



## Alkaline activation as a possibility for recycling mining waste into inert materials: Preliminary results on Elatsite, Assarel and Chelopech treated tailing materials, Bulgaria

### Алкална активация като възможност за преработване на минни отпадъци в инертни материали: предварителни резултати за третиранни материали от Елаците, Асарел и Челопеч, България

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#### Introduction

All over the world, mining industry produces huge amounts of mining waste annually, which is a significant environmental problem. In the last few decades many researchers pay attention in their studies to alkali-activation of inorganic materials for the development of some new materials through “geopolymerisation” process (Davidovits, 1991). The scientists make their studies on different materials such as tungsten mine waste (Pacheco-Torgal et al., 2008), volcanic scoria (Djobo et al., 2014), fly ash (Rosas-Casarez et al., 2014) etc. The discovery of a proper technology could help recycling millions of tons of mining waste in materials with sustainable properties appropriate for use in building industry or even in arts (Davidovits, 2015).

Suitable materials for alkali-activation are those rich in Al and Si, which require Na or K hydroxide additive and curing at moderate temperatures (Davidovits, 1991). Since aluminosilicate minerals are abundant in volcanic and sedimentary rocks, most mining wastes are workable for this experiment.

Regarding this we chose mining waste from three Bulgarian ore deposits suitable for alkaline activation. However, since crystalline quartz, which is the main constituent in these tailings, reacts pretty slowly with the alkaline source (caustic soda) and represents an obstacle for usual geopolymerization, we decided to follow a slightly different reaction pathway, using high temperature curing. This treatment leads to significant digestion of quartz,

but puts resulting products out of the frames of geopolymer definition, and should rather be considered as kinds of glass ceramics.

Elatsite and Assarel porphyry-copper deposits and Chelopech high-sulphidation epithermal copper-gold deposit are located in the Panagyurishte metallogenic district along with other porphyry-Cu and epithermal deposits as a part of the Srednogie zone, Bulgaria. Their hydrothermal systems are related to Late Cretaceous calc-alkaline igneous complexes. The intensive hydrothermal activity during the ore mineralization processes led to the formation of large haloes of K-silicate, propylitic and sericitic alteration in the wall rocks of the Elatsite and Assarel porphyry deposits (Strashimirov et al., 2002; Kanazirski et al., 2002; Hikov, 2013). The hydrothermal alteration in the Chelopech deposit is also developed in large scale around the ore bodies including advanced argillic, sericitic and propylitic zones (Mutafchiev, Chipchakova, 1969; Radonova, 1969; Georgieva, Hikov, 2016).

#### Materials and methods

The materials used in this study are collected from the tailing ponds of Elatsite and Assarel porphyry-Cu deposits and Chelopech high-sulphidation epithermal Cu-Au deposit and represent pervasive hydrothermally altered igneous rocks. K-silicate and propylitic alterations are main ore-hosting types for Elatsite, whereas in Assarel propylitic and propylitic-sericitic alterations are essential.

Advanced argillic alteration is representative in Chelopez deposit. The materials from the Elatsite and Assarel tailings were collected at intervals of several tens of meters, to establish differences in mineral composition due to natural granulometric and gravimetric separation. In the present work, the finest fractions are used to ensure greater reactivity. The material of Chelopez was kindly provided from the geological department before being deposited in the tailings pond.

Chemical analyses of the waste materials were carried out by ICP-AES. The crystalline phases of waste materials were determined by X-ray diffraction using HUBER Image Plate Guinier Camera G670. Diffraction measurements were carried out with Ge monochromator on primary beam, providing pure Cu  $K\alpha_1$  radiation ( $\lambda = 1.540598 \text{ \AA}$ ), in the range  $4\text{--}100^\circ$  and step size of  $0.005^\circ 2\theta$ . The materials from the three mining wastes were mixed with precisely calculated quantities of NaOH and demineralized water and heated at various temperatures – about  $40\text{--}80^\circ \text{C}$  for precursor drying and  $500\text{--}1000^\circ \text{C}$  for the heating after activation. The experiments were carried out in graphite crucibles. The experimental procedure was carried out at the laboratory of IMT Lille Douai, Department of Civil and Environmental Engineering, France. The materials were treated applying four different procedures: (1) mixing with NaOH and subsequently heating to max.  $1000^\circ \text{C}$ ; (2) mixing with NaOH, precursor drying up to  $80^\circ \text{C}$  and subsequently heating to maximum  $1000^\circ \text{C}$ ; (3) heating to maximum  $1000^\circ \text{C}$ , subsequently mixing with NaOH and heating to  $1000^\circ \text{C}$  again; (4) heating to maximum  $1000^\circ \text{C}$ , subsequently mixing with NaOH, drying at  $80^\circ \text{C}$  for couple of days and heating to  $1000^\circ \text{C}$  again. The main target of our experiments was to reduce the upper temperature limit for curing, as well as to experiment with the amount of added water and NaOH. All obtained products with the required hardness and insolubility were examined by XRD and SEM to obtain their mineral composition and specific microstructures.

