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COST-EFFECTIVE AND ECO-FRIENDLY EXTRACTION OF ALUMINA BASED ON KAOLIN ORE USING THERMO-CHEMICALLY ACTIVATED LIME-SINTER PROCESS

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ABSTRACT

The most commercial technology for smelter-grade alumina production is the Bayer process, which processes bauxite ore into smelter-grade alumina. The depletion of bauxite ore makes it necessary to develop innovative methods aimed at the smart processing and production of alumina and other by-products from non-traditional aluminum ores. One of these potential sources that is receiving great attention is kaolin ore. The present work aims to enhance the alumina percent recovery from kaolin ores obtained from different locations in Russia and Egypt by lime-sintering process thermochemically activated by adding charcoal. According to the results obtained before, the kaolin - limestone - charcoal mixtures were sintered at 1360°C, and the obtained sinters were then subjected to the leaching process at solid: liquid ratio (1:4), 50°C using Na_2CO_3 solutions of 80 g/L and for 10 min, at 600 rpm. The effect of the silicate module of the used kaolin ores on the alumina percent recovery and self-disintegration process has been investigated. The physico-chemical transformational changes and the efficiency of the self-disintegration process were characterized using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC), X-ray diffraction (XRD), X-ray fluorescence (XRF), and laser diffraction particle-size distribution analysis. The obtained results indicated that the used kaolin ore samples have the same thermal behavior. It is clear that, without the addition of charcoal and with decreasing the silicate module from 2.83 to 2.36, the percent recovery of aluminum oxide increases from 84.7% to 89.4%, respectively. On the other hand, with the addition of 1.5% charcoal, the performance of the process and the alumina percent recovery has been significantly enhanced with an increase from 89.3% to 93.5%, with a decrease in the silicate module from 2.83 to 2.36, respectively.

KEYWORDS: Alumina production, Thermal activation, Pyro-hydrometallurgy, Silicate module, Self-disintegration process.

استخلاص الألومينا من خام الكولين باستخدام عملية التلبيد مع الحجر الجيرى المنشطه كميائيا وحراريا و الاكثر فاعلية من حيث التكلفة وصديقه للبيئة

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الملخص

التكنولوجيا الأكثر تجارية لإنتاج الألومينا الميتالورجية هي عملية باير التي تعالج خام البوكسيت إلى ألومينا ميتالورجية. إن استنفاد خام البوكسيت يجعل من الضروري تطوير أساليب مبتكرة تهدف إلى المعالجة الذكية وإنتاج الألومينا وغيرها من المنتجات الثانوية من خامات الألومنيوم غير التقليدية. أحد هذه المصادر المحتملة لذلك والتى تحظى باهتمام كبير هو خام الكاولين. يهدف العمل الحالي إلى تحسين نسبة الألومينا المستخرجة من خامات الكاولين التي تم الحصول عليها من مواقع مختلفة في روسيا ومصر عن طريق عملية التلبيد مع الحجر الجيرى التي يتم تنشيطها كيميائيا و حراريا عن طريق إضافة الفحم. وفقا للنتائج التي تم الحصول عليها من قبل، تم تلبيد مخاليط الكاولين والحجر الجيري والفحم عند درجة حرارة 1360 درجة مئوية ثم تم اذابة الملبدات الناتجة عند الظروف الاتية نسبة الصلبة: السائلة 4:1 ، 50 درجة مئوية باستخدام محاليل كربونات الصوديوم بتركيز 80 جم / لتر. ولمدة 10 دقائق عند 600 دورة في الدقيقة. تم دراسة تأثير معامل السيليكات لخامات الكاولين المستخدمة على عملية استخلاص نسبة الألومينا والتفكك الذاتي. تم دراسة التغيرات التحويلية الفيزيائية والكيميائية وأداء التفكك الذاتي باستخدام تحليل قياس الوزن الحراري (TGA) وقياس سعرات المسح التفاضلي (DSC)، وحيود الأشعة السينية (XRD)، وفلورة الأشعة السينية (XRF)، و تحليل توزيع حجم جسيمات حيود الليزر. أشارت النتائج التي تم الحصول عليها إلى أن عينات خام الكاولين المستخدمة لها نفس السلوك الحراري. ومن الواضح أنه بدون إضافة الفحم ومع تخفيض معامل السيليكات من 2.83 إلى 2.36، فإن نسبة الاستخلاص لأكسيد الألومنيوم تزيد من 84.7% إلى 89.4% على التوالي. من ناحية أخرى، مع إضافة 1.5% فحم، تم تحسين أداء العملية و زادت نسبة الاسترجاع للألومينا بشكل ملحوظ مع زيادة من 89.3% إلى 93.5%، مع انخفاض معامل السيليكات من 2.83 إلى 2.36 على التوالي.

الكلمات المفتاحية : إنتاج الألومينا، التنشيط الحراري، الكاولين، عملية التلبيد مع الحجر الجير، المعالجة الحرارية المائية للمعادن، معامل السيليكات، عملية التفكك الذاتي.

1. INTRODUCTION

The depletion of minerals deposits of most mined minerals makes it necessary to develop an innovative method of searching for the effective utilization and extraction of valuable metals and additional important by-products based on alternative resources [1, 2].

Alumina has good physical and chemical properties, which enhance its application in the ceramics, refractories, abrasive, cement, and chemicals industries [3]. It is also considered the main source forproduction of aluminum metal. Bauxite ore is considered the main raw material used in the production of alumina and aluminum metal. Bayerand Hall-Héroult processes remain the only worldwide applicable and economical processes for alumina and aluminum metal production [4].

Due to the increasing international demand for alumina and aluminum metal as a result of their new applications in other industries and the simultaneous depletion of high-grade bauxite reserves, the World production of primary Aluminum has approximately doubled in the last ten years [5]. The global reserves of the currently available bauxite ore are limited and considered sufficient for mankind only for 50 years [6]. At the same time, countries that don't have or have limited reserves of bauxite ores attempt to reduce their imports of raw materials by finding alternative resources and technologies for the production of alumina and aluminum metal [7]. In addition to the shortage of global bauxite ore reserves, the Bayer process becomes an ineffective and non-economic technology for treating low-grade bauxite ores with high silica content (i.e., SiO_2 > 7%). The high content of silica leads to a low alumina-to-silicate ratio, which in turn leads to high caustic soda consumption, producing large quantities of bauxite residue (red mud). Until now, red mud has had limited uses and industrial applications, leading to the storage of huge amounts of it over time, resulting in unsolved environmental problems [8 -11].

