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Thermodynamic Simulation of Fly Ash and Flotation Tailings Geopolymerisation Process

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ABSTRACT

This study presents a thermodynamic modeling approach to predict the mineral composition of geopolymers synthesized from fly ash and flotation tailings. Using the GEM-Selektor software, the model simulates geopolymerization reactions based on the initial composition of raw materials, alkaline activator, and water. Experimental validation was performed by comparing the model predictions with scanning electron microscopy and compressive strength tests after 28 days of curing. The results show that increasing the proportion of flotation tailings promotes the formation of calcium- and sodium-aluminosilicate hydrate phases, which enhance mechanical properties. The developed model provides a valuable tool for optimizing geopolymer mixture design and reducing the number of trial-and-error experiments needed in sustainable construction material development.

Keywords: Geopolymer, Fly ash, Flotation tailings, Geopolymerization products, GEM-Selektor.

1. Introduction

Mining and energy activities generate over 100 billion tons of solid waste annually worldwide, presenting a significant environmental challenge that requires effective management strategies (Lèbre et al. 2017). In addition, the European Union (EU) has accumulated over 1.2 billion tons of residual waste (Wang et al. 2014).

Tailings are finely ground materials produced during the processing of mineral resources. They contain residual minerals and flotation chemicals, such as cyanide and sulfuric acid. They are highly susceptible to leaching, contaminating groundwater and surface water (Lazorenko et al. 2021: Xiaolong et al. 2021). Fly ash is generated during coal combustion in thermal power plants. Its properties include high alkalinity due to its chemical composition and the presence of heavy metals like mercury, chromium, and lead, making it hazardous if not handled properly (Abaka-Wood et al. 2022). Accumulation in dumpsites can result in dust storms and long-term contamination of soil and groundwater.

Fly ash and flotation tailings have been deposited in large quantities globally, making them important secondary resources (Vujovic et al. 2025).

The management of mining waste of all kinds is based on developing standards and its treatment or recovery. The construction industry presents a promising opportunity for the valorization and recovery of mining waste, as there is a high demand for construction materials and various potential applications for these materials.

Using waste as a secondary raw material instead of natural resources is a key strategy being developed to reduce the environmental impact of the construction sectors. There is a rising interest in sustainable construction practices, which aim to be both rational and eco-friendly. One area of innovation and research focuses on utilizing alternative materials and replacing traditional cement with other types of binders, such as geopolymers (GP) (Wang et al. 2023; Capasso et al. 2021).

The process known as geopolymerization produces geopolymers, an alkaline solution that reacts with an aluminosilicate precursor (silicon and aluminum) to form a binding matrix, which can be semi-crystalline or amorphous. GPs are materials with improved durability and strength as well as lower CO_2 emissions (Tchadjie et al. 2018; Xu et al. 2020).

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Some researchers have tried to use flotation tailings and fly ash as a source of aluminum silica in geopolymer formulations due to their mineralogical nature (Lazorenko et al. 2021: Xiaolong et al. 2021; Luhar et al. 2022). In our previous study (Štulović et al. 2024), we showed that flotation tailings could be used as aluminosilicate sources by replacing fly ash in the geopolymerization process. In this study, fly ash was replaced by a proportion of flotation tailings, which are local materials, and different mixes of flotation tailings and fly ash were used.

The goal of thermodynamic modeling in these systems is to analyze previous experimental results (Štulović et al. 2024) and to examine the impact of selected parameters on the composition of geopolymer materials. This analysis is crucial for optimizing experimental conditions. In this study, a thermodynamic model was developed and validated to predict the physicochemical composition of the geopolymer generated from fly ash, flotation tailings, alkaline reagent, and water. The GEM-Selektor software, developed by the Paul Scherrer Institute (Kulik et al. 2013; Wagner et al. 2012), was utilized to analyze the effects of selected parameters on the composition of geopolymer materials.

Given the complexity of the chemical geopolymer system, it is desirable to conduct thermodynamic modeling of the system to explain the experimental results and the influence of selected parameters on the composition of the geopolymer material (parametric study).

However, validated thermodynamic models for predicting product phases in FA/FT-based systems are lacking.

