Geosciences and Engineering, Vol. 11, No. 1 (2023), pp. 68–84.
https://doi.org/10.33030/geosciences.2023.01.006

PRELIMINARY STUDY OF LOW-GRADE CLAYS AS SECONDARY RAW MATERIAL FOR GEOPOLYMER

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Abstract: The aim of this paper is to promote the use of low-grade clays as silicon and aluminium bearing material for geopolymer applications. This study presents the definition of low-grade clays, sources, and preliminary results of low-grade clays from waste of coal mining (coal gangue) and clay deposits. The results show that low-grade clays contain kaolinite and amorphous below 20% with impurities above 64% which has significant impact in terms of reactivity. Thus, the preliminary result provided valuable idea and better understanding of low-grade clays particularly for reuse in geopolymer applications.

Keywords: *low-grade clays, kaolinite, geopolymer*

1. INTRODUCTION

1.1. Definition of low-grade clays

Clay minerals type 1 : 1 especially kaolin, are among the major precursors for geopolymer preparation. High-grade kaolin clays with kaolinite contents of over 65 wt% are the most valuable resources for obtaining pure and highly reactive amorphous metakaolin for geopolymer process [1]. Medium grade kaolin clays are with kaolinite contents of between (40%–65%) [2]. If the raw material has content of kaolinite less than 40 wt%, it can be called low-grade kaolinitic clay based on several researcher. According to Zheng et al. (2022) [3] there is no clear definition of the boundaries between high-grade and low-grade clays but agree that clay with a kaolinite content of less than 40 wt% is usually considered as low-grade clays. Yamchelou et al. (2021) [4] according to their research use the term of low-grade clays and the result of study indicate mineralogical composition of clays consists of 77.8 wt% quartz, 5.7 wt% muscovite, 3.4 wt% kaolinite, 6.9 wt% anorthoclase, 2.4 wt% rankinite and margarite 3.8 wt%. Meanwhile, Mostafa et al. (2014) [5] in their research differentiates between high grade clays and low-grade clays as shown in *Table 1*.

Table 1

Semi-quantitative mineralogical composition of clay raw materials by means of X-ray diffraction analysis wt% [5]

Phase	**Formula**	**Clay 1 wt%**	**Clay 2 wt%**	**Clay 3 wt%**	**Type of mineral**
Kaolinite	$Al_2Si_2O_5(OH)_4$	84	32	16.7	1 : 1
Illite	$K_{0.8}Al_2(Si_{3.2}Al_{0.8})$-$O_{10}(OH)_2$	16	–	16.3	2 : 1
Montmorillonite	$Al_2Si_4O_{11}\ xH_2O$	–	8	–	2 : 1
Calcite	$CaCO_3$	–	15	–	2 : 1
Quartz	SiO_2	–	15	62.5	
Hematite	Fe_2O_3	–	2	–	
Albite	$NaAlSi_3O_8$	–	7	–	
Microcline	$KAlSi_3O_8$	–	13	–	
Orthoclase	$KAlSi_3O_8$	–	–	3.2	

1.2. Properties and sources of low-grade clays

Clay minerals are hydrous aluminium phyllosilicates, with a general particle size of 2 µm or less may be either natural or synthetic, phyllosilicates or non-phyllosilicates, and have no size connotation. The structures of phyllosilicates are all based on a tetrahedral (T) and an octahedral (O) sheet that may condense in either a 1 : 1 or 2 : 1 bound as shown in *Figure 1* [6]. The basic mineral structure of low-grade clay comprising low kaolinite content. Kaolinite is formed of two sheets only; two distinct layer interlayer surfaces coexist: one with aluminate or Mg dominating groups (octahedral) and one with silicate groups (tetrahedral). Both the tetrahedral and octahedral sheets are the main components of phyllosilicates (due to their leaf-like or plate-like structure, they are known as phyllosilicates) which bound together by sharing of oxygen atoms into different layers. The adjacent layers are linked by hydrogen bonding involving aluminol (Al-OH) and siloxane (Si-O) groups. The sublayer consists of octahedral coordinates and structural water in the form of hydroxyl groups [7]. Meanwhile, the structure of illite is a 2 : 1 layer as shown in *Figure 1b*, in which the interlayer cation is potassium, which gives the structure a strong interlocking bond that holds individual layers together and prevent water molecules from occupying the interlayer position [8]. In general, clay dominated by 2 : 1 or (1 ∶ 1 + 2 ∶ 1) dioctahedral layer silicates are notably cheaper and more abundant worldwide. Clays dominated by 2 : 1 or [(1 ∶ 1 + 2 ∶ 1)] dioctahedral phases generally consist of a mixture of different non-clay minerals and clay mineral phase, including mica, smectite, chlorite and low kaolinite [9]. Low-grade clays are available in many parts of the world as shown in *Table 2*. Sources of low-grade clays could be also associated with waste or by-product of other economic activities, as dredging and mining activities or excavated clays related to large civil infrastructure works. One of the sources of low-grade clays is from waste mineral or mining activity with higher SiO_2 and Al_2O_3. Waste generated up to 65 billion tons per year due to mining activity is often associated with the risk posed by its storage and environmental management [9].

