Mineral Evolution and Elemental Migration During Reductive Bayer Digestion of Guinea Bauxite

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Abstract

Bauxite residue is an alkaline solid waste produced during alumina extraction, characterized by its significant volume and low utilization rate, which poses a serious threat to both the ecological environment and the safety of human lives and property. The reductive Bayer digestion process facilitates the source reduction of bauxite residue, enhancing opportunities for its value-added utilization while simultaneously improving the alumina extraction rate. The TESCAN Integrated Mineral Analyzer (TIMA), a comprehensive mineral analysis system, enables the quantitative assessment of the physical properties and chemical composition of various minerals present in ores. This study utilizes TIMA as the primary tool to characterize the mineral composition and elemental distribution of Guinea high-iron bauxite and reductive Bayer bauxite residue, incorporating analyses of chemical composition, particle size, and mineral phases. In Guinea bauxite, gibbsite predominantly occurs in close association with Al-goethite, while rutile/anatase and ilmenite are distributed stellately within the matrix comprised of gibbsite, Al-goethite, and hematite. Following the reductive Bayer digestion process, Aluminous Goethite is transformed into hematite, while titanium minerals remain diffusely distributed among the iron minerals. Notably, the relative content of titanium in rutile/anatase and ilmenite shifts from 75.31 % and 24.69 to 26.95 % and 73.05 % respectively, compared to the unprocessed bauxite. The Guinea bauxite is notably rich in iron (Fe), vanadium (V), titanium (Ti), and rare earth elements, with vanadium, titanium, and cerium co-enriched in rutile/anatase and ilmenite. Some of the valuable elements maintain their original mineralization during the reductive Bayer digestion process, with their concentrations further enhanced. This study provides essential data on mineral evolution and elemental migration during the reductive Bayer digestion process to the Guinea bauxite.

Key words Guinea bauxite, Bauxite residue, Reductive Bayer digestion, Mineralogy, Critical metals.

1. Introduction

Bauxite residue is a substantial solid waste generated from the alumina production process, characterized by high alkalinity, fine particle size, and a complex mineral composition [1, 2], along with a significant quantity of iron, titanium, and rare earth elements [3–5]. To achieve complete extraction of alumina, the current high-temperature Bayer digestion process typically adds 3 to 10 % lime to eliminate titanium mineral blockages [6]. However, the substantial addition of lime not only increases bauxite residue output but also raises costs and complicates the subsequent utilization of bauxite residue. To address this issue, Wang et al. [7–9] have proposed a reductive Bayer digestion process that mitigates titanium mineral blockages by incorporating a small quantity of additives, thereby increasing the digestion rate of alumina.

Guinea bauxite is a high-iron gibbsitic bauxite ore with proven reserves of 7.4 Gt [10, 11]. It is characterized by a single layer thickness ranging from 3 to 9 meters and is typically found in open, gently undulating upland areas, often covered by shrubby vegetation, making it suitable for open-pit mining [10]. Generally, the alumina content in Guinea bauxite ranges from 40 to 60 % and silica content from 0.5 to 6 %, with concentrated mineral reserves [12, 13]. Notably, more than 10 % of the Al_2O_3 present in the ore exists as insoluble aluminum minerals, such as Al-goethite [2], which results in a lower alumina extraction rate. As the port-based alumina industry continues to expand, Guinea's bauxite imports are on the rise.

To elucidate the mineral composition of Guinea bauxite and bauxite residue, researchers have conducted a series of studies. Moussa et al. [10] performed petrological, mineralogical, and geochemical investigations on bauxite ores from the Kindia region of Guinea. Their findings revealed that the primary components of the ores are gibbsite and Al-goethite, with minor quantities of anatase, rutile, diaspore, and kaolinite, alongside significant enrichments of titanium (Ti), gallium (Ga), chromium (Cr), and heavy rare earth elements. Zainudeen et al. [14] conducted a comparative analysis of the mineralogical and chemical compositions of ores from major bauxite-exporting countries in Africa. The TESCAN Integrated Mineral Analyzer (TIMA) system [15], is capable of quantitatively resolving the mineral embedding forms, as well as analyzing the elemental distribution within both bauxite and bauxite residue [16, 17]. Chen et al. examined the distribution of lithium (Li) in bauxite with TIMA and discovered that it is primarily enriched in clay minerals. Additionally, Luo et al. [18] investigated bauxite in Guizhou Province, China, and found that rare earth elements are predominantly distributed in the form of phosphates within monazite, hematite, and anatase. These studies demonstrate that TIMA not only assesses the physical properties of target minerals but also characterizes valuable metals and their relative concentrations, offering robust support for element extraction.

