Alkali-activated coal fly ash as a matrix for heavy metals immobilization

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Introduction

The utilization of industrial by-products and wastes containing heavy metal ions to synthesize materials that can be reapplied for different purposes is particularly important. Without proper treatment, hazardous ions can be washed out and pose a threat to the environment. Geopolymers – the alkali-activated aluminosilicates, are synthesized by treating reactive solid source of SiO_2 and Al_2O_3 with an alkaline solution. Their highly chemical and fire-resistant properties, and relatively high mechanical strengths make them potentially good materials for the immobilization of wastes containing hazardous ions.

Samples

Geopolymers were obtained by mixing fly ash (FA) with an alkali activator (NaOH) solution (AA) and proper wt. % borax (BX) as boron source. The amount of boric compound represented four molar ratios of boron to aluminum (B/Al).

Table 1. Geopolymer composition.

B/Al (mol/mol)	AA (mol/dm³)	AA/FA (g/g)	BX (wt.%)
0			0
0,015			1
0,030	10	0,4	2
0,075			5
0,150			10

The samples with heavy metals were prepared by adding a metal nitrate to the geopolymeric slurry. The amount of the metal salt represented the amount of metal cations in relation to fly ash, and it was 2 wt.%.

Results & Discussion

Mechanical properties

When the B/Al molar ratio was not higher than 0.075 the addition of boron compounds to geopolymers slightly enhanced the compressive strength. A higher content of boron (B/Al= 0.150) induced a decrease in the compressive strength.
A compressive strength drop was observed in materials with heavy metals addition. In this case, presence of the boron in the matrix limited the compressive strength decrease.

B/Al	Compressive strength [MPa]			Density [g/cm³]		
	Ref	2%Pb^{2+}	2%Ni^{2+}	Ref	2%Pb^{2+}	2%Ni^{2+}
0	16.0	14.1	7.5	6.0	9.9	4.9
0.015	17.0	16.0	7.9	8.9	7.4	3.2
0.030	17.1	17.0	9.3	10.0	7.9	4.2
0.075	16.3	15.8	7.8	10.7	5.0	3.3
0.150	14.9	13.7	7.0	4.8	2.5	1.0

Table 2. The compressive strength and bulk density of geopolymers without and with heavy metals addition.

XRD patterns

The XRD patterns of geopolymers with borax (Ref) have peaks from unreacted, crystalline components of the fly ash (quartz and mullite).
Common phases that form during geopoymerization (sodium carbonates and zeolite-like feldspathoids) were observed too.
There were no visible differences between the patterns of the samples with and without boron.

New peaks appeared in the XRD patterns as the result of heavy metal salt addition.
In the case of the samples with
Lead the peaks came from lead oxide. The addition of nickel nitrate caused the formation of some nickel compounds, most probably in the form of nickel hydroxide or silicate.