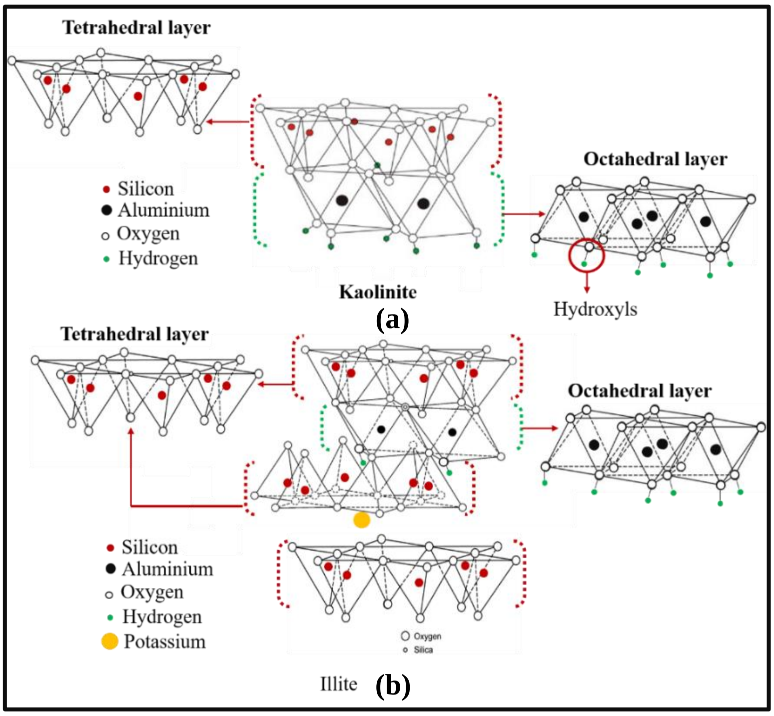

Figure 1

(a) Structure of kaolinite [10] (b) *Structure of illite* [8]

Table 2

Examples for sources of low-grade clays and applications

Author	**Ref**	**Sources of clay**	**Mineral phase**	**Wt %**	**Application**
Dixit 2021	[11]	Marine clay	Kaolinite	28–33	To replace 30% cement in mortar
Rodríguez et al. 2021	[7]	Activated coal washing rejects	Kaolinite Illite	14 6	Supplementary cementitious material
Cardinaud et al. 2021	[12]	Clay deposit	Kaolinite	6–3.6	Limestone cements
Li and Wang 2019	[13]	Coal gangues (Germany& Spain)	Kaolinite	4–30	Green concrete
Dietel et al. 2017	[14]	Clay deposit	Kaolinite illite/muscovite	11.8 19.8	Geopolymer
Zhou et al. 2017	[15]	Waste clay from excavated infrastructure	Kaolinite illite	26 32	Supplementary cementitious material
Snelling et al. 2016	[16]	Dredging sediment	Kaolinite illite/smectite	3 34	Supplementary cementitious material
El Hafid & Hajjaji. 2015	[17]	Pit from clay pottery	Illite Kaolinite	30 25	Geopolymer

