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Structural Investigation of Alkali Activated Clay Minerals for **Application in Water Treatment Systems**

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Abstract. Alkali activation technology can be applied for a wide range of alumo-silicates to produce innovative materials with various areas of application. Most researches focuse on the application of alumo-silicate materials in building industry as cement binder replacement to produce mortar and concrete [1]. However, alkali activation technology offers high potential also in biotechnologies [2]. In the processes where certain pH level, especially alkaline environment, must be ensured, alkali activated materials can be applied. One of such fields is water treatment systems where high level pH (up to pH 10.5) ensures efficient removal of water pollutants such as manganese [3]. Previous investigations had shown that alkali activation technology can be applied to calcined clay powder and aluminium scrap recycling waste as a foam forming agent to create porous alkali activated materials. This investigation focuses on the structural investigation of calcined kaolin and illite clay alkali activation processes. Chemical and mineralogical composition of both clays were determined and structural investigation of alkali activated materials was made by using XRD, DTA, FTIR analysis; the microstructure of hardened specimens was observed by SEM. Physical properties of the obtained material were determined. Investigation indicates the essential role of chemical composition of the clay used in the alkali activation process, and potential use of the obtained material in water treatment systems.

1. Introduction

Inorganic binders can be divided into fundamentally different groups according to the properties of their chemical composition. The main parameters which identify mineral binders are the content of Ca, Al and Na oxides in the chemical composition of the binder. The chemical composition of alkali activated binders (AAB) is substantially different compared to the traditional cementitious binders. AAB could be divided in high calcium (Ca) binder systems which are characterised by high Ca

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content in raw materials of AAB and low Ca systems AAB. The typical phases for AAB systems with high Ca content are C-S-H (calcium silicate hydrates) and C-A-S-H (calcium aluminate silicate hydrates) while for low Ca AAB systems N-A-S-H (sodium aluminate silicate hydrates) is the predominantly binding phase. Raw materials such as fly ash or calcined kaolin clay together with highly concentrated alkaline base (Na or K base from 6 to 10 M) or sodium silicate solution (activators) could be used to create low calcium AAB [4].

The properties of AAB are defined by the chemical composition of raw materials and the type of alkali activation solution used for activation together with their proportions in mixture composition of AAB. According to the scientific literature, a wide range of AAB could be obtained by using raw material compositions with SiO₂/Al₂O₃ (Si/Al) ratio which could vary from 0.5 < Si/Al < 300 [5]. However, in order to obtain AAB with high durability and good mechanical property performance, it is recommended to provide the chemical composition in the following range: 1<Si/Al<5 and Na_2O/Al_2O_3 (Na/Al) ~ 1 [4]. AAB created outside this range is characterised by low strength and chemical stability (durability) and it could be unstable in the water environment. If Na/Al ratio is high in mixture composition, free alkalis can remain in the structure of AAB and form carbonate crystals and efflorescence could be observed. Therefore, using different raw materials, AAB with a wide range of properties can be obtained. There is no common guidance for prediction of the properties and application should be tested experimentally.

The main compound ratios can be determined from mixture composition of AAB; therefore it has essential effect on leaching of alkalis from the structure of AAB. By reducing the Al content in the mixture composition, the amount of free alkalis increases pore amount in the material. [6]. It is concluded that low Al and high Si content in mixture composition of AAB promotes alkali leaching from the material structure and this could be the main factor that affects potential buffer capacity of water solution provided by AAB. The buffer capacity could be described as diffusion of free alkalis from material structure in the water environment. Na⁺ and K⁺ ions ensure highly concentrated alkaline environment, which enhances the dissolution of amorphous phase being an essential part of alkali activation process and binding phase development; however, these alkali ions are weakly bonded to the (N,K)-A-S-H phase and are available for leaching. Alkali ions can diffuse to AAB surface and react with CO₂ forming crystalline salts like Na₂CO₃·nH₂O, NaHCO₃, K₂CO₃, KHCO₃[7]. The content of alkalis in pore solution increases if a highly concentrated alkaline activation solution is used in the alkali activation processes [6]. Ali has reported that pore solution transfer to the surrounding environment will occur only in direct surface contact between the material surface and environment (i.e. water). Therefore the leaching rate of alkalis in highly porous AAB will be more intense because of the high specific surface available for leaching [8].

