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Influence of Na_2CO_3 and K_2CO_3 Addition on Iron Grain Growth during Carbothermic Reduction of Red Mud

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Abstract: Red mud is a by-product of alumina production from bauxite ore by the Bayer method, which contains considerable amounts of valuable components such as iron, aluminum, titanium, and scandium. In this study, an approach was applied to extract iron, i.e., carbothermic reduction roasting of red mud with sodium and potassium carbonates followed by magnetic separation. The thermodynamic analysis of iron and iron-free components' behavior during carbothermic reduction was carried out by HSC Chemistry 9.98 (Outotec, Pori, Finland) and FactSage 7.1 (Thermfact, Montreal, Canada; GTT-Technologies, Herzogenrath, Germany) software. The effects of the alkaline carbonates' addition, as well as duration and temperature of roasting on the iron metallization degree, iron grains' size, and magnetic separation process were investigated experimentally. The best conditions for the reduction roasting were found to be as follows: 22.01% of K_2CO_3 addition, 1250 °C, and 180 min of duration. As a generalization of the obtained data, the mechanism of alkaline carbonates' influence on iron grain growth was proposed.

Keywords: red mud; bauxite residue; reduction roasting; sodium carbonate; potassium carbonate; iron grain growth; magnetic separation; recycling; utilization

1. Introduction

Alumina production by the Bayer process generates a considerable amount of highly alkaline solid waste called the bauxite residue or red mud. Depending on the composition of bauxite ore and the technology used, production of one ton of alumina can generate from 0.9 to 1.5 tons of red mud [1,2]. The global bauxite residue stock grows annually and was reported to have reached approximately 4.6 billion tons in 2018 [3], including about 600 million tons in Russia [4]. This waste is typically stored in special sludge dumps [5], which leads to misuse of large land areas and to an increase of the aluminum cost. Red mud is a hazardous material because of high alkalinity, the fineness of mud

particles, and the significant content of toxic elements [6]. Storage of bauxite residue leads not only to ground and surface water pollution, but also, it can cause a discharge of red mud due to sludge dump destruction [7–9].

Many researchers have made efforts to develop a cost efficient and environmentally friendly method of bauxite residue recycling. Different applications of red mud are known, for example, in the construction industry [10–14], in catalytic processes [15], as an adsorbent [16,17], for extraction of valuable components [18–20], and others.

Red mud contains many valuable elements such as Fe, Al, Ti, and Sc, but the Fe content is highest and can reach 45% [21], so the development of a robust and cost efficient method of iron extraction is still the aim of many studies. The most common ways of iron extraction are reduction smelting at 1450–1650 °C and reduction roasting at 1050–1200 °C followed by magnetic separation of reduced iron [22]. Reduction roasting is more economically viable than reduction smelting because it consumes less energy. However, the magnetic separation of iron obtained after reduction roasting of red mud at a temperature range of the solid-phase reaction has a low efficiency due to a very small size of iron grains attached to calcium aluminosilicate phases [23]. Many authors showed that addition of sodium salts promotes the iron grain growth during carbothermic reduction, for example for limonite ($\text{FeO}(\text{OH}) \cdot n\text{H}_2\text{O}$) [24], titanomagnetite ($\text{Fe}^{2+}(\text{Fe}^{3+}, \text{Ti})_2\text{O}_4$) [25], siderite (FeCO_3) [26], and nickeliferous laterite ($(\text{Fe}, \text{Ni})\text{O} \cdot \text{OH}$) [27] ores. It was reported [28–37] that the addition of sodium salts such as sodium sulfate (Na_2SO_4), sodium carbonate (Na_2CO_3), and sodium tetraborate ($\text{Na}_2\text{B}_4\text{O}_7$) also improves the segregation of metallic iron during the carbothermic reduction of red mud. The addition of Na_2SO_4 during the carbothermic reduction of high phosphorus oolitic hematite ore promotes iron (II) sulfide' (FeS) generation [38], which increases the sulfur content in the metallic concentrate, so the use of sodium sulfate is less desired compared with other sodium salts.

It is well known that the chemical properties of potassium are similar to sodium, and potassium has a higher chemical activity than sodium. Therefore, potassium carbonate (K_2CO_3) can also probably promote iron grain growth during the carbothermic reduction of red mud.