1.3. Low-grade clays from coal gangue and clay deposit

Coal gangue is a type of industrial solid waste, which is produced in the process of coal mining, washing, and processing. Average, each ton of coal releases about 0.15 tons of gangue or accounting for 10%–25% of the total amount of coal [18]. According to data from Climate statistic (2022) [19], China produces 3969 Mt, follow by India 829 Mt and other countries. The European Commission reported that over 277 million tons consumption of brown coal in 2021 [20]. Thus, solid waste discharged from the production of coal mine has a certain impact on environmental protection by occupies valuable land resources but also commonly leads to serious pollution as well as health threats to residents [21]. Though the utilization of coal gangue has increased in recent times, the volume of its generation is still huge. Coal gangue can be viewed as potential resources instead of wastes after appropriate treatment as the main components are SiO_2, Al_2O_3, major mineralogical compositions are kaolinite, illite, and quartz. According to literature, mineralogical composition of coal gangue reported by different scholars –24] are very different, which mainly depends on the geological conditions of the study area, output type of coal gangue, and rock composition as shown in *Table 3*. The results of study by Cao et al. (2016) [23] show that kaolinite content 78.55 wt% therefore, not all coal gangue considered as low-grade clays.

Table 3

Mineralogical composition of coal gangue

Author	Ref	Countries	Kaolinite content wt%
Sitarz et al. 2022	[22]	Poland	28.20
Amrani et al. 2020	[24]	Morocco	–
Xiao et al. 2019	[25]	China	33.00
Cao et al. 2016	[23]	China	78.55
Frías et al. 2013	[26]	Spain	22–27

Clay minerals are a diverse and abundant aluminosilicate resource that has the potential to supply scalable, widely available and adaptable precursors for geopolymer application in general. Clays seldom occur in nature as highly pure deposits but rather as clay deposit, containing different clay minerals and associated non-clay minerals. According to their industrial value, clay deposits are commonly grouped into four general classes as shown in *Table 4* [27]. Considering the clay mineral content, there is significant variation in the types, amounts and exact nature of clay minerals in deposits and soils. Common clay areas have a high economic potential due to pure kaolin clays are relatively scarce. They are expensive because of the use of kaolin in paper and ceramic industry where kaolin with less 40% kaolinite rejected by the ceramic industry [28]. Besides that, metakaolin transformed by calcination of two layer silicate kaolinite already dealt with investigating its properties and its impact as additive on geopolymer properties by many researcher [29–30]. Despite its well-known good performance in geopolymer, its use as precursor is limited due to its commonly higher price.

Table 4
Classification of clay deposits [31]

	Industrial kaolin	**Bentonite clay deposits**	**Palygorskitesepiolite**	**Common clay**
Type of clays	Pure kaolin	Clay from smectite group	Similarities to bentonites	Illite/smectites
	Refractory clays			Kaolinites
	Bauxitic kaolin			Smectites
				Micas

1.4. Geopolymer

The rapid growing construction needs resulting from increased urbanization, industries, and infrastructural projects around the globe have made the demand and production of Portland cement to increase progressively with increasing year as shown in *Table 5* [32]. It is estimated that 1 ton cement production causes the release of about 1 ton CO_2 and around 10% of the total global carbon dioxide (CO_2) emission to atmosphere. Researchers have made efforts to come up with alternative of concrete to help reduce the CO_2 burden on the planet. In the purpose of reducing the environmental construction impact, the aluminosilicate inorganic polymers, also called geopolymers present attractive alternative materials [33–34].

Table 5
Global demand of production of Portland cement

Year	**2014**	**2015**	**2016**	**2017**	**2018**	**2019**	**2020**	**2030**
Global production (Billion tons)	4.18	4.10	4.20	4.05	4.10	4.20	4.40	4.80

In 1978, Davidovits, a French scientist, introduced to the world the mechanism of geopolymerization that could produce compounds possessing cementitious characteristics. Due to alkali activation of alumina-silicate source materials obtained from industrial by-products instead geopolymer, the term alkali activated material (AAM) is also used. Geopolymer is a primary material composed of an aluminosilicate substance made of a crosslinked structure of tetrahedral AlO_4 and SiO_4. Aluminosilicates rich in alumina (Al_2O_3) and silica (SiO_2) can stimulate the synthesis in a high alkalinity environment [35]. These source materials play an important role in geopolymer formation as an important source of Al^{3+} and Si^{4+} ions in the binding system. The binding property of the geopolymer results from the amorphous alkali aluminosilicate gels, which have a general formula as $Mn–(SiO_2)z–AlO_2]n \cdot wH_2O$, wherein M represents one or more alkali metals and z is 1, 2 or 3. Davidovits classified the geopolymer structure into four types as shown in *Figure 2* [36].