The non-bauxite resources are widely abundant and equitably localized in every region of the world. These non-bauxite resources include clay minerals, kaolin, nepheline syenite, and coal fly ashes, which are found in many countries that are suffering from the shortage or un occurrences of bauxite ores, and these countries are hopeful for the production of alumina and aluminum metals [12, 13]. At the same time, mining these ores is easy because it is carried out using conventional surface mining methods, which are inexpensive [14]. The high resistance of clays to mechanical abrasion during thermal treatment at high temperatures [15] enhances their utilization as raw materials for paper coating and as filler material in paper, rubber, and plastic industries, paint extender, cracking catalysts or cement, ceramic, and refractory industries [16].

Most clay contains up to 25 - 40% alumina, which enhances its use as a source for alumina extraction to be used in other industrial applications. These clays can serve as a suitable alternative for bauxite ore from which high-purity alumina can be extracted. Metallurgical-grade alumina and high-purity alumina can be extracted from clays and kaolin ores using several acidic and basic extraction processes. Acidic methods are based on the acidic leaching of the calcined ores at suitable temperatures using HCl, H_2SO_4, and HNO_3. On the other hand, the basic (alkaline) processing of these ores is based on the sintering of these ores with suitable additives, and after this, the resulting sinter is subjected to alkaline leaching using an alkaline solution [17, 18].

The sintering method has been applied in the industrial scale and can be further classified into the lime-sinter process, lime-soda sinter process, and soda-sinter process according to the sintering mediums [19-21]. Aluminosilicate ores can be processed using the lime-sinter process which consists of the following successive steps: 1) Mixing the ground aluminosilicate and calcium carbonate ores in suitable stoichiometric at a suitable temperature result in the sinter mixture consisting of dicalcium silicate ($2CaO \cdot SiO_2$) and calcium aluminate compounds ($12CaO \cdot 7Al_2O_3$, $CaO \cdot Al_2O_3$); (2) Alkaline leaching the produced sinter with dilute Na_2CO_3 solution to dissolve alumina in the form of sodium aluminate ($2NaAlO_2$) and all silica was nearly left undissolved in addition to lime and any other materials present in the sinter; (3) Carbonization of the sodium aluminate solution with CO_2 to precipitate alumina as alumina trihydrate (gibbsite) and producing the sodium carbonate solution, which can be further recycled in the leaching process or for the production of sodium carbonate powder and (4) Calcining the precipitated gibbsite at 1350°C to produce αAl_2O_3 phase [22-26].

In general, the well-known pre-treatment or activation method of the non-bauxite ores such as high aluminosilicate clays, kaolin, nepheline syenite, and coal fly ash prior to acid or alkaline leaching for enhancing the alumina extraction process is thermal activation. The thermal activation of non-bauxite ores leads to the modification of their structures to a disturbed metastable phase [27]. The crystal water in their structure transforms successively to a vapor phase and forms a dehydroxylate, an oxidation, a migration of cation to different sites, and hence the disintegration of their structure [28, 29]. Also, their structure appears amorphous and highly soluble in dilute acids and bases [30].

The thermochemical activation of the kaolin-limestone mixture via the addition of charcoal as a fluxing agent for enhancing the alumina percent recovery from kaolin ore using the lime-sintering process has been investigated. The maximum alumina recovery of about 87.40% was obtained by sintering at 1360°C with the addition of 1.5% charcoal. Combustion of ≤1.5% charcoal provided additional heat that amorphized the crystalline calcium aluminate into highly leachable amorphous phases with improved self-disintegration efficiency. Charcoal is highly recommended as a cost-effective and energy-efficient activator to enhance the alumina percent recovery from kaolin ore [31].

Egyptalum, the Egyptian aluminum company, was established in 1972 and is considered one of the leading companies in the Middle East in producing aluminum metal. But at the same time, Egypt has no alumina refinery plant to produce metallurgical grade alumina, and Egyptalum depends on imported alumina from abroad (about 1 million tons/year). Egypt is considered one of the non-bauxitic countries that don't have bauxite ore but have huge amounts of kaolin ores. These Egyptian kaolin ores can be used as a good alternative for alumina production to reduce the dependence on imported alumina and, at the same time, enhance the advanced industries that depend on the alumina in Egypt. Russia, one of the leading countries in the world in the production of alumina and primary Aluminum, also plans to maximize its production volume by utilizing its national non-bauxitic ores like nepheline syenite and kaolin ores to produce alumina instead of importing the bauxite ore [2, 12, 13].

The current study aims to investigate and enhance the alumina percent recovery from kaolin ores in different locations worldwide. The effect of the silicate module on the alumina percent recovery and the efficiency of the self-disintegration process have been investigated.

2. Materials and Methods

2.1. Raw materials

The current study was carried out using six different kaolin ore samples that were obtained from three deposits in different regions of the world - Troshkovsky (Irkutsk region), Borovichi group (Novgorod region), Russia, and Wadi Kalabsha, Egypt. The limestone ore sample collected from the Pikalevo region, Russia, was also used in the current study. The chemical and physical compositions and the thermal characteristics of the raw kaolin and kaolin-limestone mixtures were studied in detail. A high-grade commercial charcoal was purchased from Kyiv Company for Reagents (RIAP), Russia. The sodium carbonate (Na_2CO_3) of analytical grade was purchased from Vekton Company, Russia, to be used in the leaching process,

2.2. Mixture preparation and sintering

The kaolin and limestone ore samples were crushed, ground, and sieved to < 74 µm. The samples of the limestone-kaolin mixture were prepared according to the stoichiometric molar ratios based on the total oxides content: $CaO/SiO_2 = 2.0$, $CaO/Al_2O_3 = 1.8$ and $CaO/Fe_2O_3 = 1.0$ according to the optimized condition obtained before in the previous study because this composition the most suitable and high leachable alumina containing phases which in turn gives the maximum alumina percent recovery [17, 31, 32].

To study the effects of charcoal addition on enhancing the alumina percent recovery, charcoal was added to the six kaolin-limestone mixtures with charcoal contents of 1.5 wt. % of the mixture mass according to the optimized condition obtained before [33]. Then, the prepared mixtures were thoroughly mixed using a drum mixer in which the entire drum rotated at 150 rpm rotation speed around its axis. The charge and discharge of the mixtures were carried out through the charge chute fixed at the end of the drum. The grinding media is composed of alumina balls, which are added to the charge mixture to aid in the mixing process, which finally produces a highly homogenized mixture. The drum was rotated at the predetermined speed for 4 h sufficiently to obtain a highly homogenized mixture. The ground mixtures were formulated into cylindrical briquettes of 30 mm in diameter and 30 mm in height at 5 MPa pressure by a Laptuls hydraulic press [34].