The application of the reductive Bayer digestion process further enriches the valuable elements in Bauxite residue [19]; however, mineralogical studies of reductive Bayer digestion bauxite residue remain relatively scarce. This study employs the TIMA as the primary research tool to analyze the mineral composition and elemental distribution of Guinea bauxite and reductive Bayer digestion bauxite residue. The research aims to describe the changes in mineral species and elemental distribution resulting from the reductive Bayer digestion process, thereby supplying critical data to facilitate the large-scale economic utilization of bauxite residue.

2. Experimental

2.1 Materials

The Guinea bauxite and bauxite residue utilized in the experiments were sourced from an alumina plant in Shandong. The bauxite ore was crushed using a jaw crusher, while the bauxite residue underwent a washing process with hot water to eliminate any attached alkali. Subsequently, the bauxite residue was dried in preparation for mineralogical characterization.

2.2 Characterization

Mineralogical analyses of the ore and bauxite residue were conducted utilizing a TIMA-X integrated mineral analysis system (Tescan, Czech Republic). Samples were embedded in resin, followed by polishing and carbon spraying. The phase composition was analyzed using a D/Max 2500VB X-ray diffractometer (Rigaku, Japan) with a copper target, scanning at a speed of 8°/min over a range of 5° to 80°. The particle size was assessed using a BT-9300ST laser particle sizer (Dandong Baxter Instrument Co., Ltd., China). Micro-morphological analyses were performed with a Mira3 LMH high- and low-vacuum scanning electron microscope and complemented by a One Max20 X-ray energy spectrometer (Tescan, Czech Republic). The concentrations of major elements were determined using a Pro X inductively coupled plasma optical emission spectrometer (Thermo Fisher Scientific, USA), while sodium oxide (Na_2O) content was measured using a TAS-990 atomic absorption spectrophotometer (Beijing Pudian General Instrument Co., Ltd., China).

3. Results and Discussion

3.1 Mineralogical Analysis of Guinea Bauxite

Table 1 presents the chemical composition of Guinea bauxite, characterized by high iron content (Fe_2O_3: 26.02 %), low silica levels (SiO_2: 2.48 %), and a high alumina-silica ratio (A/S: 17.65). Additionally, the ore exhibits significant concentrations of rare earth elements, as well as valuable elements such as vanadium and gallium, which may become concentrated during the alumina extraction process. Figure 1 displays the XRD pattern of Guinea bauxite, highlighting its principal components: gibbsite, Al-goethite, and hematite, alongside minor amounts of boehmite, anatase, rutile, kaolinite, and quartz. The diffraction peak intensity of Al-goethite is higher than that of hematite, indicating that both Al-goethite and hematite serve as the primary iron-bearing minerals present in bauxite.

Table 1 Main chemical composition of Guinea bauxite.

	Al_2O_3	Fe_2O_3	SiO_2	TiO_2	V_2O_5
wt.%	43.77	26.02	2.48	2.12	0.09
	CaO	Sc_2O_3	Y_2O_3	CeO_2	Ga_2O_3
Ppm	1438	35	30	52	94