In this study, we aim to develop and validate such a model using GEM-Selektor, to reduce experimental workload and improve material design.

2. Materials and methods

In our previous study (Štulović et al. 2024), fly ash (FA) from thermal power plants in Serbia (TE “Morava”-Svilajnac) and flotation tailings (FT), obtained from the Majdanpek copper mine (Serbia), were mixed to create three geopolymer mixtures. The percentages of FA and FT were 80, 65, and 50 %, and 20, 35, and 50 %, respectively.

A detailed mineralogical analysis was performed for all raw materials (flotation tailings, and fly ash). The results of the characterization are shown in Table 1.

Mineralogical analysis of raw materials confirmed the presence of Si in the form of SiO_2 and Al in the form of Al_2O_3. Iron is present in two phases (FeS and Fe_2O_3) depending on the type of raw material. FeS is contained in flotation tailings, while Fe is found in zeolites and fly ash in the form of Fe_2O_3. Loss on ignition at 950 °C was 9.1, 10.5, and 11.7% for samples FT and FA, respectively.

Sodium hydroxide solution (10.0 g NaOH/25 cm^3 H_2O) was used as the alkaline reagent (AR). The activating solution is tempered to room temperature before use. Compositions of geopolymer mixtures are given in Table 2.

In our mixture’s optimization research (Štulović et al. 2024), physico-chemical, mineralogical, and environmental characterizations were conducted on the raw material FT and FA, and the three geopolymer mixtures (FT20FA80, FT35FA65, FT50FA50).

Geopolymer samples with the highest share of tailings (50%), aged for 28 days, were analyzed by SEM-EDS methods. The scanning electron microscopy (SEM) method was carried out using a JEOL JSM–7001F field emission scanning electron microscope (SEM) (JEOL, Tokyo, Japan) equipped with an INCA energy-dispersive X–ray analysis unit (EDS).

The hardened specimens were tested at 28 days for compressive strength (UCS). UCS was measured using a hydraulic-testing-machine-type Shimadzu UH-F1000Kni (Shimadzu, Kyoto, Japan) with a clip speed of 2 $mmmin^{-1}$. The results were the mean measurement values of the three samples.

A standard leaching method, toxicity characteristic leaching procedure (TCLP) (*Method 1311*, 1992.), was used to determine the leaching of flotation tailing and hardened geopolymer specimens as granular waste under the experimental conditions specified hereafter. The pH of acetic acid was adjusted to 2.88 ± 0.05 before leaching experiments. The crushed samples and acetic acid solution were placed into beakers with a liquid/solid ratio of 20 and extracted for 18 h.

3. Modeling approach

Modeling was performed using the Gibbs Energy Minimization Software (GEM-Selektor) (Kulik et al. 2013), a geochemical modeling tool that calculates equilibrium speciation and the quantities of aqueous and solid phases in a complex chemical system. This is achieved through the use of Gibbs free energy minimization algorithms.

Table 1. Chemical composition of FT, and FA (Štulović et al. 2024)

Phase	FT (wt.%)	FA (wt.% DS)	FT20FA80	FT35FA65	FT50FA50
FeS	4.21	/	0.42	0.74	1.05
Fe_2O_3	3.58	8.14	3.61	3.27	2.93
Na_2O	1.26	0.29	0.24	0.31	0.39
SiO_2	45.61	37.03	19.37	20.02	20.66
CaO	6.21	23.41	9.99	8.70	7.41
$CaCO_3$	20.70	/	2.07	3.62	5.18
Al_2O_3	11.14	10.14	5.17	5.25	5.32
K_2O	2.69	0.86	0.61	0.75	0.89
MgO	3.35	0.72	0.62	0.82	1.02
SO_3	/	0.97	0.39	0.32	0.24
H_2O	1.19	13.44	3.66	3.66	3.66

* DS—dry substance content.