After that, the cylindrical briquettes of the different mixtures were sintered in a closed system in a high-temperature chamber furnace (PVK-1.6-5 -TEPLOPRIBOR) with 10°C min^{-1} heating rate up to 1360°C, which was selected as the best previously recommended sintering temperature that gives the highest alumina percent recovery [33]. The residence time for all samples was 1 h at 1360°C. Subsequently, the sinters were cooled inside the furnace to room temperature at the same heating rate of 10°C $min^{-1,}$ which allowed them to be annealed to achieve the effective self-disintegration process [33, 35].

2.3. Sinter-leaching process

The obtained sintered mixtures were processed by the leaching process with Na_2CO_3 solutions. The dissociation reaction mechanisms of the leaching process can be presented according to the following Equations 1 and 2 [32].

$$12CaO \cdot 7Al_2O_3 + 12Na_2CO_3 + 5H_2O \longrightarrow 14NaAlO_2 + 12CaCO_3 + 10NaOH \quad \text{Eq. (1)}$$

$$CaO \cdot Al_2O_3 + Na_2CO_3 \longrightarrow 2NaAlO_2 + CaCO_3 \quad \text{Eq. (2)}$$

The leaching process was carried out using a HEL Auto-Mate II reactor system equipped with a magnetic stirrer. The reactor system has three reactors, in which each leaching experiment was carried out in parallel mode to reduce the error percentage. The liquid solution inside the reactor system was maintained at constant atmospheric pressure by reversing the condensed vapor to the reactor system to keep the solid: liquid ratio of the mixture constant. Stirring was carried out using a magnetic stirrer inside the working volume of each reactor. The rotation speed of the magnetic stirrer ranged from 250 to 1500 rpm. Sensors for temperature measuring were installed in the reaction medium and linked to the jacket of each reactor. Each cell was equipped with an independent heating element, and the cooling process was carried out by continuously supplying water as a coolant to fix the predetermined temperature. The operating temperature of the system varies from 20 –160°C ± 0.1°C. According to the procedure described before, each obtained sintered powder was stirred in a fresh Na_2CO_3 solution of 80 g L^{-1} concentration for 10 min., at 1:4 S: L at 50°C and 600 rpm rotation speed [36]. The resulting suspended slurry, i.e., the pulp, was filtered out by a vacuum pump, resulting in a sludge that was washed with hot distilled water and then dried at 110°C in a drying oven. According to the difference in the chemical compositions of the original sinters and their corresponding sludges, obtained by analyzing alumina content using X-ray fluorescence (XRF), the Al_2O_3 percent Recovery was calculated in accordance with Equation 3:

$$Al_2O_3 \text{ extracted} = (Al_2O_3 \text{ sintered} - Al_2O_3 \text{ sludge}) / Al_2O_3 \text{ sintered} \quad \text{Eq. (3)}$$

Each experiment or measurement was repeated three times for each condition, and the average was taken to reduce the error percentage and increase the accuracy of the obtained results.

2.4. Characterization methods

The changes accompanying thermal treatment of kaolin ore, kaolin-limestone and kaolin-limestone-charcoal mixtures were investigated using differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) carried out by a simultaneous TGA-DSC instrument (SDT Q600, TA Instruments, USA) in the temperature range 25–1300°C, at 20°C min^{-1} heating rate, using a platinum crucible and under vacuum conditions. The mineralogical composition of the kaolin ore samples was investigated using X-ray diffraction (XRD) of a Bruker D8 focus X-ray diffractometer, with Cu-Kα radiation (30 mA, 40 kV, $\lambda = 1.5406$ Å) in the range of 10–60° 2θ, at 0.008° 2θ scanning step and 10 s $step^{-1}$ counting time. The chemical composition of kaolin ore samples and resulting sinters and sludges were determined using XRF with a sequential XRF spectrometer (XRF-1800, Re anode, 90 mA, 40 kV, Shimadzu, USA). The particle-size analyses of the obtained sinters and sludges powders were carried out by a laser 201C Microsizer analyzer (InTechSA Ltd, Russia) in the 0.2 - 600 µm sizes range.

3. RESULTS AND DISCUSSION

3.1. Physico-chemical characterization of the raw materials

The chemical composition of kaolin samples from three different regions of the world, Troshkovsky (Irkutsk region), Borovichi group (Novgorod region), Russia, and Wadi Kalabsha, Egypt, is presented in **Table 1**. The column "Other" includes the mass fraction of P_2O_5, SO_3, and small impurities V_2O_5, Cr_2O_3, and MnO. It is clear that the alumina content in these samples ranges from 31.17% to 33.74%, and this content represents an economical percentage for alumina recovery in comparison with bauxite ores [13]. **Table 1** shows the effect of the chemical composition of kaolin ore samples on their corresponding value of the Silicate Module. Silicate Module ($\nu\ SiO_2 / \nu\ Al_2O_3$) is the molar ratio of SiO_2 to the molar ratio of Al_2O_3. For example, the Silicate Module of the Troshkovsky kaolin ore sample is equal to [(52/60) / (31.9/102)] = 2.78.

Table 1. Chemical composition of kaolin ores from different regions of the world.

Sample No.	Kaolin location	Mass fraction of oxides, %										
		SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	Na_2O	K_2O	others	LOI	Silicate Module
1	Troshkovsky	52.2	31.9	1.40	0.58	0.59	0.53	0.15	0.15	0.13	13.00	2.78
2	Wadi Kalabsha	48.69	31.17	2.21	3.90	0.26	0.13	0.23	0.09	0.86	12.47	2.65
	Borovichi group											
3	BLKPS1	46.77	33.74	1.65	3.22	0.17	0.37	0.44	0.41	0.31	12.91	2.36
4	BLKPS2	48.61	33.74	1.61	3.20	0.16	0.34	0.22	0.43	0.51	11.80	2.45
5	BLKPS3	50.31	32.87	1.59	3.18	0.15	0.36	0.25	0.39	0.12	10.76	2.60
6	BLKPS.3B	53.12	31.94	1.53	3.12	0.12	0.34	0.25	0.40	0.16	9.02	2.83

The chemical composition of the Pikalevsky limestone sample obtained by X-reflorescence (XRF) is presented in **Table 2**. It is clear that the limestone ore sample consists mainly of CaO oxide of about 53.3% and loss on ignition, which is 43.7%.