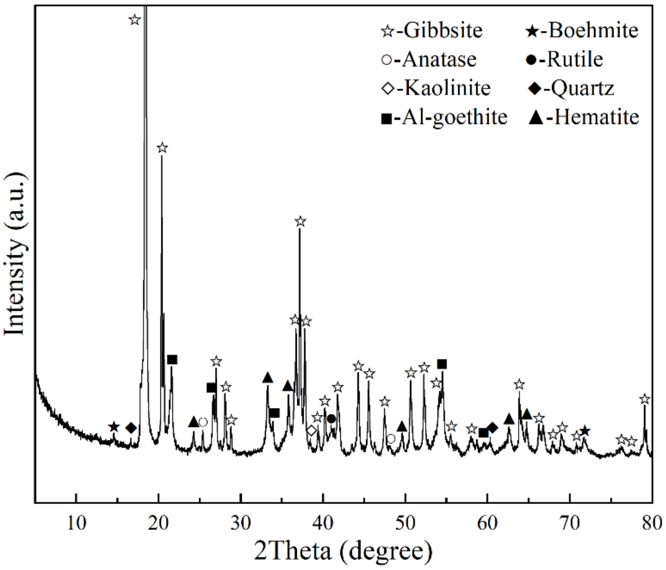
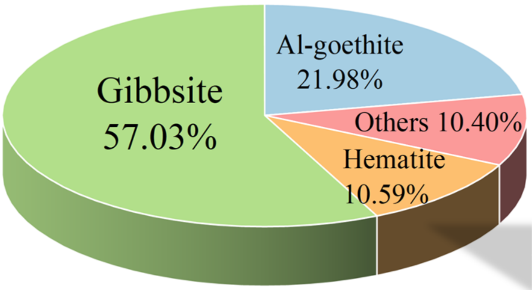


Figure 1. XRD pattern of Guinea bauxite.

The Mineral properties module in the TIMA system can effectively quantify the mineral content of the bauxite. Figure 2 illustrates the proportions of various minerals present, with gibbsite, Al-goethite, and hematite comprising 57.03 %, 21.98 %, and 10.59 %, respectively. Additionally, goethite constitutes 2.76 % of the total bauxite, while the titanium minerals rutile/anatase and ilmenite account for 1.38 % and 0.91 %, respectively. Since rutile and anatase have the same chemical composition, no distinction is made in TIMA. Quartz and kaolinite are the primary silica-containing minerals, representing 1.44 % and 1.66 % of the ore, respectively. Their SiO_2 content is, however, lower than that indicated by chemical analysis. This discrepancy may be attributed to the fine particle sizes of certain silica-containing minerals, which fall below the detection accuracy of the TIMA analysis.



Others	wt.%
Goethite	2.76
Rutile/Anatase	1.38
Boehmite	1.68
Kaolinite	1.66
Ilmenite	0.91
Quartz	1.44
Zircon	0.57

Figure 2. Percentage of major minerals in Guinea bauxite (wt.%).

To elucidate the mineral embedding relationships within Guinea ore, the bauxite samples selected for this study were solely crushed using a jaw crusher, thereby preserving the original embedding characteristics of the ore as much as possible. Utilizing an automatic mineral analysis system, various minerals in the bauxite were identified, as illustrated in Figure 3. Figures 3(a-b) depict representative ore particles, while Figs. 3(c-f) present localized magnifications of these particles. In general, the ore contains a significant amount of Al-goethite in addition to gibbsite and hematite, with these minerals banded around the gibbsite. The hematite particles are relatively intact, though fine iron mineral particles are present where they interface with Al-goethite. From Figures. 3(c-d), it is evident that rutile/anatase and ilmenite are arranged in a stellate pattern within the mineral matrix of gibbsite, suggesting gradual reactivity with the sodium aluminate solution during the digestion process. The hematite matrix in Figure 3(d) contains some titanium minerals and goethite. Finally, Figure 3(f) illustrates a close nesting of Al-goethite, hematite, and gibbsite, alongside minor distributions of goethite, titanium minerals, and boehmite.

The application of automated mineral analysis facilitates the quantitative characterization of the associations between different minerals. This process is based on the collection and counting of pixel points representing the overlapping areas of two minerals, which are then normalized to determine the percentage of each mineral associated with a specific counterpart, as presented in Table 2. The percentage of free particles is relatively low due to the absence of further milling of the ore. Gibbsite is primarily associated with Al-goethite and rutile/anatase, while its association with hematite accounts for only 5.2 %. The Al-goethite is mainly embedded with gibbsite and hematite, comprising 50.86 % and 33.89 % of its associations, respectively. The primary minerals associated with hematite are goethite and Al-goethite; however, given the low content of goethite, this indicates a significant presence of large grains of monomer-dissociated hematite. Goethite is predominantly embedded within hematite, while titanium minerals are mostly associated with gibbsite, Al-goethite, and hematite. Notably, the highest association rates of two silica-bearing minerals—kaolinite and quartz—occur with Al-goethite. The pronounced association between kaolinite and quartz further emphasizes this relationship.