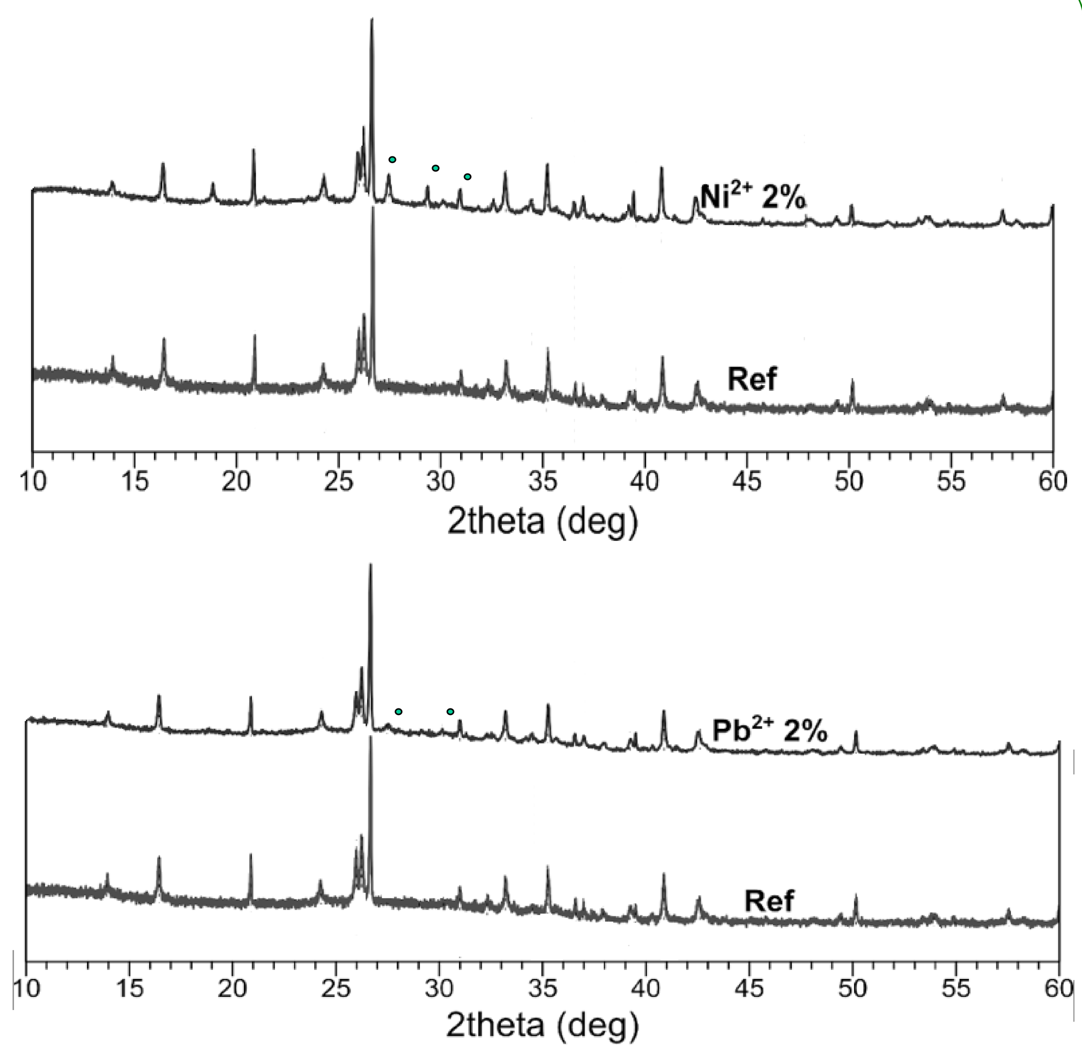

Figure 1. The XRD patterns of geopolymers with borax without (Ref) and with heavy metals addition (Ni^{2+} 2%- upside, Ni^{2+} 2%- downside). Dots show peaks from heavy metal crystalline phases.

FT-IR spectra

The differences between the spectra of geopolymers with and without heavy metals could be observed in regions related with:

- presence of nitrate ions (1384 cm^{-1}),
- main band (1000 cm^{-1}) that might be related to conection of heavy metal ions with geoploymer framework,
- pseudolattice vibrations in the range of 710 – 650 cm^{-1}, as a result of the ion-exchange of Na^{+} cations for heavy metal cations.