Table 2. Chemical composition of Pikalevsky limestone ore.

Oxides	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	L.O.I.
%	2.01	0.41	0.56	0.58	53.3	43.72

The results of the X-ray analysis of kaolin ores samples are shown in **Fig. 1**. It is clear that all the studied kaolin ore samples are composed mainly of kaolinite ($Al_2O_3.2SiO_2.2H_2O$) and quartz minerals (SiO_2) as the main phases.

The results of TGA and DSC analysis of the original kaolin samples from various deposits are shown in **Fig. 2**. The second endothermic DSC peak appeared in the temperature range 519.75 - 535.79°C, which corresponds to the second TGA region, is an indicator of the enthalpy of dehydroxylation of kaolinite to metakaolinite. In addition, the sharp exothermic peak observed in the temperature range of 938.47-981.30°C is due to the metakaolinite phase transformation to Al-Si spinel (mixture of γ-alumina, amorphous silica, and mullite).

From the above chemical, physical, and thermal characterization of the different kaolin ore samples, it is indicated that all the used kaolin samples have the same thermo-chemical behavior with a little difference depending on the degree of their purity. This enhances the possibility of utilizing kaolin ore of different grades for the production of metallurgical grade and high-purity alumina.

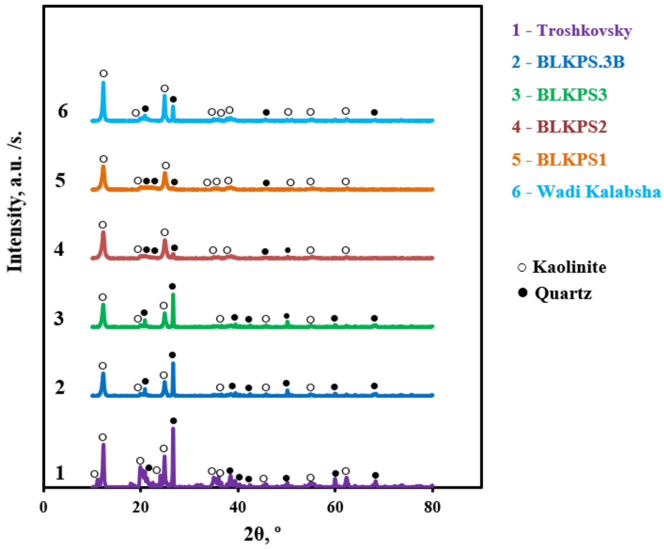

Fig. 1. X-ray diffractograms of kaolin ore samples from different locations.

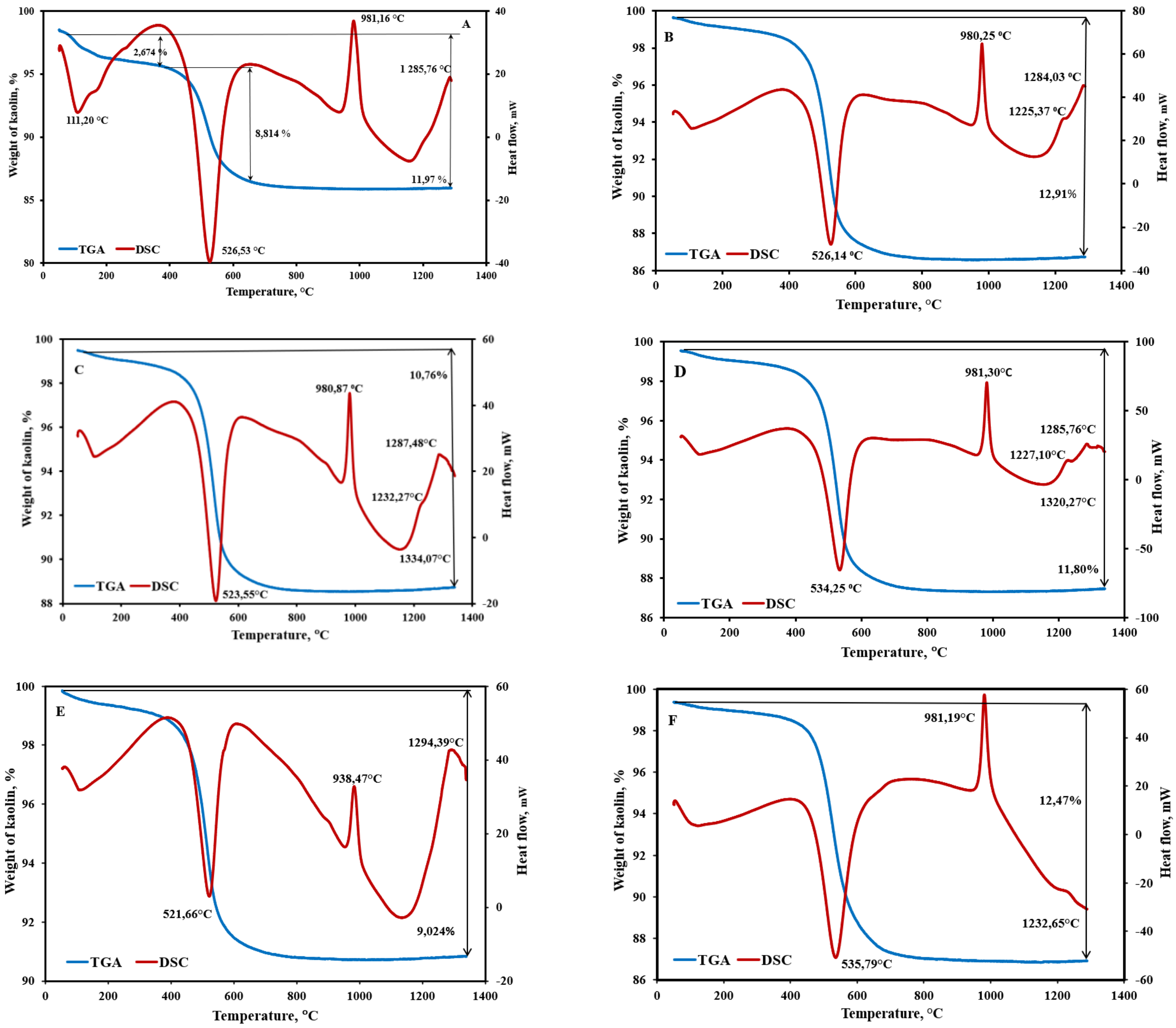

Fig. 2. TGA and DSC curves of initial kaolin ore samples from different deposits: (A) Troshkovsky; (B) BLKPS1; (B) BLKS2; (D) BLKS3; (E) BLKPS.3B; (E) Wadi Kalabsha.

