste management and the potential for long-term release through other mechanisms such as volatilization at high temperatures or residue erosion [27].

3.2.3 Environmental Implications Based on the Leaching Process

The environmental implications of changes in element behavior during pre-treatment were evaluated by interpreting mobilization patterns in the context of groundwater quality. Enrichment analysis results showed that elements with significant negative Δ% values are candidates for further dissolution screening. Among these, Fe and Mn were confirmed present in the leachate through AAS analysis and

are therefore discussed here as elements with demonstrated mobility, while other depleted elements (Mg, Al, Zn, Ni, Co) remain candidates for mobility pending equivalent leachate confirmation. Iron and manganese showed the most sensitive response to oxidative conditions, with a very significant increase in solubility at higher H_2O_2 concentrations. High concentrations of Fe and Mn in groundwater can cause aesthetic and operational problems, including water discoloration, sediment formation, and disruption of piping systems. Although not toxic at low concentrations, the accumulation of Fe and Mn in water systems can disrupt ecological balance and reduce water quality for various uses [28].

Direct leachate analysis using AAS confirmed the presence of dissolved Fe and Mn following pre-treatment. The pre-treatment solution itself remained acidic throughout the 10-day process, with pH ranging from 4.00-4.11 under 3% H2O2 treatment, while TDS increased to more than 3,000 mg/L by the final day at 60 mesh particle size, and residual H2O2 remained above 1% even after 10 days. Comparison with the Indonesian coal mining wastewater quality standard (Permen LHK No. 5 Tahun 2022) and TDS standard (PP No. 22 Tahun 2021) showed that subsequent leaching was highly effective at reducing TDS, with removal effectiveness exceeding 90% and resulting concentrations below the applicable standard. Manganese removal effectiveness also remained below the standard threshold across all particle sizes tested. Iron removal effectiveness, however, varied by particle size: at 40 and 60 mesh, effectiveness reached only 25.2% and 11.3%, respectively, exceeding the permissible standard, while at 100 mesh effectiveness reached 30.4% and fell below the standard. Solution pH remained acidic (below 6) after leaching across all conditions, which does not meet the applicable water quality standard. These results indicate that while the leaching process is effective at removing bulk dissolved solids and Mn, residual acidity and incomplete Fe removal, particularly at coarser particle sizes, represent the primary environmental risk factors requiring control if this pre-treatment process is applied at field scale.

Magnesium and aluminum, although relatively common elements in natural water systems, can cause problems when dissolved in high concentrations. Dissolved aluminum can be toxic to aquatic organisms at certain pH levels, while high Mg can contribute to increased water hardness. Alkali elements such as Na and Li also show a solid-phase depletion trend consistent with high mobility, which could affect the salinity and chemical characteristics of groundwater if confirmed. Trace elements such as Zn, Ni, and Co, which show a similar depletion trend under oxidative conditions, remain candidates for further mobility assessment pending leachate confirmation, and are more critical elements from an environmental toxicity perspective if that mobility is confirmed. Although these elements are essential at low concentrations, concentrations exceeding threshold levels can have toxic effects on aquatic organisms and potentially enter the food chain. The mobility of these elements during pre-treatment indicates the need for control of operational conditions to minimize release into the environment [29], [30].

In the context of applying Subsurface Cultivation and Gasification (SCG) technology or other methods of subsurface coal, the mobilization of these elements is a serious concern. The SCG system involves the injection of oxidants and the interaction of fluids with in-situ coal, which has the potential to produce geochemical conditions similar to the pre-treatment tested in this study [8]. If the process is not properly controlled, the release of major and trace elements into the aquifer can occur on a significant scale. The results of this study provide a basis for the initial identification of risk elements that need attention in environmental impact assessments. Elements such as Fe, Mn, Zn, Ni, and Co, which show high mobility during pre-treatment, are priority candidates for further evaluation through leaching tests that simulate actual release conditions into water systems. The integration of enrichment analysis and leaching tests will provide a more comprehensive risk assessment framework to support decision-making in the application of sustainable and environmentally friendly coal utilization technologies [31], [32].

It should be noted that the present findings are derived from a 10-day, room-temperature, bench-scale batch experiment, and direct extrapolation to field-scale aquifer conditions requires caution, as actual SCG operations involve different pressure, temperature, residence time, and groundwater flow conditions that were not simulated in this study.

This study has several limitations that should be considered when interpreting the results. First, precise sampling coordinates, seam depth, and the number of sampling increments were not recorded during

field collection. Second, mineralogical characterization (XRD or SEM-EDS) was not performed, so phase associations discussed in this study remain interpretive hypotheses rather than confirmed assignments. In addition, only proximate analysis (moisture, ash, volatile matter, fixed carbon) was performed; ultimate analysis and total sulfur content were not determined for the coal samples in this study. Third, detailed analytical QA/QC parameters, including digestion protocol, instrument model, certified reference materials, procedural blanks, matrix spikes, and detection/quantification limits, were not documented for the ICP-MS and AAS analyses in the underlying study, and could not be reconstructed retrospectively; this is acknowledged as a limitation rather than resolved in the present manuscript. Fourth, a complete element-specific mass balance (initial elemental mass versus mass recovered in residue plus leachate) was not established for any element, because leachate concentrations were measured only for Fe and Mn rather than the full element suite; Δ% values for other elements should therefore be interpreted as relative changes in the solid residue rather than confirmed absolute transfers to the aqueous phase. An ash-tracer estimate of bulk solid mass recovery (Methodology; Results, Section 3.2.2) provides partial support for this interpretation but is not a substitute for a full element-level mass balance.