In this study, we compared the influence of Na_2CO_3 and K_2CO_3 additions on iron recovery and iron grain growth during the carbothermic reduction of red mud using thermodynamic analysis and laboratory experiments. The effects of temperature and carbothermic reduction roasting duration, as well as the amount of alkaline carbonate additions on metallization degree and large sized iron particles' fraction were studied. Magnetic separation of the reduced samples was carried out to find out the roasting parameters for gangue–grain output. Thus, the desirable conditions of reduction roasting to recover iron from red mud were determined, and the mechanism of alkaline carbonates' influence on iron grain growth was proposed.

2. Materials and Methods

2.1. Raw Materials

The original red mud was taken from Ural Aluminum Plant (Russia, Kamensk-Uralsky, 56.302094° N 61.981120° E). To study and compare the influence of Na_2CO_3 and K_2CO_3 additions on iron grain growth during the carbothermic reduction of red mud, and initially present sodium was removed by leaching with a lime slurry in a glass reactor at 90 °C for 3 h [39]. The chemical composition was analyzed by an X-ray fluorescence spectrometer AXIOSmax Advanced (PANalytical, Almelo, the Netherlands). Table 1 shows the chemical composition of red mud. The X-ray diffraction (XRD) patterns were obtained by a ULTIMA IV diffractometer (Rigaku, Tokyo, Japan) using $\text{Cu-K}\alpha$ radiation. The phase composition was determined by Match! Software (Crystal Impact, Bonn, Germany) [40]. Figure 1 shows the XRD pattern of red mud with the identified phases. Long flame coal containing 15% of ash and 18% of moisture was used as a reductant. The additives were chemically pure reagents of Na_2CO_3 and K_2CO_3 . Red mud, coal, and additives were ground and sieved up to the particle size of less than 0.2 mm.

Table 1. Chemical composition of red mud (wt.%) from Ural Aluminum Plant (Russia, Kamensk-Uralsky).

Fe ₂ O ₃	SiO ₂	Al ₂ O ₃	TiO ₂	CaO	MgO	MnO	Na ₂ O	P ₂ O ₅	S	Sc	LOI
36.9	8.71	11.8	3.54	23.8	1.01	0.95	0.27	0.42	0.14	0.008	12.46

Figure 1. The XRD pattern of red mud from Ural Aluminum Plant (Russia, Kamensk-Uralsky).

2.2. Thermodynamic Calculation

The equilibrium calculations were carried out by HSC Chemistry 9.98 software (Outotec, Pori, Finland) [41] at 25–1100 °C in a nitrogen atmosphere at atmospheric pressure for 100 kg of red mud; the species with small fractions were excluded from the calculation. Based on the elemental and phase compositions, the following red mud composition was used: 29.89% Fe₂O₃; 7.80% FeOOH; 21.76% Ca₃Al₂Si₃O₁₂H₁₂; 5.55% Ca(OH)₂; 6.02% CaTiO₃; 15.61% CaCO₃; 10.53% Al(OH)₃; 0.59% CaSO₄; 1.01% MgO; 0.27% Na₂O; 0.97% P₂O₅. The carbon to red mud ratio was 1:2, so the carbon amount was 50 kg.

Thermodynamic calculation of the liquid phase amount was performed using FactSage 7.1 software (Thermfact, Montreal, Canada; GTT-Technologies, Herzogenrath, Germany) [42] with the FToxide database for iron-free red mud with K₂O or Na₂O addition to the following composition: 17.48% SiO₂; 23.69% Al₂O₃; 7.11% TiO₂; 47.78 CaO; 2.03% MgO; 1.91% MnO.

2.3. Experimental Procedure

Before the reduction roasting, the red mud and alkaline carbonates were dried at 105 °C in an air oven for 2 h. Then, the dried red mud and additives were mixed up in a V-shell blender for 24 h. The amounts of the additions were selected so that after conversion of carbonates into oxides, their amounts corresponded to 2.5, 5, 7.5, and 10 wt.% of sodium oxide and to 3, 6, 9, 12, and 15 wt.% of potassium oxide, respectively. The pellets from the mixed powders were obtained using a hand hydraulic press N3630A (Nordberg, Hunan, China): 1 g of the prepared mixtures was added into the mold of 17 mm in diameter and compacted with a pressure of 215 MPa.

The pellets were then placed into a corundum crucible 62 mm high and 45 mm in diameter filled up with coal in a way to prevent the pellets from touching each other. Then, to increase the reducing agent potential, the crucible was sealed, turned upside down, and placed into another corundum crucible 68 mm high and 58 mm in diameter, which was also half-filled with coal.