3.2. Effect of silicate module on the effectiveness of self-disintegration process

One of the economic features of the proposed technology is the occurrence of the self-disintegration process for the sintered mixture at the end of the sintering time. The self-disintegration process normally takes place as a result of the crystalline β-C_2S ($2CaO{\cdot}SiO_2$) formation under high temperatures and then its transformation into the γ phase during the cooling of the sintered mixture according to Equations 4 and 5 [17, 31].

$$2CaO + SiO_2 \xrightarrow{1145^{\circ}C} \beta - Ca_2SiO_4 \quad \text{Eq. 4}$$

$$\beta - Ca_2SiO_4 \xrightarrow{675^{\circ}C} \gamma - Ca_2SiO_4 \quad \text{Eq. 5}$$

Fig. 3 shows the influence of the silicate module of kaolin ore from different deposits on the efficiency of the Self-disintegration process of the sintered kaolin-limestone mixtures in the absence of charcoal addition. **Fig. 3A** shows the frequency curves of the particle size distribution of the different sinters obtained from different kaolin-limestone mixtures in which all the produced sinters showed a unimodal distribution. **Fig. 3B** shows the cumulative curves of the particle size distribution of the different sinters. It is clear that the resulting sinters can be classified into three different particle size groups: fine, medium, and coarse, respectively. The first group includes sinter obtained by sintering kaolin ore from the Troshkovsky deposit, which has the smallest particle size among other groups where D_{50} = 10.3 μm. The second group includes the sinters obtained by sintering kaolin ore from the BLKPS2, BLKPS3, Wadi Kalabsha, and BLKPS-3B deposits, which have an average particle size among other groups where D_{50} ranging from 15.9 – 17.7 μm. The third group includes sinter obtained from sintering kaolin ore from the BLKPS1 deposit, which has the largest particle size among other groups where D_{50} = 33 μm, as shown in **Table 3** and **Fig. 3B**. It is shown that kaolin ore from BLKPS1 location, which has the smallest silicate modulus, has the largest particle size, which explains the relationship between the silicate modulus and the occurrence of the self-scattering process and, consequently, the particle size of the resulting sinter.

The specific parameters of the particle-size homogeneity (Span = $(D_{90} - D_{10})/D_{50}$), the gradation curvature coefficient ($C_c = D_{30}^2/(D_{60}D_{10})$), and the uniformity coefficient ($C_u = D_{60}/D_{10}$) which were calculated as presented in Table 3 [31]. There was no significant correlation between the origin of kaolin deposits and the particle-size homogeneity of any of the sinters, as the size span values ranged from 1.81 (in the sinter produced from the corresponding BLKPS1 kaolin ore) to 3.27 (in the sinter produced from the corresponding Troshkovsky kaolin ore), with an average value of 2.33. The source of kaolin ore showed a non-significant positive correlation (R^2 = 0.50) with the curvature coefficient (C_c) and a non-significant positive correlation (R^2 = 0.31) with the uniformity coefficient (C_u). The C_c values of all the produced sinters being >1 indicated that all the sinters produced consisted of well-graded particles [31].

Fig. 3C shows the frequency curves of the particle size distribution of the different corresponding sludges obtained from leaching the corresponding sinters, which all showed a unimodal distribution. **Fig. 3D** shows the cumulative curves of the particle size distribution of the different sludges. **Fig. 3C** and **Fig. 3D** show that there is an increase in the size of the corresponding sludges particles, even though the particle sizes of the corresponding sinters were smaller. This can be attributed to the agglomeration of very fine calcium carbonate particles that were deposited on the surface of the solid residual of calcium silicate particles [32].