Table 2. Compositions of geopolymer mixtures (Štulović et al. 2024)

Geopolymer	Binder		AR		Water/ (Binder + AA)	AR/ Binder	Si/Al	Strength (MPa) at 28 days
	FT	FA	NaOH	Water				
	g	g	g	g				UCS
FT20FA80	10.0	40.0	10.0	25.0	0.42	0.2	2.4	4.87
FT35FA65	17.5	32.5	10.0	25.0	0.42	0.2	2.7	14.03
FT50FA50	25.0	25.0	10.0	25.0	0.42	0.2	3.0	44.37

General thermodynamic data for aqueous, solid, and gaseous species were obtained from the PSI-GEMS thermodynamic database (Thoenen et al. 2014). The Cemdata18 database (Lothenbach et al. 2019) and the calcium (alkali) aluminosilicate hydrate C-(N)-A-S-H model from reference (Myers et al. 2014) were utilized for cementitious materials. The thermodynamic properties of zeolites reported in references (Ma et al. 2020; Ma et al 2020; Park et al. 2022) were used to represent and sodium-aluminum-silicate-hydrate (N-A-S-H) gels, as their solubility products show significant similarity (Lothenbach et al. 2019; Gomez-Zamorano et al. 2017; Lothenbach et al. 2017).

The input data for the software corresponds to the initial composition of the mixture in its oxide forms (see Tables 1 and 2). The GEMS software then predicts the precipitation or dissolution of each mineral in the system by calculating the saturation index at thermodynamic equilibrium, starting from the dissolution of the anhydrous phases. The effective saturation index for each solid phase was used to deduce the reaction's evolution (dissolution or precipitation): oversaturated solution (ISeff>0), thermodynamic equilibrium (ISeff=0), and undersaturated solution (ISeff<0). The model will be validated by comparing its predicted composition with the experimentally measured Unconfined Compressive Strength (UCS) of geopolymers that have aged for 28 days.

4. Results and discussion

4.1. Validation of the thermodynamic model

The validation of the model consists in comparing the experimental (TCLP test, SEM-EDS, and UCS) and numerical quantification (GEMs) of geopolymerization products.

All the measured values for the elements (Cu, Pb, Fe, Mn, and Zn) are significantly lower than the limit values for the TCLP test (Table 3), and these sources of aluminosilicates are classified as non-toxic waste (Štulović et al. 2024). Also, the metal immobilization process is the most effective in geopolymers based on fly ash with the largest share of flotation tailings.

Characteristic SEM-EDS images of the obtained geopolymer (FT50FA50) are shown in Figure 1 (Štulović et al. 2024). The micrograph of FT50FA50 geopolymers shows a well-developed gel-like hydration product of the geopolymer matrix with a high degree of homogeneity. From the micrographs and results of EDS analyses, it can be seen that the hydrated structure and gel-like phase correspond to the C-(N-)A-S-H (CaO–(Na_2O,Al_2O_3)–SiO_2–H_2O) gel).

The results of the unconfined compressive strength (UCS) testing of fly ash (FA)-based geopolymers with varying contents of flotation tailings (FT) are presented in Table 2. The highest UCS value, measured at 44.4 MPa, was recorded for the geopolymer containing 50% FT after 28 days of curing.

These findings align with the observed increase in the Si/Al molar ratio, which rose from 2.7 to 3.1 (see Table 2). This suggests effective activation of the flotation tailings within the fly ash geopolymer system, leading to a potential increase in Si-O-Si bonds and residual silica.

4.2. Modeling quantification of geopolymerization products

The results of thermodynamic modeling (Figure 2) of the previously mentioned geopolymer mixtures (FT20FA80, FT35FA65, FT50FA50) showed that increasing the proportion of FT in the mixture increased the content of the C-A-S-H phase and a decrease in the content of unreacted aluminosilicate sources. The obtained results are in agreement with the experimental optimization results from our previous study (Štulović et al. 2024). Also, the thermodynamic model also predicted an increase in the proportion of geopolymerization products (N-A-S-H and C-A-S-H) with the addition of FT, which is also in accordance with the experimental results and with the improvement of the mechanical performance of the geopolymer.

Based on the agreement of the obtained results of thermodynamic modeling with the experimental results, the influence of selected process parameters on the composition of the obtained geopolymers by numerical simulations could be investigated.