The carbothermic reduction experiments were carried out in a muffle furnace at the temperature range of 1000–1350 °C. The crucibles with the pellets were placed into the preheated furnace. After roasting, the reduced samples were taken out and quenched into liquid nitrogen to prevent secondary oxidation of iron. The temperature was set by a microprocessor automatic controller using an S-type Pt/Pt-Rh thermocouple.

To analyze the roasted samples chemically, they were ground and sieved to a size less than 0.05 mm. The content of the total iron was determined by an atomic absorption spectrometer AA240FS (Varian Inc., Palo Alto, Santa Clara, CA, USA). The content of metallic iron in the samples was determined using the potassium dichromate titration method according to the Russian State Standard GOST-23581.11-79.

The Mössbauer analysis was performed using a spectrometer MS-1104Em (ZAO Kordon, Rostov-on-Don, Russia) at room temperature. The ^{57}Co nuclei with 47 mCi activity in a Rh matrix were used as the source. The Mössbauer spectra were processed using SpectrRelax 2.4 software (Lomonosov MSU, Moscow, Russia) [43].

2.4. Iron Grain Size Calculation

The microstructure of the reduced samples was observed on the polished sections by reflected light using a METAM LV-34 (LOMO-Mikrosistemy, Saint Petersburg, Russia) optical microscope. Photomicrographs were obtained in 250× magnification. After that, 16 photomicrographs were combined (stitched) and then used for image analysis. Image Pro Plus software (Media Cybernetics, Rockville, MD, USA) was applied to analyze the images and to calculate the sizes of the iron grains. The average Feret diameter in all directions was used as a characteristic of the average grain size. The Feret diameter is the distance between two parallel lines that bound an object perpendicular to a certain direction. Grains with size less than 0.2 µm were neglected from the calculation.

2.5. Magnetic Separation

Magnetic separation was carried out by dry method. Reduced samples were ground and sieved to a size less than 0.054 mm. After separation, the magnetic and non-magnetic fractions were weighted and analyzed for iron content. The iron metallization, yield of magnetic concentrate, and iron recovery indexes in the magnetic fraction were calculated as follows [31]:

$$\eta = \beta/\alpha \times 100\% \quad (1)$$

where η is the iron metallization ratio, %; α the total iron content of the reduced sample, %; and β the metallic iron content of the reduced sample, %;

$$\gamma = m_1/m_0 \times 100\% \quad (2)$$

where γ is the yield of magnetic concentrate, %; m_0 the feed mass of reduced sample subjected to magnetic separation, g; m_1 the mass of obtained magnetic concentrate, g;

$$\varepsilon = \gamma \times (\lambda/\alpha) \times 100\% \quad (3)$$

where ε is the recovery of iron, %; λ the total iron content of magnetic concentrate, %.

3. Results

3.1. Thermodynamic Calculations

3.1.1. Thermodynamic Analysis of the Carbothermic Reduction of Iron in Red Mud

It can be seen from Figure 1 (XRD results) that the main iron containing phases of red mud were hematite (Fe_2O_3) and goethite (FeOOH). Goethite decomposes into hematite directly at about 300 °C [44], so the carbothermic reduction process occurred as the following chemical reactions:

It should be noted that Boudouard–Bell reaction regenerates carbon monoxide above 700 °C [45], so Reaction (6) was actually a total reaction of the following interactions:

Figure 2 shows the equilibrium amounts of iron containing phases as a function of the roasting temperature during the carbothermic reduction of red mud. It can be seen that full reduction of iron into the metallic form according to Reactions (3)–(11) was possible above 710 °C. However, a previous experimental study [33] pointed out that a high iron metallization degree after the carbothermic reduction of red mud can be achieved only at temperatures above 1050 °C.

Figure 2. Effect of the temperature on the equilibrium amount of iron phases.

3.1.2. Thermodynamic Analysis of the Influence of K_2CO_3 and Na_2CO_3 on the Carbothermic Reduction Process

Figure 3 shows the effect of Na_2CO_3 addition on the equilibrium behavior of iron-free phases at 1100 °C. It indicates that an increase of Na_2CO_3 content lead to a decrease of gehlenite ($2CaO \cdot Al_2O_3 \cdot SiO_2$), an increase of Ca_3SiO_5 , $3CaO \cdot 2SiO_2$, and also the formation of sodium phases such as $Na_2O \cdot Al_2O_3$ and $Na_2O \cdot SiO_2$. These processes can be described by the following chemical reactions:

Figure 3. Effect of Na_2CO_3 addition on the equilibrium amounts of different phases at 1100 °C.