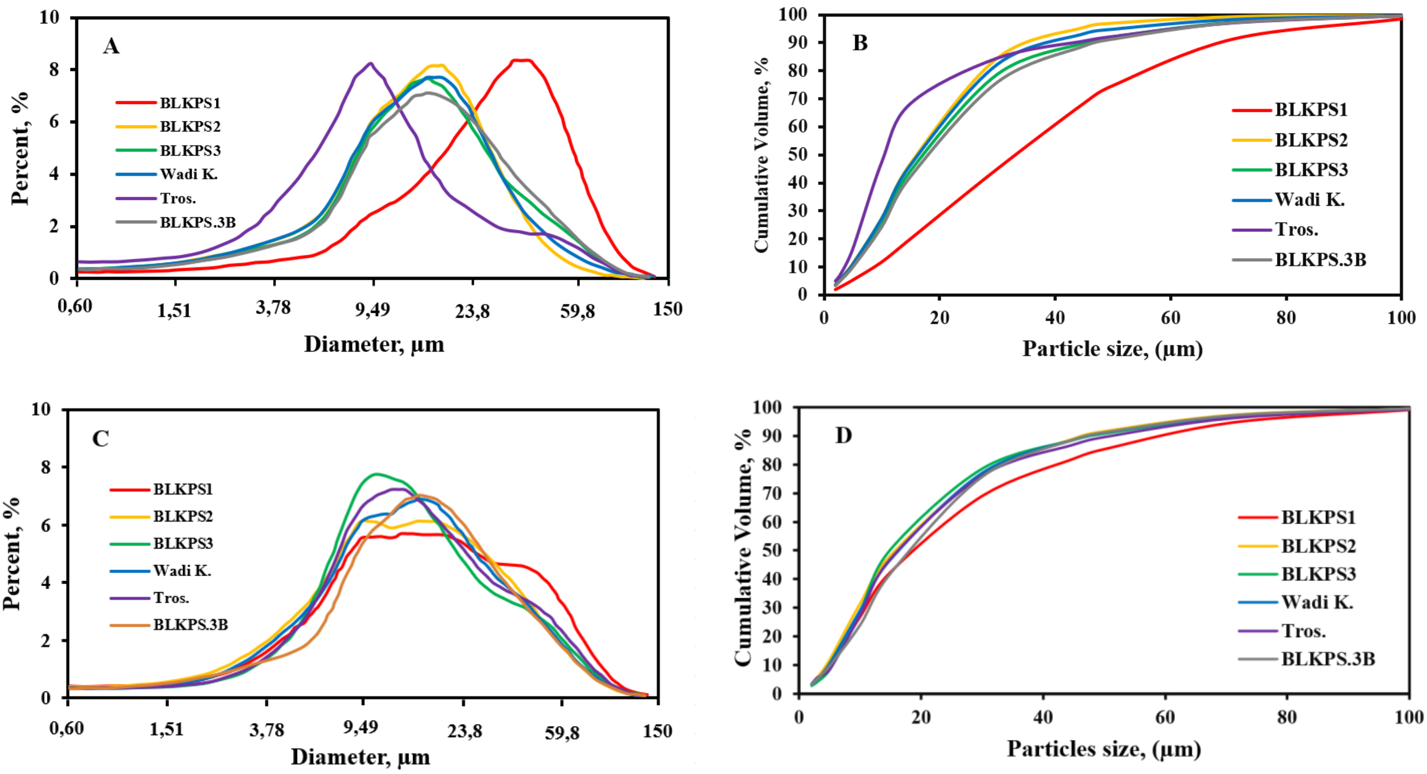

Fig. 3. Effect of silicate module on the efficiency of the Self-disintegration process of the sintered kaolin-limestone mixtures from different locations in the absence of charcoal addition: (A) frequency curves and (B) cumulative curves of the sinters; (C) frequency curves and (D) cumulative curves of the related sludges obtained after the leaching process.

Table 3. Particle size distribution of sinters obtained during sintering of kaolin ores from different deposits at a temperature of 1360°C.

Kaolin samples	Particle size distribution, µm									Size homogeneity and gradation parameters		
	10%	20%	30%	40%	50%	60%	70%	80%	90%	Span	C_u	C_c
BLKPS1	8.87	15.0	21.1	27.0	33.0	39.3	46.3	55.1	68.7	1.81	4.43	1.28
BLKPS2	4.53	8.13	10.6	13.1	15.9	18.9	22.4	27.2	35.5	1.94	4.17	1.31
BLKPS3	4.95	8.69	11.2	13.9	16.7	20.1	24.4	31.4	45.5	2.43	4.06	1.26
Wadi Kalabsha	4.65	8.18	10.7	13.2	16.1	19.2	23.1	28.4	38.5	2.10	4.13	1.28
Troshkovsky	3.20	5.28	7.06	8.70	10.3	12.3	15.4	21.1	36.9	3.27	3.84	1.27
BLKPS.3B	5.06	8.85	11.5	14.3	17.5	21.3	26.3	33.7	47.6	2.43	4.21	1.23

Fig. 4 shows the influence of the silicate module of kaolin ore from different deposits on the efficiency of the Self-disintegration process of the sintered kaolin-limestone mixtures with the addition of 1.5% charcoal to the mixture. **Fig. 4A** shows the frequency curves of the particle size distribution of the different sinters obtained from different kaolin-limestone mixtures in which all the produced sinters showed a unimodal distribution. **Fig. 4B** shows the cumulative curves of the particle size distribution of the different sinters. It is clear that the resulting sinters can be classified into two different particle size groups: fine and medium, respectively. The first group includes sinter obtained by sintering kaolin ore from the Troshkovsky deposit, which has the smallest particle size among other groups where D_{50} = 10.5 µm. The second group includes the sinters obtained by sintering kaolin ore from the BLKPS1, BLKPS2, BLKPS3, Wadi Kalabsha, and

BLKPS-3B deposits, which have an average particle size among other groups where D_{50} ranging from 15.8 – 20.9 µm as shown in **Table 4** and **Fig. 4B**.

The specific parameters of the particle-size homogeneity Span, C_c, and C_u are presented in **Table 4** [31]. There was no significant correlation between the origin of kaolin deposits and the particle-size homogeneity of any of the sinters, as the size span values ranged from 1.74 (in the sinter produced from the corresponding BLKPS1 kaolin ore) to 3.82 (in the sinter produced from the corresponding Troshkovsky kaolin ore), with an average value of 2.32. The source of kaolin ore showed a non-significant positive correlation (R^2 = 0.00) with the curvature coefficient (C_c) and a non-significant positive correlation (R^2 = 0.03) with the uniformity coefficient (C_u). The C_c values of all the produced sinters being >1 indicated that all the sinters produced consisted of well-graded particles [31].

Fig. 4C shows the frequency curves of the particle size distribution of the different corresponding sludges obtained from leaching the corresponding sinters, which all showed a unimodal distribution. **Fig. 4D** shows the cumulative curves of the particle size distribution of the different sludges. **Fig. 4C** and **Fig. 4D** show that there is an increase in the size of the corresponding sludges particles, even though the particle sizes of the corresponding sinters were smaller. This can be attributed to the agglomeration of very fine calcium carbonate particles that were deposited on the surface of the solid residual of calcium silicate particles [32].