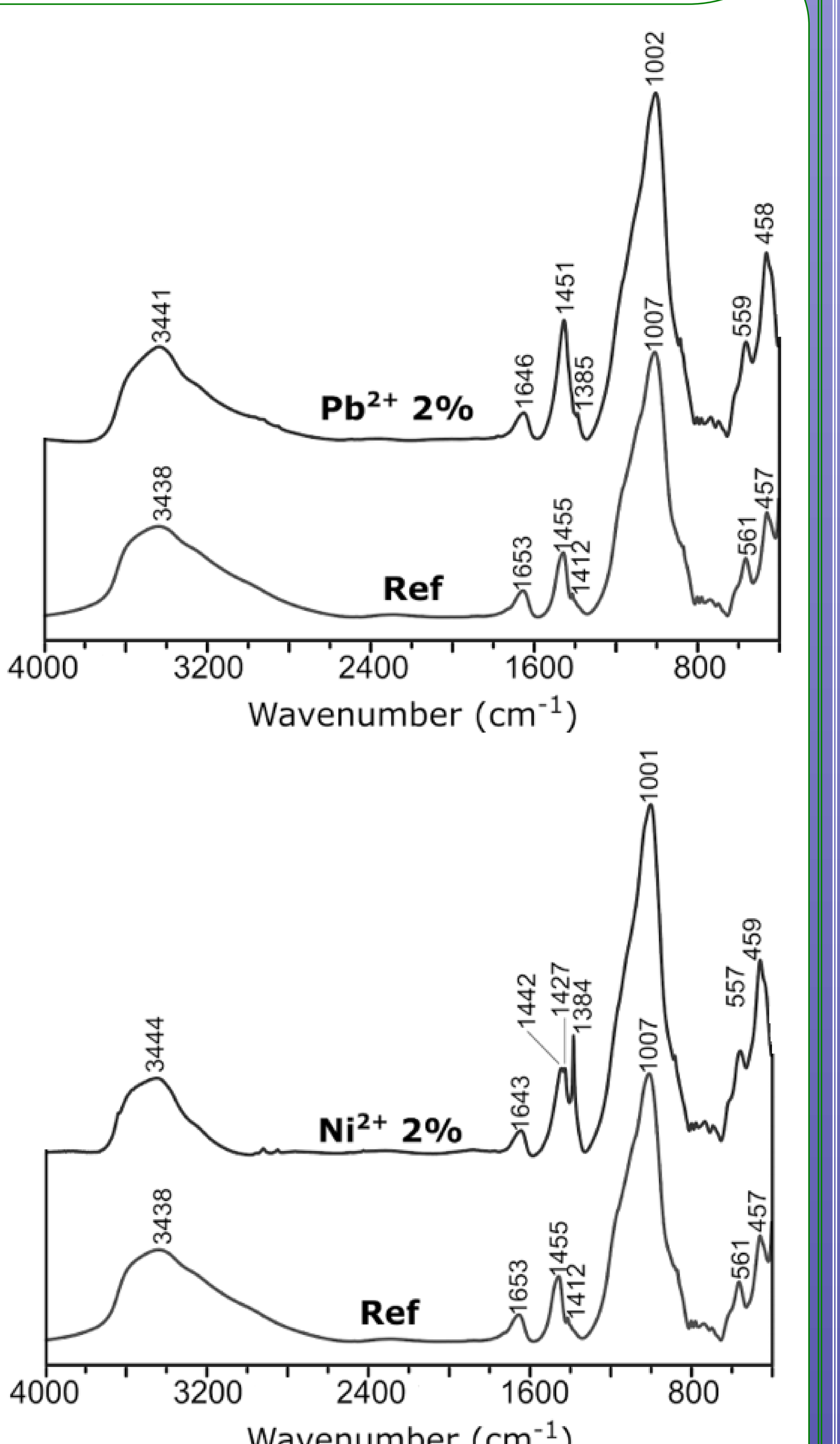

Figure 2. The FT-IR spectra of geopolymers with borax. Without heavy metals addition (Ref) and with addidtion of: 2%wt. Pb^{2+} upside and 2%wt. Ni^{2+} downside).

SEM images

There were no significant changes in the general microstructure caused by addition of Pb^{2+} nor Ni^{2+} .
The elemental mapping of the structure of the sample with lead and nickel showed that elements were distributed regularly throughout the sample.