To accurately evaluate the digestion properties of Guinea bauxite and achieve complete extraction of aluminum minerals, it is essential to study the distribution of critical elements among the different minerals. Figure 4 illustrates the distribution of aluminum (Al), silicon (Si), iron (Fe), and titanium (Ti) across various minerals using the Elemental deportment module. Approximately 10.42 % of the aluminum content is found in the form of Al-goethite, which poses challenges for extraction during the low-temperature Bayer process. Additionally, aluminum constitutes 3.50 % in boehmite and 1.73 % in kaolinite. The aluminum substitution coefficient can be calculated to be around 0.33 based on the aluminum content in Al-goethite ($Fe_{1-x}Al_xO\cdot OH$). Silicon is predominantly found in quartz, kaolinite, and zircon, accounting for 58.06 %, 32.22 %, and 9.72 %, respectively. In terms of iron, Al-goethite contains a higher concentration than hematite, comprising 49.78 % and 40.69 %, respectively. Lastly, titanium is primarily distributed between rutile/anatase and ilmenite, accounting for 75.31 % and 24.69 %, respectively.

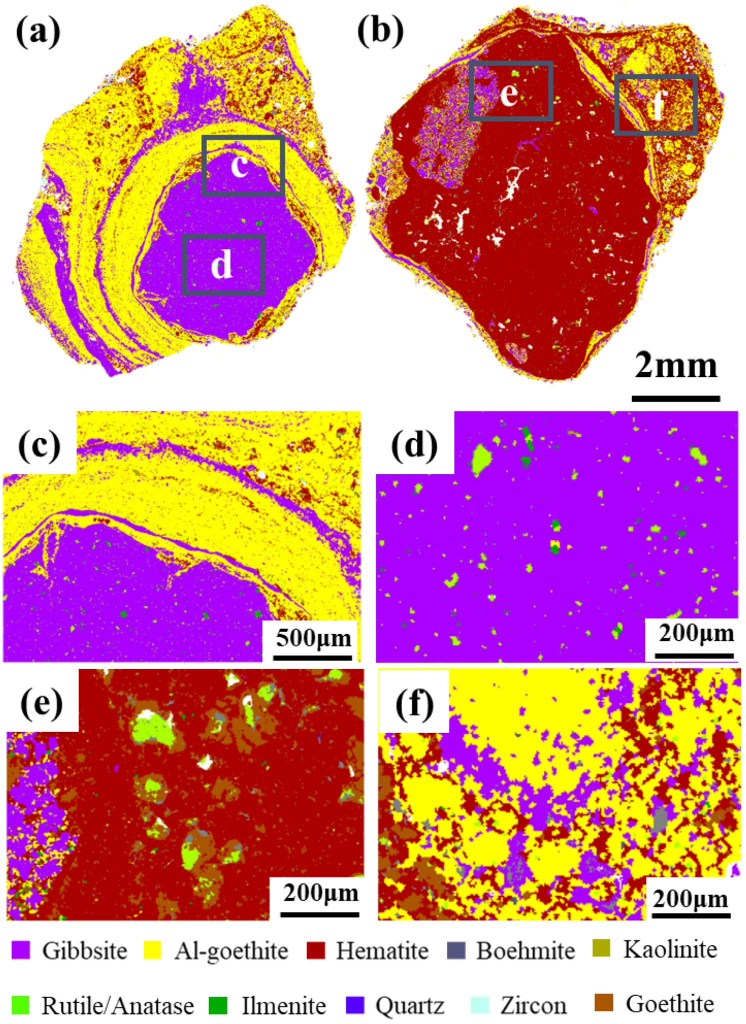


Figure 3. TIMA identification and map-scanning of the main minerals in Guinea bauxite.