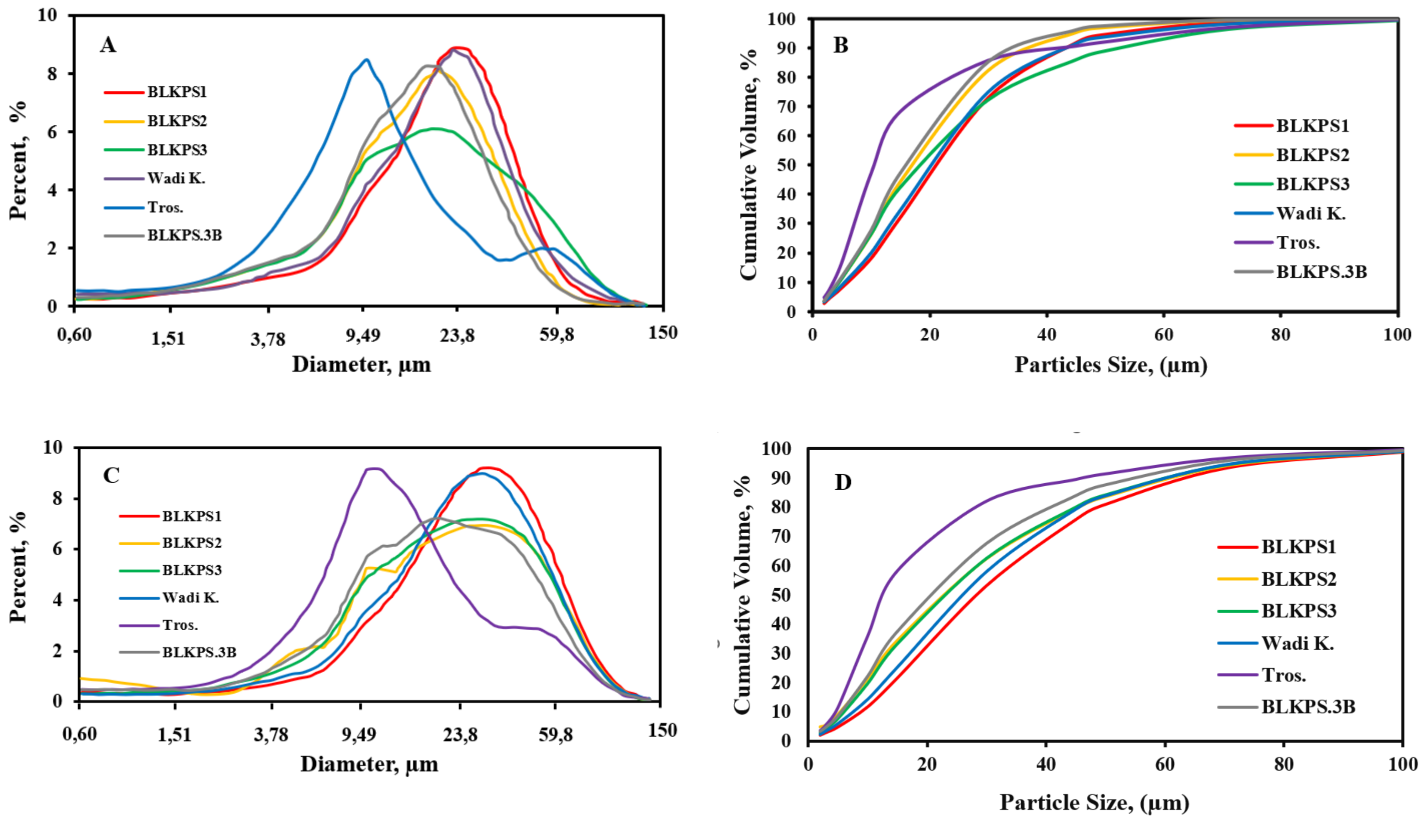

Fig. 4. Effect of SiO_2 / Al_2O_3 ratio on the Self-disintegration process efficiency of kaolin-limestone mixture from different locations in the presence of 1.5% charcoal: (A) frequency curves and (B) cumulative curves of the sinters; (C) frequency curves and (D) cumulative curves of the related sludges obtained after the leaching process.

Table 4. Particle size distribution of sinters obtained during sintering of kaolin ores from different deposits at a temperature of 1360°C with 1.5% charcoal addition.

Kaolin samples	Particle size distribution, μm.									Size homogeneity and gradation parameters		
	10%	20%	30%	40%	50%	60%	70%	80%	90%	Span	C_u	C_c
BLKPS1	6.21	10.7	14.3	17.7	20.9	24.5	28.6	34.0	42.6	1.74	3.94	1.34
BLKPS2	4.52	8.27	11.0	13.8	16.8	20.0	23.7	28.7	36.9	1.93	4.42	1.34
BLKPS3	4.51	8.18	11.0	14.2	17.9	22.4	28.4	37.4	52.3	2.67	4.97	1.20
Wadi Kalabsha	5.59	10.0	13.4	16.8	20.1	23.6	27.7	33.1	42.9	1.86	4.22	1.36
Troshkovsky	3.63	5.68	7.37	8.90	10.5	12.5	15.9	23.6	43.7	3.82	3.44	1.20
BLKPS.3B	4.32	7.98	10.6	13.1	15.8	18.7	22.1	26.8	34.8	1.93	4.33	1.39

3.3. The effect of the silicate module of kaolin ore on the alumina percent recovery

The effect of the silicate modulus on the alumina percent recovery from kaolin ores with different chemical composition and belongs to different regions of the world. In accordance with the chemical composition of kaolin ore (**Table 1**), the silicate modulus of the samples varied from 2.36 to 2.83, and their effect on the alumina percent recovery is shown in **Table 5**.

Table 5. Effect of the silicate module of kaolin ore on the Al_2O_3 percent recovery from sintered kaolin-limestone mixtures with and without charcoal addition.

Sample No.	Locations	Silicate Module	Recovery Al_2O_3, %	
			Without charcoal addition	**With charcoal addition**
1	BLKPS1	2.36	89.4	93.5
2	BLKPS2	2.45	88.3	92.4
3	BLKPS3	2.6	86.9	90.8
4	Wadi Kalabsha	2.65	86.4	90.4
5	Troshkovsky	2.78	85.2	89.3
6	BLKPS.3B	2.83	84.7	88.8

Fig. 5 shows the dependence of Al_2O_3 percent recovery on the silicate module of kaolin ore from the sintered kaolin-limestone mixture sintered at 1360°C with and without charcoal addition, according to the data presented in **Table 5**. It is clear that the silicate module of kaolin ore has a significant effect on the alumina percent recovery from kaolin ore using the sintering method. It is shown that, at the same time, without the addition of charcoal and with a decrease in the silicate module from 2.83 to 2.36, the percent recovery of aluminum oxide increases from 84.7% to 89.4%. On the other hand, the sintering of these samples of kaolin raw materials with the addition of 1.5% charcoal of the charge mass has a positive effect on enhancing the performance of the process with an increase in the Al_2O_3 percent recovery from 89.3% to 93.5%, respectively.

The data obtained make it possible to radically change the prevailing opinion about the impossibility of processing low-quality aluminosilicates with high rates of Al_2O_3 extraction and Al_2O_3 yield in general. Also, the possibility of using any grade of kaolin ore with the aim of the extraction of alumina using this method is also possible. These results fully agreed with the previously obtained data on the possibility of efficient processing of aluminosilicates with the extraction of Al_2O_3 at the level of 84-85%, even when using low-grade raw materials (nepheline syenite) with an Al_2O_3 content of 29-30% to 17.5%, but at the same time, the decisive influence of silicate modulus on the extraction of Al_2O_3 [8].