Figure 3 demonstrates that a high amount (>16 wt.%) of sodium carbonate addition led to the formation of $Na_2O \cdot Al_2O_3$ according to Reaction (13) without gehlenite formation. The authors in [46,47] showed that the formation of the sodium aluminate instead of gehlenite during roasting of red mud improved aluminum extraction by soda and carbonate leaching. However, Na_2CO_3 addition over 18 wt.% led to the formation of the sodium metasilicate according to Reaction (15).

Figure 4 shows the effect of K_2CO_3 on the equilibrium amounts of different phases at 1100 °C. It can be seen that an increase of K_2CO_3 content either led to a decrease of gehlenite or to an increase of Ca_3SiO_5 . It should be noted that to obtain $KAlO_2$, it is necessary to add a higher amount of K_2CO_3 than Na_2CO_3 to obtain sodium aluminate. $KAlO_2$ formation can occur according to the following reaction:

It can be seen from Figure 4 that, if K_2CO_3 was added, phosphorus remained in apatite. The chemical behavior of other elements during the carbothermic reduction of red mud with K_2CO_3 addition was similar to their behavior with Na_2CO_3 addition.

Figure 4. Effect of K_2CO_3 addition on the equilibrium amounts of different phases at 1100 °C.

3.1.3. Thermodynamic Simulation of the Liquidus Temperatures in the Red Mud- Na_2O and Red Mud- K_2O Systems

Figure 5 shows the effects of Na_2O and K_2O addition on the liquid phase amount of red mud. The small amount of liquid phase in red mud without carbonate additions appeared only around 1250 °C. Increasing of carbonates' addition led to smoother growth of the liquid phase amount. Below 1200 °C, the addition of 10% Na_2O had the most significant effect on the amount of the liquid phase and the solidus temperature (about 1160 °C). The addition of 15% K_2O also led to the appearance of the liquid phase below 1200 °C, but a lesser amount.

Figure 5. Effect of Na_2O and K_2O addition on the liquid phase amount of iron-free components of red mud.

3.2. Experimental Results of Iron Reduction

3.2.1. The Effects of the Roasting Temperature and Duration Time on the Iron Metallization Degree

Figure 6 shows the influence of the roasting temperature and duration on the iron metallization degree for red mud without carbonate additions. The presented data indicated that the first 20 min

of the roasting was sufficient to metallize more than 78% of the iron in the temperature range of 1000–1200 °C. After that, the metallization degree grew slowly and remained in the range of 78–90%. An increase of temperature also promoted the iron metallization process insignificantly.

Figure 6. Effects of the roasting temperature and duration on the iron metallization degree of red mud (accuracy of measurements is 1%).

3.2.2. The Effects of Na_2CO_3 and K_2CO_3 Additions on the Iron Metallization Degree

Figure 7 shows the influence of Na_2CO_3 and K_2CO_3 additions to red mud on the iron metallization degree at 1000 and 1200 °C. All the curves have minima at 4–8 and at 10–13 wt.% addition for K_2CO_3 and Na_2CO_3 , respectively. Subsequent increasing of carbonate amounts approximately increased the iron metallization degree to the values obtained for the samples without carbonate addition. To determine all of the iron-containing phases present in the reduced samples unambiguously, the Mössbauer spectroscopy method was used. Figure 8 shows the obtained Mössbauer spectra of the reduced samples with and without additions of alkaline carbonates. Table 2 provides the spectra parameters and iron phase distribution.

Figure 7. Effect of Na_2CO_3 and K_2CO_3 addition on iron metallization degree (accuracy of measurements is 1%).

Figure 8. Mössbauer spectra of the samples roasted 60 min at 1200 °C without additions (a), 12.83% Na₂CO₃ (b), and 8.8% K₂CO₃ (c). The experimental spectra (black); α -Fe sextet (red); α -Fe_{1-x}A_x sextets (green); θ -Fe₃C sextet (blue); χ -Fe₅C₂ sextet (cyan); FeC doublet (orange); γ -Fe-C doublet (gray); FeP₂ singlet (violet).