Table 2. Mineral association in the Guinea bauxite.

	Gibbsite	**Al-goethite**	**Hematite**	**Goethite**	**Rutile/ Anatase**	**Boehmite**	**Kaolinite**	**Quartz**	**Ilmenite**
Gibbsite	/	50.86	4.99	1.05	35.92	49.55	13.64	5.40	31.55
Al-goethite	65.67	/	27.29	5.30	29.45	35.66	41.77	32.63	28.66
Hematite	5.20	33.89	/	86.67	17.02	1.77	16.74	5.23	20.06
Goethite	0.17	0.93	61.17	/	8.96	0.11	1.32	0.89	5.06
Rutile /Anatase	20.45	8.72	4.56	5.99	/	3.74	10.10	16.74	12.28
Boehmite	6.49	2.33	0.08	0.02	1.20	/	5.67	3.88	1.81
Kaolinite	0.49	1.25	0.69	0.12	1.09	4.52	/	30.40	0.27
Quartz	0.02	0.40	0.02	0.01	0.78	1.06	8.11	/	0.04
Ilmenite	1.17	0.72	0.99	0.48	1.96	0.66	0.32	0.14	/
Free particles	0.35	0.92	0.22	0.37	3.61	2.92	2.32	4.96	0.27
Total	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00

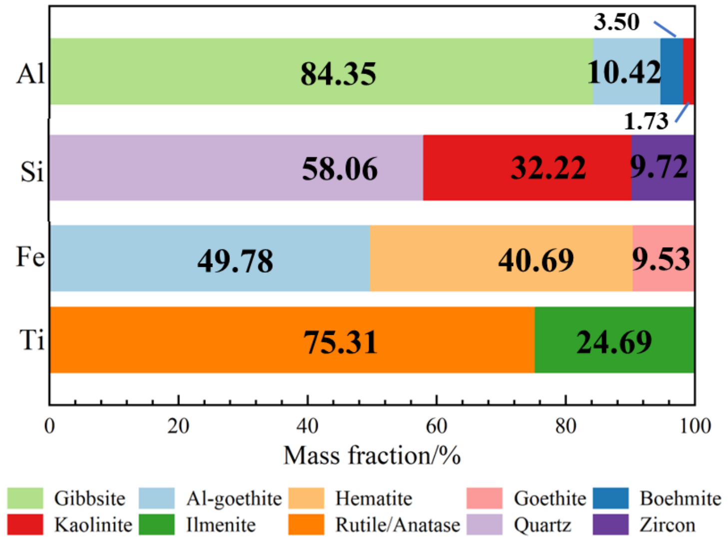


Figure 4. Distribution of Al, Si, Fe, Ti elements in different minerals.

Figure 5 presents the energy spectra of selected elements in bauxite, revealing similar distribution characteristics as observed from the map-scanning results. Aluminum and iron are the predominant elements in bauxite. Titanium primarily exists in the form of rutile/anatase and ilmenite, associated with gibbsite and Al-goethite. Additionally, titanium (Ti), vanadium (V), and cerium (Ce) are co-enriched in rutile/anatase and ilmenite. Elements such as hafnium (Hf), calcium (Ca), tantalum (Ta), and germanium (Ge) are found to be more abundant in iron and titanium minerals than in gibbsite. In contrast, scandium (Sc) and yttrium (Y) are more diffusely distributed among the bauxite minerals, posing challenges for the observation of their enriched phases at lower concentrations.