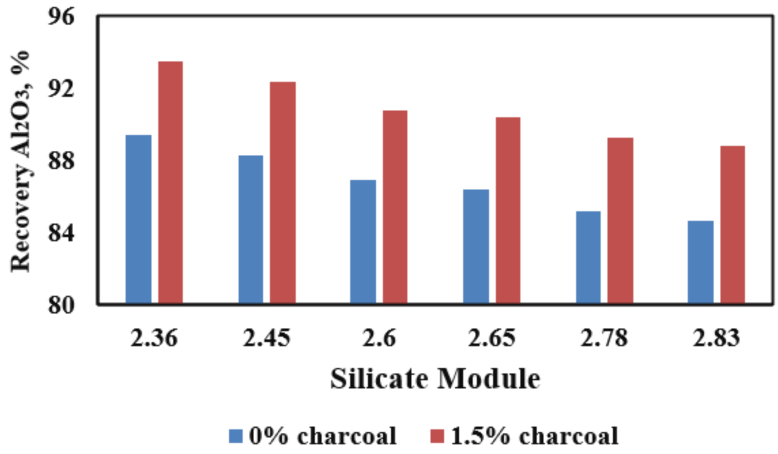

Fig. 5. Dependence of the Al_2O_3 percent recovery from the sintered kaolin-limestone mixture on the silicate module of kaolin ore with and without the addition of charcoal at 1360°C.

Hence, the recommended flowsheet for processing kaolin ore using a thermo-chemically activated lime-sinter process is presented in **Fig. 6**.

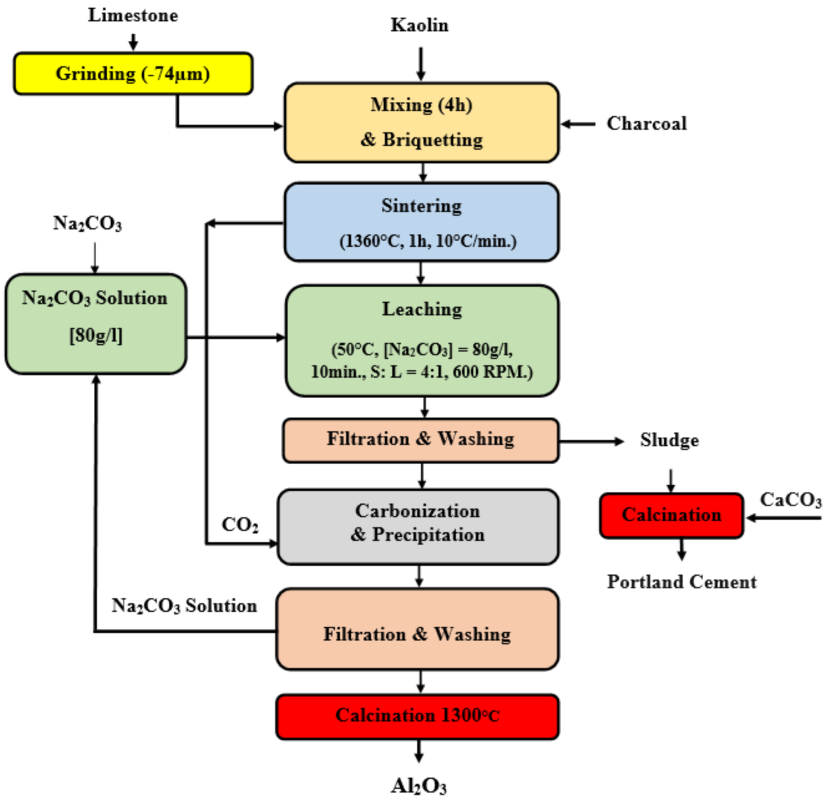

Fig. 6. The proposed technology for the Pyro-hydro metallurgical processing of kaolin ore using a thermo-chemically activated lime-sinter process for alumina extraction.

This technology has many advantages, differing from the traditional Bayer process, which suffers from economic and environmental disadvantages. Economically, this technology utilizes the nationally available and inexpensive kaolin ore instead of importing the costly bauxite ore. In addition to that, the current technology is simple and, at the same time, gives high-purity alumina as a final product. The self-disintegration process of the obtained sinter is considered one of the promising economic features of this process as it saves the cost of the successive high-costly grinding process in contrast to the same technology when used in processing nepheline ore.

Environmentally, the current technology overcomes the seriously solid pollutants (red mud) which are currently difficult and partially utilized in other applications. The kaolin sludge can be utilized totally in the production of portland cement ore; it can be further processed for the production of fine-depressed high-purity calcium carbonate, which has many industrial applications in addition to valuable calcium silicate, that has many industrial applications including wastewater treatment. In addition to the solid waste, the gaseous waste, composed mainly of CO_2, can be used in the carbonization process to precipitate the high-purity alumina from the alumina-bearing solution. In conclusion, it can be said the proposed technology has no waste, which gives it many advantages over the other technologies.

Conclusions

The present study aims to investigate the possibility of Alumina production from kaolin ore samples with different chemical compositions obtained from three locations worldwide. The kaolin ore has been processed using an improved lime-sinter process in which the kaolin-limestone mixture has been thermochemically activated using charcoal addition and sintered at 1360°C. The effect of the silicate module of the used kaolin ores on the alumina percent recovery and the efficiency of the self-disintegration process have been investigated.

The obtained results showed that the kaolin samples with different compositions have nearly the same thermal behaviour, which enhance it utilization with different grades in the alumina production. The lime-sinter process approved its effectiveness in the extraction of alumina from kaolin ores with a wide range of different chemical compositions. Also, thermochemical activation of kaolin-limestone mixture by charcoal addition showed noticeable improvement in the effectiveness, efficiency, and alumina percent recovery from kaolin ores with different origins. The obtained results indicated that the silicate module has noticeable effects on the alumina percent recovery and the efficiency of the self-disintegration process. Without the addition of charcoal and with decreasing the silicate module from 2.83 to 2.36, the percent recovery of aluminum oxide increases from 84.7% to 89.4%, respectively. On the other hand, with the addition of 1.5% charcoal, the efficiency of the process has been significantly enhanced, and the alumina percent recovery increased from 89.3% to 93.5%, decreasing the silicate module from 2.83 to 2.36, respectively. The optimum operation conditions for the effective extraction of alumina from kaolin ore processed using lime-sinter process is as follows: 50°C leaching temperature for 10min., at 1:4 solid : liquid ratio, using sodium carbonate solution of concentration 80gm.L^{-1}.

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