The obtained data pointed out that the iron containing phases of all the samples were qualitatively almost similar. It can be seen that the major iron containing phase in all the samples was α -Fe [48]. The sextets of α -Fe_{1-x}A_x had slightly different parameters compared to the α -Fe sextet and probably corresponded to iron atoms with an inhomogeneous surrounding that was characteristic of iron alloys [49,50]. Evidently, these sextets described α -Fe with dissolved elements in it. The singlet denoted as γ -Fe-C refers to γ -Fe [51], which is a face centered-cubic phase of metallic iron stable normally above 910 °C. Apparently, the roasting conditions promoted the formation of γ -Fe, and dissolved carbon can stabilize this austenite structure [52]. All the samples contained the sextets with parameters similar to the cementite phase θ -Fe₃C [53,54]. The samples with a lower degree of metallization (see Figure 7) also had another sextet, which probably refers to χ -Fe₅C₂ [55]. In addition, it should be noted that these samples had also higher carbide content. Furthermore, it is possible that the carbide sites included also some phosphides due to the similarity of spectra parameters [56]. It may be assumed that the doublet denoted as Fe-C corresponded to either low iron containing carbon clusters [57] or high carbon austenite [58], and another doublet adequately matched with iron phosphide FeP₂ parameters.

Thus, the Mössbauer analysis showed that the carbothermic reduction roasting of red mud led to almost full metallization of iron. Subtle differences in the iron metallization degree obtained by Mössbauer spectroscopy and the potassium dichromate titration method were probably due to the partial indissolubility of iron carbides, while using the Russian State Standard GOST-23581.11-79 developed for iron ores, concentrates, and direct reduction pellets.

Table 2. Mössbauer spectra parameters and iron phase distribution of the samples roasted 60 min at 1200 °C (at.%).

Roasting Charge	Phase	δ , (mm/s)	ε , (mm/s)	Γ_{exp} , (mm/s)	H_{eff} , (kOe)	S, (at. %)
Red mud without additions	α -Fe	0.01			331.4	63.1
	α -Fe _{1-x} A _x (1)	0.03			304.6	9.6
	α -Fe _{1-x} A _x (2)	0.05	−0.01	0.37	277.7	4
	α -Fe _{1-x} A _x (3)	0.06			250.9	1.9
	α -Fe _{1-x} A _x (4)	0.08			224.1	0.8
	θ -Fe ₃ C	0.01	−0.08	0.31	190.3	4.5
	FeC	0.02	0.30	0.22	-	2.9
	γ -Fe-C	−0.08	-	0.31	-	9.6
	FeP ₂	0.00	0.85	0.22	-	1.9
Red mud + 12.83% Na ₂ CO ₃	α -Fe	0.00			332.0	42.1
	α -Fe _{1-x} A _x (5)	0.02	0.01	0.36	308.2	6.9
	α -Fe _{1-x} A _x (6)	0.03			284.5	3.1
	α -Fe _{1-x} A _x (7)	0.04			260.8	2.4
	θ -Fe ₃ C	0.19	0.01	0.57	187.8	37.9
	χ -Fe ₅ C ₂	0.14	−0.01	0.57	109.0	2.8
	FeC	0.01	0.35	0.30	-	1.2
	γ -Fe-C	−0.14	-	0.30	-	3.2
	FeP ₂	−0.01	0.85	0.30	-	0.4
Red mud + 17.1% Na ₂ CO ₃	α -Fe	0.01			331.2	63.8
	α -Fe _{1-x} A _x (8)	0.04	0.00	0.35	306.7	8.7
	α -Fe _{1-x} A _x (9)	0.07			282.1	4.1
	α -Fe _{1-x} A _x (10)	0.10			257.5	3.3
	θ -Fe ₃ C	0.13	−0.04	0.43	194.4	11.4
	FeC	0.02	0.27	0.24	-	2.6
	γ -Fe-C	−0.08	-	0.24	-	3.7
	FeP ₂	0.01	0.84	0.24	-	2.3
Red mud + 8.8% K ₂ CO ₃	α -Fe	0.01			332.0	42.5
	α -Fe _{1-x} A _x (11)	0.04	−0.01	0.37	304.9	7.1
	α -Fe _{1-x} A _x (12)	0.07			277.8	4.0
	α -Fe _{1-x} A _x (13)	0.10			250.7	2.1
	θ -Fe ₃ C	0.17	0.00	0.60	188.1	24.7
	χ -Fe ₅ C ₂	0.15	−0.05	0.60	113.4	2.0
	FeC	0.01	0.32	0.25	-	5.7
	γ -Fe-C	−0.08	-	0.31	-	10.9
	FeP ₂	−0.00	0.83	0.25	-	1.0
Red mud + 22.01% K ₂ CO ₃	α -Fe	0.00			330.1	82.8
	α -Fe _{1-x} A _x (14)	0.02			302.6	5.4
	α -Fe _{1-x} A _x (15)	0.04	0.00	0.29	274.1	1.9
	α -Fe _{1-x} A _x (16)	0.05			245.5	0.9
	α -Fe _{1-x} A _x (17)	0.07			217.0	0.4
	θ -Fe ₃ C	0.07	−0.07	0.26	191.6	5.2
	Fe-C	0.01	0.32	0.26	-	0.5
	γ -Fe-C	−0.1	-	0.26	-	1.3
	FeP ₂	0.01	0.85	0.26	-	2.4

δ , chemical shift; ε , quadrupole shift; Γ_{exp} , line width; H_{eff} , magnetic field; S, site area.