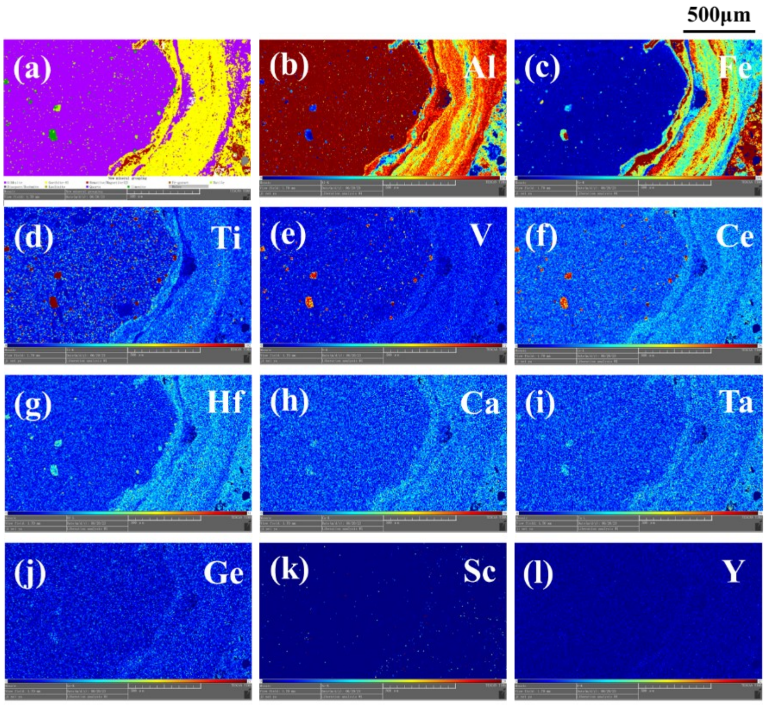


Figure 5. Map-scanning of selected elements in bauxite.

3.2 Mineralogical Analysis of Reductive Bayer Bauxite Residue

The reductive Bayer digestion process eliminates the need for lime addition, instead employing a minimal quantity of additives to regulate the digestion potential. This approach prevents the blockage of alumina extraction by titanium minerals, significantly enhances the conversion of Al-goethite to hematite, and improves the overall digestion rate [8]. The chemical composition of the reductive Bayer bauxite residue, which contains 73.18 % Fe_2O_3, is presented in Table 3. Meanwhile, the valuable elements such as scandium (Sc) and vanadium (V) in the bauxite residue have been further enriched. Figure 6 displays the XRD pattern of the reductive Bayer bauxite residue, which reveals a straightforward phase comprising primarily hematite, cancrinite, and small quantities of Al-goethite. Based on a Na_2O/SiO_2 mass ratio of 0.55, it can be inferred that the primary compositions of sodium aluminosilicate are $Na_2O·Al_2O_3·1.7SiO_2·2H_2O$ and $Na_2O·Al_2O_3·2SiO_2·2H_2O$.

Table 3 Chemical composition of reductive Bayer bauxite residue (wt.%).

wt.%	Fe_2O_3	Na_2O	Al_2O_3	SiO_2	TiO_2	CaO
	73.18	3.45	6.74	6.25	5.82	0.27
ppm	Sc_2O_3	V_2O_5	Y_2O_3	CeO_2		
	86	2107	71	101		

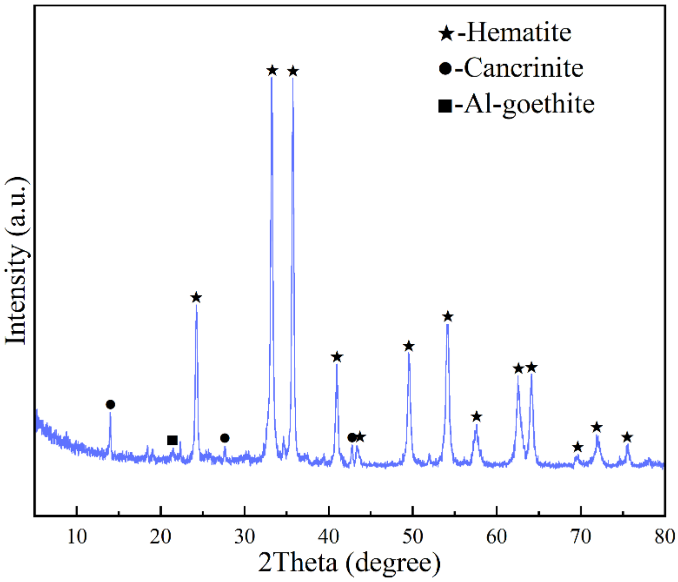


Figure 6. XRD pattern of reductive Bayer bauxite residue.