In water treatment systems, where continuous ensuring of stable pH is vital for purification of water, this leaching effect from the structure of AAB could be regarded as a positive factor for passive pH or buffer capacity controlling systems. To enhance leaching from AAB structure, low calcium AAB with low Al and high Si content would be an advantage while for AAB designed for construction industry it would be an advantage to use raw materials with high amount of Al. However, the strength of AAB must be considered also in water treatment systems due to high water pressure during filtration through material.

2. Materials and methods

2.1. Materials

Two types of clay were used to obtain low calcium alkali activated binders (AAB): metakaolin (MK) obtained from kaolin clay from "Surin-Kaolin" Ltd (Poland) and calcined local illite clay (IC) obtained from raw illite clay from "Lode" Ltd (Latvia). The additional secondary raw materials used in this investigation were aluminium scrap recycling waste (ASRW) received from aluminium scrap recycling industry facility "Dilers" Ltd (Latvia), glass waste (G) received from the glass recycling factory "Lampu Demerkurizacijas Centrs" Ltd (Latvia). In order to increase material homogeneity and fineness, raw materials were ground for 30 minutes by using planetary ball mill Retsch PM 400. Chemical composition of raw materials is given in table 1.

Chemical component	ASRW	IC	MK	G
Al ₂ O ₃	63.2	14.6	34.2	1.0
SiO ₂	7.9	73.8	51.8	68.1
CaO	2.6	0.9	0.1	1.4
SO_3	0.4	-	-	-
TiO ₂	0.5	0.6	0.6	-
MgO	4.4	1.1	0.1	-
Fe ₂ O ₃	4.5	4.1	0.5	0.2
PbO	-	-	-	20.0
Na ₂ O	3.8	0.1	0.6	8.0
K ₂ O	3.8	2.8	-	1.2
CaCO ₃ *MgCO ₃	-	-	-	-
Others	2.6	1.1	0.5	0.1
LOI, 1000 °C	6.21	0.98	0.2	-

Table 1. Chemical composition of raw materials (wt. %).

According to XRD analysis, calcined IC has crystalline structure and, in addition to quartz (SiO₂) and illite (K(AlFe)₂AlSiO₃O₁₀(OH)₂·H₂O), it also contains microcline (KAlSiO₈) while MK is largely amorphous with the amorphous phase in 20 region from 18 to 33°. The content of reactive SiO₂ was 1.3% for MK and 1.1% - for IC, but total amount of R₂O₃ was 55.9% for MK and 19.5% for IC respectively. The ASRW is the final waste product in the aluminium scrap recycling factories. According to the XRD analysis data, the ASRW contains metallic aluminium (Al), iron sulphite (FeSO₃), aluminium nitride (AlN), corundum (Al₂O₃), aluminium iron oxide (FeAlO₃), magnesium dialuminium (MgAl₂O₄), quartz (SiO₂), aluminium chloride (AlCl₃) and aluminium hydroxide (Al(OH)₃). Glass powder is used as an additive to AAB mixture to change SiO₂ amount in the composition. The results of grading analysis showed that the additionally ground glass contains a wide range of particle sizes: from 8 µm to 30 µm with the average grain size of 26.3 µm. The specific surface area of G ground for 30 minutes was 1.126 m²/g. The chemical compositions of ASRW, IC, IM and G are given in table 1.

The alkali activation solution was prepared by using commercially available sodium silicate solution from "Vincents Polyline" Ltd characterized by the silica modulus M_s =3.22. To obtain alkali activation solution with the required chemical composition, the modification with an addition of sodium hydroxide was done. Commercially available sodium hydroxide flakes from "Tianye

Chemicals" (China) with 99% purity were used. By the change of NaOH content, sodium silicate solution with silica modulus from M_s =1.3 to M_s =3.22 was obtained.