The use of low-grade clay in geopolymer application from waste brings additional benefits to society by creating added value by recycling resources, reducing the generation of waste, and avoiding the occupation of land area for disposal purposes. Furthermore, limited availability and relative high prices for type clay 1 : 1 (kaolin) make low-grade clays from secondary resources successful strategy to enhance sustainability in geopolymer industry. It has been proven that calcined materials, like ground granulated blast furnace slag (GGBS), fly ash and metakaolin (which are mainly amorphous) has higher reactivity during geopolymerization reaction unlike uncalcined materials. In geopolymers, the reactivity of raw material depends on its particle size [37–38], glass content and glass composition [39].

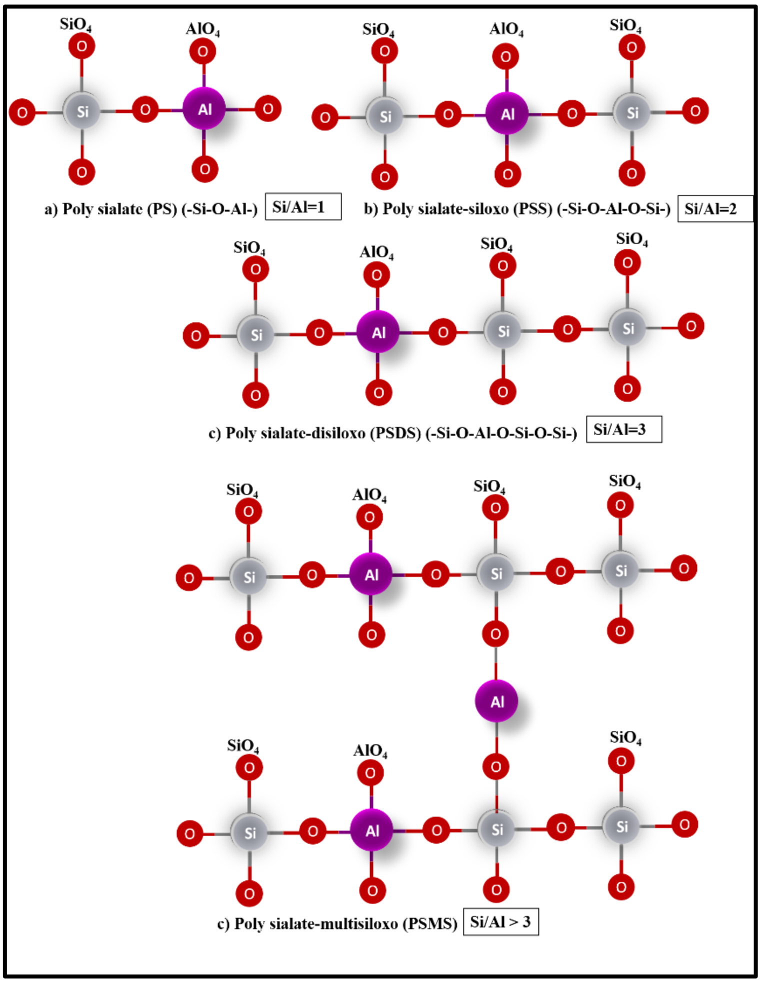

Figure 2
Geopolymer structure

Table 6 compares the result obtained from the analysis of chemical composition coal gangue, clay deposit, fly ash, metakaolin and ground granulated blast furnace slag. Each component such as calcium oxide (CaO) has been an important factor in geopolymer. According to many researcher [40–41] the limiting factor has hindered use of fly ash in geopolymer is low calcium content (CaO) due to requires longer setting times, porosity. Furthermore, the behaviour of aluminosilicate solutions can be significantly influenced by alkali and alkali earth metal cations. When an alkali cation is present, aluminium can be found in tetrahedral coordination, and these tetrahedral can directly replace those in the silica glass network [42].