To investigate the mineral embeddedness in bauxite residue, representative particles were selected from a total of 2000 bauxite residue particles utilizing the Particle Viewer module of TIMA, as depicted in Figure 7a. The bauxite residue contains a large number of monolithic dissociated hematite particles and some surface-bound aluminosilicate minerals, such as cancrinite ($Na_2O·Al_2O_3·1.7SiO_2·2H_2O$) and hydrogarnet ($3CaO·Al_2O_3·xSiO_2·(6\text{-}2x)$ H2O). Additionally, some unreacted titanium minerals and Al-goethite are associated with hematite. Large-sized cancrinite is also present in the bauxite residue, enabling more efficient separation from iron minerals during the sorting process. Figure 7b depicts a partial enlargement of the reductive Bayer bauxite residue sample, revealing fine particles of iron minerals and cancrinite.

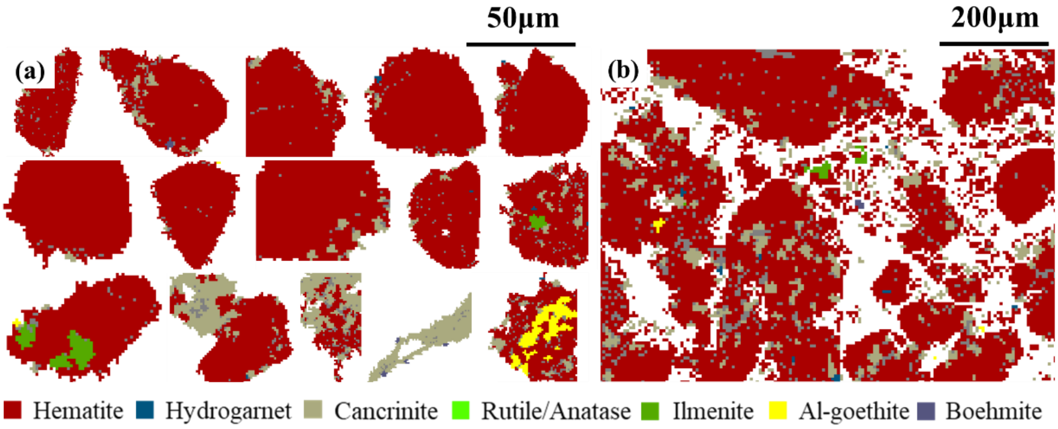


Figure 7. Representative particles (a) and partial enlargement area (b) of the reductive Bayer bauxite residue sample.

To perform a quantitative analysis of the mineral content and elemental distribution in bauxite residue, the mineral composition of the reductive Bayer bauxite residue is detailed in Table 4. Hematite constitutes over 70 % of the bauxite residue, corroborating the findings from the chemical composition analysis. The silicon-bearing mineral present in bauxite residue is predominantly cancrinite, comprising 17.96 % of the total composition. Titanium minerals primarily occur in the forms of rutile/anatase and ilmenite, with titanium content from ilmenite accounting for 73.05 % an that from rutile/anatase accounting for 26.95 %. Compared to bauxite, the titanium minerals formed during the reductive Bayer digestion process exhibit interactions with iron minerals, resulting in titanium-iron compounds. These findings align with previously reported literature data [9, 20].

Table 4 Mineral composition of reductive Bayer bauxite residue (wt.%).

Minerals	Minerals Contents (Reductive)
Hematite	74.31
Cancrinite	17.96
Al-goethite	2.80
Hydrogarnet	0.33
Boehmite	0.16
Ilmenite	3.39
Calcite	0.03
Rutile	1.02
Sum	100.00

The reductive Bayer digestion process eliminates the need for lime addition, thereby achieving a reduction in the source of bauxite residue while ensuring the digestion of aluminum minerals. To investigate the reaction behavior of elements during the digestion process, Figure 8 presents the energy spectra of selected elements in the bauxite residue. The mineral distribution in Figure 8(a) reveals several primary phases, including hematite in red, rutile/anatase in light green, ilmenite in dark green, and cancrinite in gray. Almost all iron in the digested bauxite residue is contained within hematite, while the primary minerals, Al-goethite and goethite, predominantly transform into hematite. Although cancrinite typically exhibits a fine grain size, some individual particles display a coarser grain size. Furthermore, titanium (Ti), vanadium (V), and cerium (Ce) remain co-enriched in rutile/anatase and ilmenite minerals, indicating that V and Ce did not undergo significant migration or transformation during the reductive Bayer digestion process.