2.2. Methods

Mineralogical composition of raw materials and AAB was determined by X-ray diffraction (XRD) (PAN analytical X'Pert PRO) and chemical composition for raw materials was determined according to LVS EN-196-2 with sensibility ±0.5w%. Elements were analysed by EDX (energy dispersive X-ray spectrometry - EDS, Oxford instruments 7378). Reactive SiO₂ and R₂O₃ for calcined clays were determined according to LVS EN 196-2 and gravimetric analysis was used to determine content of SiO₂ and Al₂O₃ (Florentine method). Structural characterization of different functional groups of raw materials and AAB was performed by using Fourier transform infrared (FTIR) spectrometer (VARIAN 800 FT-IR) between 400 and 4000 cm⁻¹. The particle size distribution for powdered raw material was determined by laser granulometer Analysette 22 Nano Tec. Specific surface area was detected by BET method ("Nova 1200 E-Series, Quantachrome Instruments"). The thermoanalysis of AAB was performed with DTA/DSC Baehr DTA 703. Scanning electron microscope (SEM) (Tescan Mira/LMU) was used for microstructural investigation of AAB and for description of raw materials. The XRD, FTIR, SEM and DTA analyses were performed for 28 days old AAB specimens.

2.3. Sample preparation

AAB specimens based on MK or IC with ASRW and with or without glass (G) additive were created. Sodium silicate solution with $M_s=1.63$ was used. The mixture proportion of AAB is given in table 2.

Mixture	MK	IC	ASRW	G	Sodium silicate solution to
composition					solid content ratio
MK-A1-G0	1	-	1	-	0.75
MK-A1-G1	1	-	1	1	0.75
IC-A1-G0	-	1	1	-	0.75
IC-A1-G1	-	1	1	1	0.75

Table 2. Mixture composition of alkali activated binders, mass ratio.

The solid raw materials were mixed together and alkali activation solution was added according to mixture composition. After mixing, pastes were immediately poured into sealed prismatic moulds measuring $4 \times 4 \times 16$ cm. The amount of paste poured into the mould was calculated according to the expansion of each mixture to avoid limited expansion of the paste. Moulds were covered and samples were cured at 80°C for 24 h. Afterwards the demoulded samples were cured at room environment until planned tests were performed.

3. Results and discussion

According to the XRD diffractograms, AABs are typically "X-ray amorphous"[9]. The broad peak observed from 20 to 30° 20 in MK has been broadened up to 40° 20 after the reaction with the activation solution M_s =1.67 and shifted higher. This shift demonstrates the formation of new amorphous phases, usually described as geopolymeric gels (MK-A1-G0 and MK-A1-G1) (figure 1) [10].



C-A1-G0 IC-A1-G1 5 15 25 35 45 55 Degree 2θ

Figure 1. Diffractograms of AAB for 28 day old specimens made of metakaolin.

Figure 2. Diffractograms of AAB for 28 day old specimens made of illite clay.

XRD diffractograms showed that the mineralogical composition of AAB made with IC was not affected significantly by the amount of glass in the composition; however, the structure is not completely X-ray amorphous, comparing with AAB made with MK (figure 2). The halo of IC-A1-G0 and IC-A1-G1 is not very expressive in the diffractograms in comparison with MK. It could be explained by the mineralogical composition of IC calcined at temperature 800°C and low amount of Al₂O₃. The only crystalline phase is clearly identified by XRD analysis of AAB made with IC, which is quartz. Comparing the results obtained by XRD, it was concluded that alkali activation of IC creates weak amorphous structure of AAB; however, IC could be used to create AAB but the weak reactions could define mechanical properties of AAB.

Restructuration of mineral compounds in raw materials and formation of new compounds occurs during alkali activation and new bonds could be detected by FTIR analysis. FTIR spectroscopy technique was used for raw materials and the results compared to those obtained for AAB (figures 3 and 4). All AAB samples based on MK or IC have a vibration mode at 446 cm⁻¹ which corresponds to Si-O-Si or Al-O-Si bending vibration [11]. This absorbtion mode was not characteristic for raw materials and indicates the formation of new bonds. Mode at 540 cm⁻¹ is typical for MK and it is associated to Si-O-Al bonds, where Al is present in octahedral coordination. After alkali activation this bond vibration disappears in the structure of AAB. The small modes at 668 cm⁻¹ could also be attributed to O-Si-O (zeolite species) bond band (figure 3) and was characteristic for calcined clay. The absorbtion spectra become less intense after alkali activation.



Figure 3. FTIR patterns of raw materials and 28 days old AAB based on MK.



Figure 4. FTIR patterns of raw materials and 28 days old AAB based on IC.