Table 6

Chemical composition of coal gangue, clay deposit and amorphous raw material;(MK: metakaolin, GGBS: ground granulated blast furnace slag)

Component										
Material	**Ref**	**SiO_2**	**Al_2O_3**	**MgO**	**Na_2O**	**CaO**	**K_2O**	**Fe_2O_3**	**MnO**	**TiO_2**
Coal gangue	[43]	33.9	13.54	0.51	0.25	0.34	1.19	3.49	0.51	0.53
	[44]	59.7	20.16	–	0.23	1.96	2.52	5.5	–	–
	[45]	56.5	36.78	0.22	0.42	0.62	–	1.95	–	2.10
	[46]	55.9	24.81	–	–	0.28	2.02	8.73	0.01	1.17
	[47]	56.5	36.78	0.22	0.42	0.62	–	1.95	–	2.10
Clay deposit	[48]	59.3	20.7	1.6	0.94	0.85	2.7	6.4	–	–
Fly ash	[49]	46.6	16.2	2.96	0.50	9.36	1.64	9.4	0.147	0.54
	[50]	60.9	27.10	–	3.31	1.55	1.38	4.98	–	–
	[51]	48.1	14.42	3.34	–	11.7	1.66	10.97	0.17	–
MK	[29]	58.0	35.6	1.0	–	0.2	1.1	2.0	–	–
GGBS	[30]	32.8	17.06	7.71	0.48	37.6	0.20	–	–	–
	[52]	31.6	12.40	5.80	0.91	43.1	0.18	0.37	0.58	–

To date most of the investigations are about low-grade clays [53-54] is well documented in the literature, however, definition, sources and properties of low-grade clays are not well understood. Thus, the main aim of the current research was to establish clear definition of low-grade clays and properties. Moreover, a few samples of low-grade clays from different location are characterization.

2. MATERIAL AND METHOD

The experimental works utilized low-grade clays from clay deposits (LGC1, LGC2) waste of mining coal, coal gangue (LGC3, LGC4, LGC5) at different locations in Miskolc, Hungary. The particle density was determined by pycnometer method using alcohol as media. The particle size distribution of the raw material was measured by dry sieving and characteristic of particle X_{10}, X_{50} and X_{90} were identify. To determine the chemical composition of material samples, the X-ray fluorescence technique was performed using XRF, Rigaku Supermini X-ray Fluorescence apparatus. The crystallographic structure of raw material was determined by X-ray diffraction (XRD) on a Bruker D8 Advance diffractometer using Cu Kα radiation (40 kV, 40 mA). Data was collected between 10 and 65° of two theta angle, with a step size of 0.05° and a count time of 5 s per step. Samples were further analysed using Rietveld phase quantification method to determine the amount of crystalline and amorphous components.

3. RESULT AND DISCUSSION

3.1. Particle size analysis

The moisture content, bulk density and particle density as shown in *Table 7*. The evaluation of particle size is a vital aspect, and the particle size distribution of the raw material is shown in and *Figure 3*. The characteristic particles size of X_{10} range (0.066–0.125 mm) for LGC1-LGC5. The observed median particle size X_{50} of LGC1 and LGC2 between 0.508 and 0.725 mm and LGC3-LGC5 between (1.262–1.849 mm). The X_{90} of LGC1-LGC3 indicate the size approximately 12.029–12.397 mm, sixth times biggest than the LGC1 and LGC2. Kumar and Kumar (2011) [55] conducted series of geopolymer with different particle size and found that compressive strength improved with particle size X_{50} = 2.27 μm. This view also supported by Mucsi et al. (2015) [56] who writes that the quality parameter for geopolymer influences by particle fineness when X_{50} = 4.49 μm.

Table 7
Raw materials characterization

Type of clay	**Sample name**	**Moisture content (%)**	**Bulk density (g/cm^3)**	**Particle density (g/cm^3)**
Clay deposit 1	LGC1	2.54	0.88	1.91
Clay deposit 2	LGC2	1.86	0.90	2.32
Coal gangue 1	LGC3	1.37	0.73	2.28
Coal gangue 2	LGC4	0.94	0.89	2.62
Coal gangue 3	LGC5	1.09	1.16	2.26

Table 8
Characteristic particle sizes of materials

Type of clay	**Sample name**	**X_{10} [mm]**	**X_{50} [mm]**	**X_{90} [mm]**
Clay deposit 1	LCG1	0.085	0.508	2.301
Clay deposit 2	LGC2	0.125	0.725	2.574
Coal gangue 1	LGC3	0.078	1.262	12.029
Coal gangue 2	LGC4	0.066	1.435	12.147
Coal gangue 3	LGC5	0.079	1.849	12.397