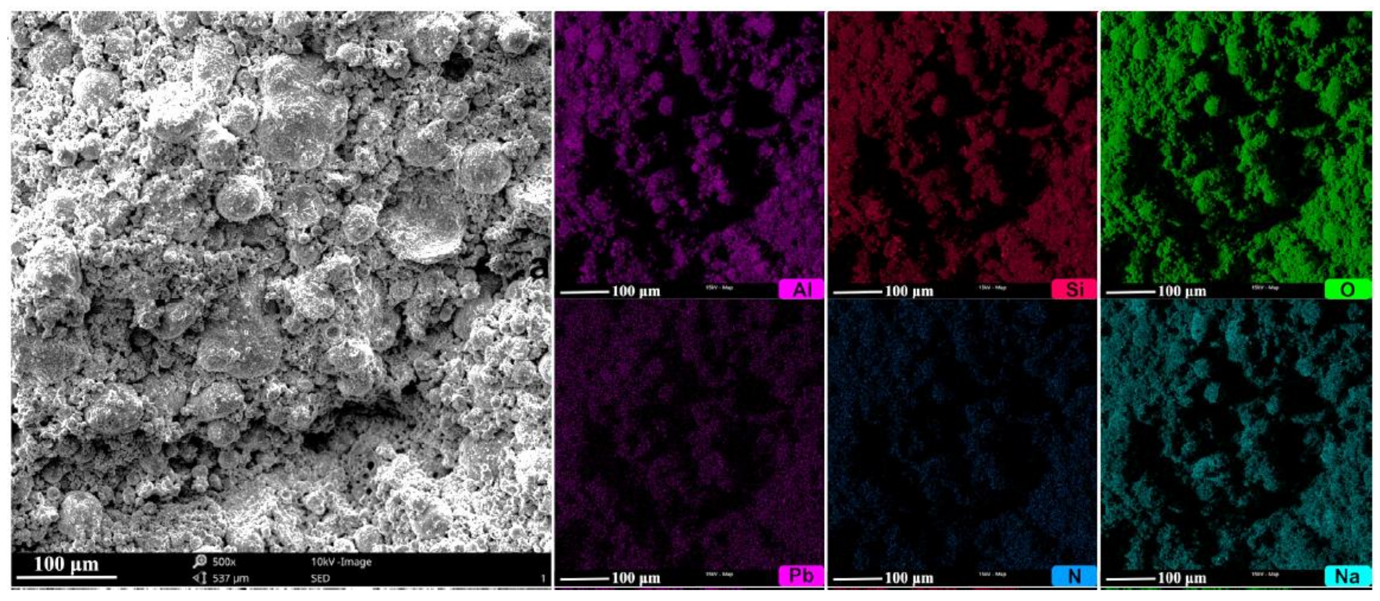

Figure 3. SEM image and EDS maps of geopolymer with 2% Pb^{2+} addition.

Heavy metal ions leaching

Higher boron content affected with increasing lead ions leaching.
Nevertheless, the immobilization rates were excellent, especially when considering that heavy metals were added in extremal amounts of 20,000 mg/kg of fly ash.

B/Al	Immobilization rate [%]	
	2% Pb^{2+}	2% Ni^{2+}
0	99,97	>99,99
0,015	99,96	>99,99
0,030	99,95	>99,99
0,075	99,87	>99,99
0,150	99,84	>99,99

Table 3. Heavy metal immobilization in geopolymers.

Conclusions

Addition of boron decreases the mechanical properties of geopolymers but limits their decrease in case of heavy metal salts addition.

XRD patterns show cristallization of small amounts of heavy metal compounds that can be soulable in water and impact the leaching effect in obtained geopolymers. FT-IR spectra proves that lead and nickel ions could be incorporated in geopolymers structure. SEM observations show that microstructure of all composites were quite similar and typical for alkali-activated coal fly ash.

Leachability of Pb^{2+} ions increased with addition of boron. Nevertheless, the immobilization rates were remarkable. For the reference sample, they were >99.9% for Pb^{2+} and >99.99% for Ni^{2+} .

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