Vibration spectra with the maximum at 1085 cm⁻¹, which is characteristic for raw materials (MK and IC), moves to higher frequencies after alkali activation, while vibration mode at 770 cm⁻¹ in MK was not detected in AAB. The shift of vibration spectra between raw materials and AAB indicates the structural changes under process of alkali activation. The shoulder at 1100 and 1200 cm⁻¹ is assigned to amorphous SiO₂, which indicates that unreacted amorphous SiO₂ could remain after alkali activation. This phenomenon was observed for samples with glass additive (MK-A1-G1 and IC-A1-G1) which contained more amorphous SiO₂ in the mixture composition. Vibration spectra with the maximum at 1085 cm⁻¹, which is characteristic for raw materials (MK and IC), moves to higher frequencies (1018 to 1030 cm⁻¹) after alkali activation, while vibration mode at 770 cm⁻¹ in MK was not detected in AAB.

The results from DTA provide limited information on the phase composition of the system. It is evidently the consequence of the amorphous or near-amorphous character of the ingredients for the studied materials, thus a use of any method is rather restricted. DTA histograms are characterized by the occurrence of first endoeffect in the region about 110–150°C due to the loss of evaporable water (figure 5) [12]. The endoeffect in the region of 250–300°C most likely characterizes decomposition of pore solution, which probably is a mixture of NaOH (melting point 318°C) and NaHCO₃ (melting point 50°C) [13]. The loss of chemically bonded water was observed during the heat treatment of AAB. Glass additive in the mixture composition increased the intensity of endoeffects of AAB under heat treatment, which indicates that pore solution was more saturated with chemically bonded water.



Figure 5. DTA curves of AAB based on IC and MK.

The density of obtained materials was from 319 to 382 kg/m³ and the density of mixture composition made without glass additive was slightly lower in comparison with the mixture composition made with glass. The open porosity was from 16 to 29%, but the total porosity of the obtained materials increased from 84 to 87% (table 3). AAB mainly have close pore system. The BET specific surface area of MK-A1-G1 and MK-A1-G0 was from 5.1 to 6.1 m²/g, while for IC-A1-G1 and IC-A1-G0 specific surface increased to 45 and 60 m²/g. SEM images reveal the structure of AAB, where crystalline substances are concentrated on the pore surface. Crystals on the material surface were well built for AAB based on IC, while for AAB based on MK crystals were enclosed in the material structure (figure 6 and figure 7).

Table 3. Mass ratio of main compounds in mixture composition and physical properties of alkali activated material.

Mixture		Mass ratio		Density		Porosity, %
composition	SiO ₂ /Al ₂ O ₃	SiO ₂ /Na ₂ O	Na ₂ O/Al ₂ O ₃	(kg/m^3)	Open	Total
IC-A1-G0	1.6	2.9	0.6	319	26	84
IC-A1-G1	2.5	3.7	0.7	382	24	82
MK-A1-G0	1.1	2.8	0.4	327	29	84
MK-A1-G1	1.8	3.7	0.5	355	16	84



Figure 6. SEM images of AAB for 28 day old specimens made with metakaolin.



Figure 7. SEM images of AAB for 28 day old specimens made with illite clay.

4. Conclusions

Alkali activated binders based on metakaolin (MK), which contain reactive components (total R_2O_3) up to 55.9%, have expressive amorphous structure that characterizes changes (restructuration) of the MK minerals in the highly concentrated alkaline environment. Whereas binders based on illite clay (IC) (reactive components $R_2O_3 - 19.5\%$) have less explicit amorphous structure according to the results of XRD. Restructuration of the existing chemical bonds and formation of new bonds of calcined kaolinite and illite clay takes place in the highly concentrated alkaline environment indicating the formation of a new binder structure. The shift of vibration spectra between raw materials and AAB (1085 cm⁻¹ to 1018 cm⁻¹) indicates the structural changes under process of alkali activation.

Glass additive in the composition of alkali activated binder increases presence of semi-crystalline sodium carbonate and sodium bicarbonate in the pore solution, which is not possible to detect by XRD, but they are clearly identifiable in FTIR spectra (1436 cm⁻¹) and SEM. The pH level of such compounds could be from pH 8.4 to 11.6 and up to 14.0 for NaOH depending on the concentration in the water solution. This pH range ensured by salts and basis could be effectively used in the waste water treatment systems where optimal pH range is from 9.5 to 11.5. Therefore, it is possible to create AAB with high OH⁻ ion leaching rate by using glass additive in the mixture composition and AAB could be used as the material for passive pH stabilization in waste water treatment systems.

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