3.3. Experimental Results of Iron Grain Growth

3.3.1. The Effects of Na₂CO₃ and K₂CO₃ Addition and Temperature on the Iron Grain Growth

Figure 9 shows the influence of temperature and the amount of alkaline additions on iron grain growth. Grains with a size of 1–5 μ m represented the reduced iron particles with the biggest part of the relative area.

Figure 9. Effect of Na₂CO₃ addition at 1000 °C (a), 1100 °C (c), and 1200 °C (e) and K₂CO₃ addition at 1000 °C (b), 1100 °C (d), and 1200 °C (f) on the size of iron grains after 60 min of roasting.

After roasting at 1000 °C, only the samples with 17.1% Na₂CO₃, as well as 4.4%, 13.2%, and 17.61% K₂CO₃ had iron grains with a size over 40 μm. An increase of roasting temperature up to 1100 °C had an insignificant effect on the grain size distribution. The influence of alkaline additions at 1200 °C was similar compared to 1000 °C and 1100 °C, but there was a slight increase of the grain fraction above 40 μm. In general, the effect of Na₂CO₃ and K₂CO₃ addition on the iron grain growth after 60 min of the roasting was insignificant.

3.3.2. The Effect of Roasting Time on the Iron Grain Growth

Figure 10 shows the influence of roasting time on the iron grains' growth with the addition of 17.1% Na_2CO_3 and different temperatures.

Figure 10. Effect of roasting time on size of iron grains with addition of 17.1% Na_2CO_3 : (a) 1000 °C; (b) 1100 °C; (c) 1200 °C.

An increase of roasting time in the temperature range of 1000–1100 °C led to the growth of the iron grains, but the size of iron grains obtained without addition of Na_2CO_3 was larger or slightly different compared with the size of iron grains obtained with 17.1% Na_2CO_3 addition. An increase of roasting time at 1200 °C led to the opposite effect on the iron grain growth. The iron grain size in the samples with the addition of 17.1% Na_2CO_3 after 120 and 180 min of roasting was significantly larger compared with the samples without additions. An increase of roasting time from 120 to 180 min led to increasing the amount of iron grains above 40 μm from 28% to 52%.

Figure 11 demonstrates that an increase of temperature above 1200 °C after 180 min of the roasting with the addition of 17.1% Na_2CO_3 had an insignificant effect on the iron grain size.

Figure 12 shows the influence of roasting time on the iron grains' growth with the addition of 22.01% K_2CO_3 at different temperatures. In the samples with K_2CO_3 obtained at 1000 °C, an increase of the roasting time led to iron grain growth compared with the sample without K_2CO_3 addition (Figure 12a). On the contrary, at 1100 °C, the iron grains' size in the samples without alkaline additions after 120 and 180 min of roasting was considerably larger compared with the sample with the addition of K_2CO_3 (Figure 12b). The influence of roasting time at 1200 °C and 22.01% K_2CO_3 was similar to its

influence for 17.1% Na_2CO_3 addition, but the iron grain size in the sample with K_2CO_3 addition was significantly smaller than in the sample with Na_2CO_3 addition and was less than 27% (Figure 12c).

Figure 11. Effect of temperature at the addition 17.1% of Na_2CO_3 and 180 min roasting time on the size of iron grains.

Figure 12. Effect of roasting duration on the size of iron grains with the addition of 22.01% K_2CO_3 at 1000 °C (a), 1100 °C (b), and 1200 °C (c).

Figure 13 shows that iron grains dramatically grew after 180 min of roasting at 1250 °C of the sample with 22.01% K_2CO_3 addition. A further increase of the temperature up to 1300 °C had no effect on iron grains' growth.

Figure 13. Effect of temperature on iron grains' size after 180 min of roasting with the addition of 22.01% K_2CO_3 .

As a generalization, reduced samples with considerable iron grain size could be obtained at temperatures no less than 1200 °C for Na_2CO_3 addition and no less than 1250 °C for K_2CO_3 addition. Furthermore, the cumulative evidence suggested that the best results were obtained for roasting duration of more than 120 min.