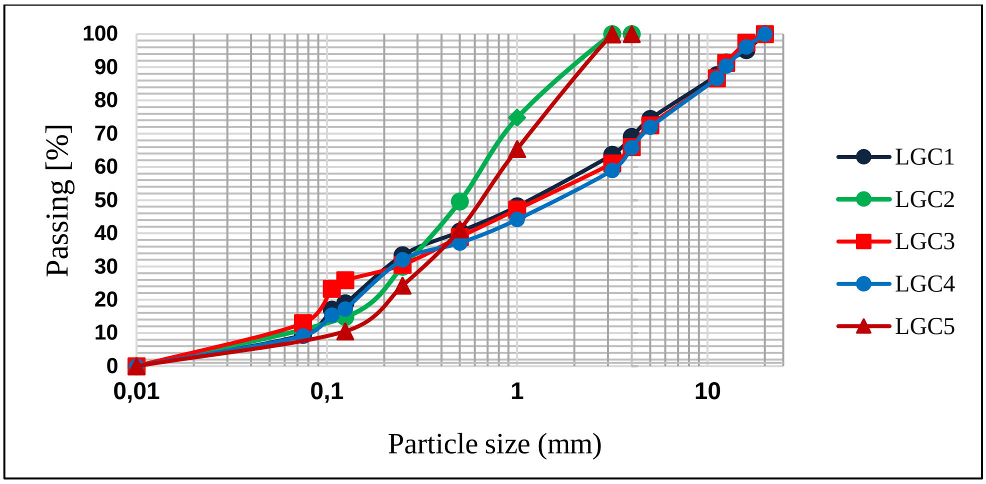

Figure 3

Particle size distribution of raw materials

3.2. Chemical composition of raw materials

Chemical composition shows a very heterogeneous material, containing several components with different characteristics as shown in *Table 9.*

Table 9

Chemical composition of raw materials

Component	LGC1	LGC2	LGC3	LGC4	LGC5
SiO_2	59.4	60.1	59.2	61.1	72.1
Al_2O_3	18.1	17.5	20.8	17.8	13.4
MgO	2.80	2.32	2.30	1.92	1.07
CaO	2.45	2.83	0.68	0.67	0.65
Na_2O	0.54	0.57	0.55	0.69	0.86
K_2O	3.17	3.05	3.50	2.99	2.20
Fe_2O_3	6.53	7.05	7.08	5.67	4.33
MnO	0.109	0.126	0.127	0.104	0.123
TiO_2	0.926	0.912	1.076	0.959	0.624
P_2O_5	0.111	0.117	0.093	0.103	0.084
S	0.43	0.03	0.14	0.13	0.02
F	<0.3	<0.3	<0.3	<0.3	<0.3
Total	94.6	94.6	95.5	92.1	95.5
$SiO_2+Al_2O_3+Fe_2O_3$	84.03	84.65	87.08	84.57	89.33
LOI	5.4	5.4	4.5	7.9	4.5

All samples (LGC1–LGC5) are composed of $SiO_2 + Al_2O_3 + Fe_2O_3$ between 84.03–89.33% meet the minimum requirement by ASTM C618 [57]. According to ASTM C618, term of chemical composition of $SiO_2 + Al_2O_3 + Fe_2O_3 = 70\%$ is minimum %

under Class N classification. All samples (LGC1–LGC5) present a lower loss on ignition (LOI), indicating a lower percentage of organic carbon between 4.5–7.9% below the requirement based on C618 the LOI maximum is 10%. LOI is a critical factor when assessing the geopolymerization. Unburned carbon absorbs the activator solution thus results in lower mechanical strength and higher costs [40].

Another important major oxide to be considered in this low-grade clays, calcium oxide (CaO). LGC3–LGC5 are low in CaO content (0.65–0.68%) compared to LGC1 and LGC2. Although fly ash geopolymer as an amorphous material and has been explored by many researchers, the limiting factor which has hindered the use of fly ash in geopolymers is its calcium oxide (CaO), resulting in long setting time, high porosity, and slow strength development [58]. Majority of low calcium coal fly ash have significantly less charge balancing cations than Al [59]. In additional, the reaction product of low-grade clays based geopolymers is mainly sodium aluminosilicate hydrate (N–A–S–H).