However, GEM-Selektor assumes thermodynamic equilibrium, which may not be fully realized in geopolymer systems, especially during early curing. Additionally, the lack of kinetic modeling or accounting for phase metastability (e.g., incomplete dissolution of fly ash or tailings) may affect the accuracy of predicted mineral assemblages. A sensitivity analysis examining the effect of initial Si/Al or Ca/Si ratios, or small changes in the composition of the alkaline reagent, would further strengthen the robustness and applicability of the model.

Table 3. The concentration of contaminants with pH-Eh values in the leachates (TCLP test)

TCLP	FT20FA80	FT35FA65	FT50FA50	Lim. value. mg/l
Cu	0.02	0.02	0.25	25
Pb	0.1	0.1	0.1	5
Fe	0.50	1.65	0.16	-
Mn	3.12	4.21	7.20	-
Zn	0.33	0.67	1.25	250
pH	6.9	6.3	5.7	-
Eh. mV	99.9	40.1	79.4	-

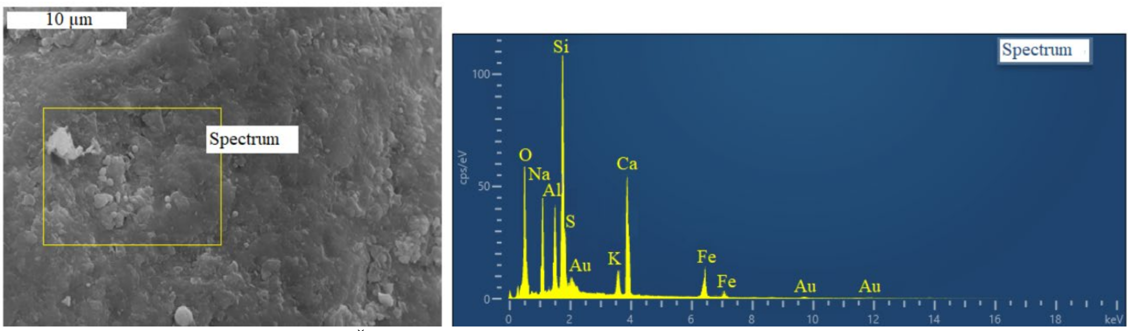

Fig. 1. SEM-EDS analysis of the geopolymer FT50FA50 (Štulović et al. 2024)

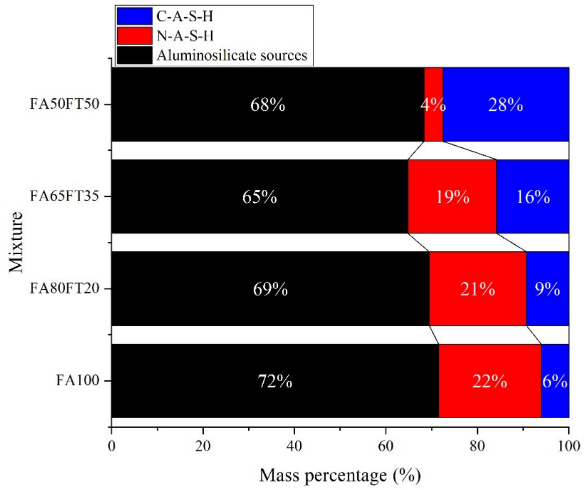

Fig. 2. Phase composition of geopolymer mixtures obtained by thermodynamic modeling

5. Conclusion

The primary goal of this work was to develop a thermodynamic model for predicting the physicochemical composition of geopolymers based on flotation tailings and fly ash. The model was validated by analyzing experimental results of the optimization of the geopolymer synthesis process. Thermodynamic modeling was based on the initial composition of the mixture (flotation tailings/fly ash + alkaline reagent+ water) using the Gibbs Energy Minimization Software (GEM-Selektor).

The simulation of the process with the thermodynamic model confirmed that with an increase in the proportion of flotation tailings in the initial geopolymer mixture, the amount of C-A-S-H phase also increases, in accordance with the results of our previous study. By understanding the ratio of the developed C-A-S-H and N-A-S-H phases, the stability of the material can be predicted.

In future research, the developed thermodynamic model can be used to better understand the effect of selected parameters on the final composition of geopolymer to reduce the number of experimental tests.

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