3.4. Magnetic Separation of Reduced Samples

Table 3 shows the results of the magnetic separation of reduced samples.

Table 3. The magnetic separation indexes of reduced samples.

Roasting Conditions	Addition	Iron Concentrate Yield (γ), %	Tailings Yield, %	Iron Recovery (ϵ), %	Iron Grade (λ), %	Iron Metallization (η), %	Iron in Tailings, %
1200 °C, 180 min	Without addition	n/s *	n/s	-	-	-	-
	17.1% Na_2CO_3	n/s	n/s	-	-	-	-
	22.01% K_2CO_3	n/s	n/s	-	-	-	-
1250 °C, 180 min	Without addition	n/s	n/s	-	-	-	-
	17.1% Na_2CO_3	15.89	84.11	25.37	55.65	81.88	8.23
	22.01% K_2CO_3	50.2	49.8	92.39	70.77	88.87	8.74
1300 °C, 180 min	Without addition	n/s	n/s	-	-	-	-
	17.1% Na_2CO_3	40.59	59.41	77.27	72.05	88.84	6.76
	22.01% K_2CO_3	44.1	55.9	85.54	72.5	90.47	8.1
1350 °C, 180 min	Without addition	n/s	n/s	-	-	-	-

* n/s, no separation.

The represented data indicate that the best results of magnetic separation were achieved with 22.01% K_2CO_3 at 1250 °C after 180 min of roasting where the iron recovery was 92.39%. The best results for roasting with the sodium carbonate addition were obtained for 1300 °C, 17.1% Na_2CO_3 , and 180 min duration. Under these conditions, iron recovery appeared to be 77.27%, which was significantly less than with 22.01% K_2CO_3 addition. After roasting without additions at 1300–1350 °C, as well as after roasting at 1200 °C with both additions, there was no separation into concentrate and tailings.

Figures 14 and 15 show the XRD patterns of iron concentrates (magnetic fraction) and tailings (non-magnetic fraction), and Table 4 indicates the elemental composition of the tailings. The XRD pattern

of the concentrates obtained after magnetic separation of the samples with alkaline additions showed that the main phase was metallic iron with minor content of iron-free minerals contained in the tailings. This result demonstrated that no full gangue-iron grains' separation could occur at these conditions. The main tailings' phases at both roasting conditions were gehlenite ($2\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{SiO}_2$), tricalcium aluminate ($3\text{CaO}\cdot\text{Al}_2\text{O}_3$), tricalcium silicate ($3\text{CaO}\cdot\text{SiO}_2$), perovskite ($\text{CaO}\cdot\text{TiO}_2$), and non-extracted metallic iron. The tailings obtained from the sample with 22.01% K_2CO_3 besides the above mentioned phases also contained potassium aluminate (KAlO_2) and mayenite ($12\text{CaO}\cdot 7\text{Al}_2\text{O}_3$). The main sodium phase of the tailings obtained in the sample with 17.1% Na_2CO_3 was NaAlSiO_4 .

Figure 14. The XRD pattern of tailings and iron concentrate obtained by roasting of red mud with 17.1% Na_2CO_3 at 1300 °C and 180 min duration time and following magnetic separation. (a) Tailings; (b) iron concentrate.

Figure 15. The XRD pattern of tailings and iron concentrate obtained by roasting of red mud with 22.01% K_2CO_3 at 1300 °C and 180 min duration time and following magnetic separation. (a) Tailings; (b) iron concentrate.

Table 4. Chemical composition of the tailings obtained by roasting of red mud at 1300 °C and 180 min duration time and following magnetic separation: 17.1% Na_2CO_3 (a) and 22.01% K_2CO_3 (b).

Sample	Fe	Si	Al	Ti	Ca	P	Sc
(a)	6.76	7.52	10.65	3.86	32.01	0.13	0.015
(b)	8.1	7.64	9.9	3.81	31.04	0.053	0.014

4. Discussion

Thermodynamic analysis and experimental research of the carbothermic reduction of red mud have shown that iron could be almost completely reduced already at 1000–1200 °C after 20 min of the roasting. Investigation of the reduced samples by Mössbauer spectroscopy indicated that an increase of alkaline carbonates' addition promoted Reaction (7) of Fe_3C formation. The mechanism of this influence needs to be further investigated.