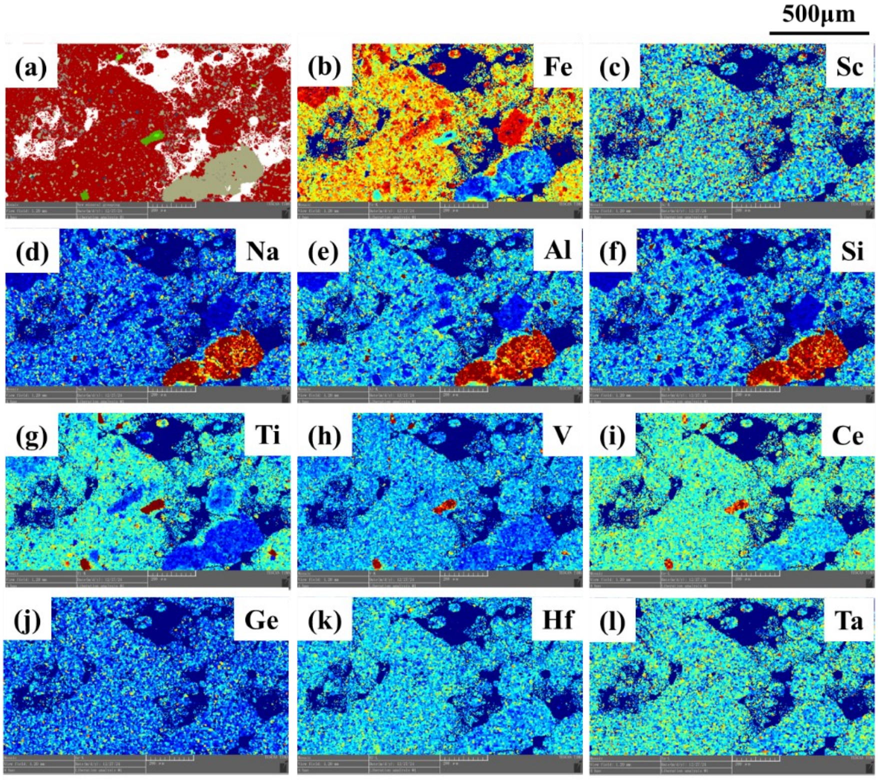


Figure 8. Map-scanning of reductive Bayer bauxite residue.

4. Conclusions

In this study, TIMA served as the primary analytical tool to characterize and analyze the minerals and elements present in bauxite and bauxite residue during the Bayer digestion process. The conclusions are as follows:

1. The principal phases in the Guinea bauxite include gibbsite, Al-goethite, and hematite, which account for 57.03 %, 21.98 %, and 10.59 %, respectively. Al-goethite and rutile/anatase are found embedded in both the periphery and interior of the ore, with hematite also embedded alongside Al-goethite. The ore is notable for its richness in rare earth elements, and vanadium (V) and cerium(Ce) are identified within rutile/anatase and ilmenite.

2. The main phases of reductive Bayer bauxite residue consist of hematite and cancrinite, along with small amounts of ilmenite, rutile/anatase, and unreacted Al-goethite. Cancrinite and various fine-grained iron minerals are interspersed, while titanium minerals are predominantly embedded within the iron mineral matrix.

3. Reductive Bayer bauxite residue shows an increased concentration of valuable elements, including vanadium (V) and cerium (Ce) in the rutile/anatase and ilmenite phases. Specifically, the distribution of titanium in the reductive Bayer bauxite residue is 26.95 % in rutile/anatase and 73.05 % in ilmenite.

5. Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

6. Acknowledgement

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