Data availability. The ICP-MS and AAS datasets generated and analyzed during this study are available from the corresponding author upon reasonable request.

4. Conclusion

Pre-treatment of low-rank coal using hydrogen peroxide has been shown to affect the geochemical behavior and redistribution of major and trace elements. Identification based on ICP-MS analysis before and after pre-treatment shows that elemental concentrations undergo significant redistribution, exhibiting either relative depletion or enrichment as a direct response to oxidative conditions. Fe and Mn are the elements most sensitive to hydrogen peroxide pre-treatment. Elements such as Zn, Co, Ni, Mg, and Al show relative depletion in the solid residue under oxidative conditions and remain candidates for further mobility assessment pending leachate confirmation, while K, Ba, Sr, Cu, and Eu tend to accumulate in solid residues. The enrichment index ($\boldsymbol{\Delta}\%$) is effectively used as a screening tool to identify major and trace elements that are environmentally relevant. Leachate analysis confirmed that Fe and Mn, the two elements most responsive to $\mathbf{H_2O_2}$ pre-treatment, were mobilized into the aqueous phase. Manganese concentrations remained below the applicable mining wastewater quality standard (Permen LHK No. 5/2022), whereas Fe exceeded the permissible limit at 40 and 60 mesh particle sizes. The persistence of acidic pH after leaching further indicates that control of pre-treatment conditions, particularly particle size and $\mathbf{H_2O_2}$ concentration, is important to minimize the risk of groundwater contamination.

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Supplementary Table S1. Condition-Specific Enrichment Index (Δ%) Values for All Elements Across Particle Sizes and H2O2 Concentrations

Element	40 mesh 0% H2O2	40 mesh 3% H2O2	60 mesh 0% H2O2	60 mesh 3% H2O2	100 mesh 0% H2O2	100 mesh 3% H2O2
Cd	+194.06	+40.27	+97.27	+27.03	+110.71	+99.51
Pb	+52.38	-10.01	-13.25	-31.01	+136.78	+290.73
Tl	+973.60	+153.30	+341.15	+85.79	+219.38	+85.88
Bi	+3496.15	+101.39	+436.98	+69.41	+173.89	+55.96
Ag	+301141.64	+2069.65	+9527.87	+1754.23	+2789.71	+1309.52
Fe	-38.55	-77.06	-39.18	-52.46	-23.65	-51.24
Mn	+46.44	-29.19	+41.71	-27.82	+57.91	-8.52
Cu	+85.95	+22.26	+39.64	+61.35	+212.05	+100.84
Zn	+8.14	-16.03	-12.60	-28.99	+7.64	+28.53
Co	+49.31	-24.33	+40.75	-13.85	+41.36	-9.15
Ni	+25.62	-20.69	+25.52	-10.39	+41.40	+1.35
La	+4.56	-2.20	-1.67	+6.56	+22.71	+23.11
Ce	-22.90	-30.08	-27.14	-20.33	-6.56	-7.38
Nd	-4.92	-16.10	-11.59	-7.80	+12.41	+9.64
Sm	+14.59	-19.45	-15.00	-17.70	+9.93	+5.69
Gd	-2.37	-23.73	-17.35	-16.12	+11.56	-0.85
Y	-3.81	-27.27	-6.50	-16.53	+21.29	+7.31
Dy	+9.65	-24.61	-10.84	-15.50	+18.65	+6.89
Er	+22.25	-34.91	-15.66	-27.13	+7.43	-5.74
Yb	+62.20	-17.74	+11.20	-2.46	+39.16	+20.65
Lu	+401.94	-4.52	+55.60	+7.26	+59.64	+28.82
Tm	+334.91	-13.77	+31.69	-8.02	+41.88	+11.47
Ho	+135.89	-12.53	+9.53	-4.80	+30.96	+16.29
Pr	+15.23	-13.46	-5.98	-8.04	+15.14	+11.87
Eu	+85.99	+32.74	+51.59	+39.09	+62.03	+58.41
Na	-16.86	-35.90	-24.18	-16.69	+2.90	-24.27
Mg	-94.24	-96.03	-93.15	-95.37	-90.70	-94.42
K	+505.55	+184.48	+497.59	+166.76	+562.81	+256.25
Ca	+27.04	-0.05	+12.10	-21.60	+39.93	+61.73
B	+37.80	-45.60	-25.72	+37.64	-23.45	-47.60
Li	+67.98	-70.42	-37.56	-67.28	-41.47	-68.07
Al	-34.16	-85.06	-34.26	-78.34	-20.23	-61.69
Sc	-12.97	-64.83	-28.75	-55.86	-14.37	-41.73
Cr	+4.35	-16.72	+46.88	+31.11	+291.70	+123.62
Ga	-22.06	-56.41	-30.71	-47.84	-12.18	-37.32
Sr	+33.35	-6.29	+25.77	-9.40	+39.71	+13.87
In	+166.26	-32.12	-5.84	-35.98	-24.28	-38.47
Ba	-99.85	+30.99	+47.36	+33.00	+54.17	+41.50
Tb	+104.11	-24.52	-6.63	-16.64	+16.05	+5.05

Note: Values are relative enrichment index (Δ%) in the solid residue, calculated as (C_after - C_before)/C_before x 100%. Positive values indicate relative enrichment in the residue; negative values indicate relative depletion in the residue (see Methodology for full interpretation).