The magnetic separation process showed that separation of metallic iron from a gangue phase could be achieved only above 1250 °C and after 180 min of roasting with the additions of alkaline carbonates. Furthermore, there was no separation into concentrate and tailings after roasting of the samples without alkaline additions even at 1350 °C. These results can be explained by examining the microstructure after roasting. Figure 16 shows the microstructure of different reduced samples.

Figure 16. Microstructure of reduced samples after 3 h of roasting at 1200 °C with 17.1% Na_2CO_3 (a) and 22.01% K_2CO_3 (b), as well as without additions at 1300 °C (c) and 1350 °C (d).

Evidently, iron grains in the samples obtained without additions (Figure 16c,d) attached to the gangue phase and mainly had a size of 1–5 µm (Figure 13), so it was difficult to separate them from each other. These observations were consistent with other studies [23,30]. Although iron grains in the samples obtained with 17.1% Na_2CO_3 and 22.01% K_2CO_3 additions had a larger size, they also attached to the gangue phase, which resulted in the failure of magnetic separation (Figure 16a,b).

Figure 17 shows the microstructure of the separated samples. They contained iron grains with the size above 100 µm divided from the gangue phase. There was an insignificant amount of fine iron particles attached with gangue that passed into the tailings (Table 4). These fine grains grew slightly even at higher temperature (Figures 11 and 13). Small effect on iron grain growth at temperatures above 1200 °C for Na_2CO_3 and 1250 °C for K_2CO_3 additions was also due to local attached iron particles with gangue. In summary, it is necessary to increase the amount of additions for better separation of iron concentrate and tailings.

Figure 17. Microstructure of reduced samples at 1300 °C and 3 h of roasting time with 17.1% Na_2CO_3 (a) and 22.01% K_2CO_3 (b) additions.

The most common hypothesis of the mechanism of the iron grain growth during the carbothermic reduction of different high iron raw material is associated with the appearance of a liquid phase, which promoted diffusion and aggregation of iron [26]. It can be seen from Figure 5 that the addition of 10% Na_2O and 15% K_2O at the temperature of 1250 °C led to increasing the amount of liquid phase to 45% and 50%, respectively. At the same temperature and addition of 17.1% Na_2CO_3 and 22.01% K_2CO_3 , there were similar amounts of liquid phase. This implies that such an amount of liquid phase was sufficient for the formation of large metal particles. Similarly, if the liquid phase amount was below 45%, significant iron grain growth was unlikely to occur.

However, it has to be taken into account that the presence of a considerable amount of liquid phase is the necessary, but insufficient condition for iron extraction. As can be seen from Figure 5, the sample obtained at 1350 °C without alkaline additions contained about 50% of liquid phase, which was similar to other successfully separated samples. In contrast with these samples, no separation into concentrate and tailings happened for this sample. It is possible to suggest that, besides the presence of the liquid phase, there were other factors affecting iron separation from the gangue. Surface (interfacial) tension at the gangue–metal interface might have a significant effect on iron grain growth during roasting and gangue–grain separation during grinding. It was evident that alkaline carbonate additions affected both the liquid phase amount and the gangue–metal interfacial tension.

Thus, it was found possible to extract iron effectively from red mud by reduction roasting followed by magnetic separation. After the separation of metallic iron, the tailings were proposed to be leached by hydrochloric acid for Al, Ca, and Sc dissolution and subsequent extraction. Previous research has shown the best efficiency of hydrochloric acid compared to sulfuric and nitric acid for leaching of aluminosilicate minerals [59]. It is then possible to recover selectively scandium from the chloride solutions by resins or extraction methods [60–62]. The separation of aluminum and calcium chlorides was previously studied in coal fly ash utilization [63]. In the present case, the high calcium content in the tailings made it possible to use the salting out method and precipitate $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ with further pyrolysis to sandy grade alumina production [64–66].

5. Conclusions

Iron containing phases of neutralized red mud were successfully reduced, and metallic iron was separated by reduction roasting with the addition of sodium and potassium carbonates followed by magnetic separation. Iron reduction and iron grain growth processes were carefully investigated, and optimal conditions were determined. The optimal conditions for the roasting with sodium carbonate were 17.1% of Na_2CO_3 addition, 1300 °C, and 180 min of roasting duration, which led after magnetic separation to iron recovery of 77.27% and the iron concentrate grade of 72.05%. The best results for the roasting with potassium carbonate addition were 22.01% of K_2CO_3 addition, 1250 °C, and 180 min of roasting duration, so after magnetic separation, iron recovery reached 92.39%, and the iron concentrate grade was 70.77%.

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