3.3. Phase composition

The XRD analysis of the raw materials in *Table 10* shows that the main mineral components of LGC1-LGC5 are kaolinite type 1 : 1 clay mineral, illite type 2 : 1 clay mineral, and the dominant mineral is quartz. Moreover, these clays have impurities such as calcite (carbonate), dolomite (carbonate) muscovite (mica), and quartz content more than 64 wt% compared to clay mineral content between 18.9–30.4 wt%, with amorphous content is less than 20 wt%. Based on the chemical composition in *Table 9*, the CaO content in low-grade clays is mostly associated with carbonate minerals. As a result, LGC1 and LGC2 from clay deposits have the highest percentage of calcium oxide (CaO).

Table 10

Phase composition of raw materials

Clay mineral	**LGC1 wt%**	**LGC2 wt%**	**LGC3 wt%**	**LGC4 wt%**	**LGC5 wt%**
Kaolinite $Al_2Si_2O_5(OH)_4$	1.1	1.8	6.2	4.5	6.3
Chlorite IIb	1.4	0.1	1.7	1.6	–
Illite 2M1 $K_{0.65}Al_2(Al_{0.65}Si_{3.35}O_{10})(OH)_2$	24.5	24.1	22.5	16.2	12.6
Total clay mineral	27	26	30.4	22.3	18.9
Quartz (SiO_2)	32.7	30.9	30.7	45.2	56.3
Muscovite 2M1 ($KAl_2(AlSi_3O_{10})(OH)_2$	10.1	8.1	14.1	9.6	5.6
Albite $NaAlSi_3O_8$	5.0	6.3	4.5	5.7	6.1
Calcite ($CaCO_3$)	3.6	3.0	–	–	–
Dolomite $CaMg(CO_3)_2$	3.1	1.8	–	–	–
Microcline $KAlSi_3O_8$	1.3	1.5	2.8	2.6	2.1
Halite NaCl	1.0	–	1.3	0.9	–
i/sm 11A	3.0	–	–	–	–
Goethite	–	3.1	–	–	–
Amorphous	15.7	19.5	16.3	13.8	8.8

LCG1 and LGC2 shows high amorphous content that related to thermally decomposed of kaolinite, illite and other clay minerals and calcium carbonate. The present findings seem to be consistent with Keppert et al. (2018) [60] which found the highest calcium carbonate contribute to highest amorphous. It shows that this type of raw material LGC1–LGC5 are crystalline phases which hardly dissolve during geopolymer reactions. Usually, most crystalline phases hardly dissolve during geopolymer reactions [61]. When the amorphous phase content was above 50%, the materials had larger impact on the developed strength of the alkali activated cement [62].

4. CONCLUSION

This paper discusses the definition, properties and occurrence of low-grade clays resources that are potentially suitable for use as geopolymers. The definition of low-grade clays with kaolinite content below 40 wt%, medium clays between 40–65 wt% match those reported by several researcher. Based on the results of the preliminary study of low-grade clay, the following conclusions can be drawn:

- Overall, the initial particle size was almost 100% below 2.57mm for LGC1 and LGC2, however, for LGC3–LGC5 was almost 100% below 12.397 mm.
- The chemical composition results show that LGC1–LGC5 are aluminosilicate sources and are key parameters in the geopolymerization reaction. Besides that, the CaO content varies widely from 0.68 up to 2.83 wt%.
- All samples (LGC1-LGC5) show kaolinite type 1:1 clay content below 10% and illite content 12.6–24.6% type 2 : 1 clay has a relatively stable (crystalline) chemical structure at room temperature with amorphous content below 20%.
- From the preliminary result LGC2 and LGC3 have the highest potential with amorphous content of 19.5 wt% and 16.3 wt% respectively but are still the lowest resulting in slow binding and early strength development. However, calcium oxide (CaO) also element contribute to properties of geopolymer.
- The low reactivity limits of low-grade clay which can be improve by using mechanical activation with high-energy mills.

ACKNOWLEDGMENTS

The authors are grateful to Ferenc Móricz associate professor at the University of Miskolc for the XRF measurement.

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