## Results and discussion

The Elatsite waste materials are composed mainly of feldspars, quartz, clinocllore, muscovite, and Na-plagioclase. Small quantities of apatite, rutile, gypsum, calcite, biotite, magnetite, pyrite and actinolite are presented. Characteristic for the Assarel materials is the predominance of quartz along with albite, layered silicates (clinocllore, muscovite) and pyrite, with minor K-feldspar, calcite and rutile. The Chelopez waste material consists mainly of quartz, dickite, kaolinite and pyrite, with minor svanbergite, barite, calcite and anatase.

Regarding the chemical composition, the Elatsite material has 29.96 wt% Si, 8.73 wt% Al and low quantity of S – 0.27 wt%. The Assarel material has 28.51 wt% Si, relatively low Al – 5.27 wt% and considerably high content of S – 3.92 wt%. The Chelopez material contains 30.78 wt% Si and 6.57 wt% Al, and the highest content of S – 7.41 wt% that has a significant effect during the experiments. The chemical composition is represented in elements and not in oxides, as accepted in the geological literature, since the ratio of the elements in the material is required for the present study.

The materials from the three mining wastes were treated following the four different procedures specified above, thus more than 90 experiments were implemented. About 25 of them produced solid, porous, insoluble products, which when soaked in distilled or demineralized water kept the pH values of the liquid close to neutral. The experimental products were soaked in demineralized water immediately after their cooling for one week. Three years later, the solubility was rechecked with soaking for a time of 2 weeks. During all this time the materials retained stable and the pH of the water was close to neutral. Successful results were obtained for all three waste materials, but especially from the mining waste of the Elatsite deposit. Due to the higher content of pyrite in the Chelopez material, it was very difficult to achieve successful sample, therefore the content of NaOH was increased, compared to that used for the other two tailings.

The XRD study of alkali-activated materials showed very pronounced differences both with respect to presented mineral phases and the amount of amorphous matter. Unlike typical geopolymers, where the bulk of material is amorphous, and crystalline phases (if any) are residues of unreacted primary minerals, the products obtained in this study contain moderate quantities of amorphous phase and newly formed crystalline phases, not represented in the initial material. In general, layered silicates like clinocllore, micas (muscovite, biotite,) and clays (kaolinite, dickite and illite) were found to disappear and K-feldspar (orthoclase) and plagioclase were found to be transformed into their high temperature forms. Pyrite is transformed to hematite and apparently sulfur is actively involved in the formation of nosean –  $\text{Na}_8(\text{Al}_6\text{Si}_6\text{O}_{24})\text{SO}_4 \cdot \text{H}_2\text{O}$ , a member of sodalite-group minerals. Nepheline is formed in all cases. All other mineral phases identified in the raw materials were also not detected, except for the quartz, which is identified in all XRD patterns and represents unreacted residual phase, and albite, which is identified especially in those materials with a high initial content as in the Elatsite deposit. The main crystalline phases in the Elatsite alkali-activated materials are sanidine (disordered high

temperature form of K-feldspar), quartz, nepheline, albite, and diopside with minor amount of hematite, nosean and apatite. Typical phases for the Assarel material are quartz, nepheline, albite, minor hematite, and nosean. In the Chelopech materials the main phases are quartz, nepheline, hematite, nosean and rarely cristobalite. The coexistence of nepheline with quartz is not contradictory because the system is not in equilibrium and quartz is present only as residue. In all alkali-activated materials an overall increase of background intensity is observed, which corresponds to the formation of amorphous phase. Most notably, the amorphous hump is developed in the alkali activated materials from Elatsite and Chelopech, in the range of  $2\theta$  values between approximately 15 and 35°.

SEM examination of the obtained alkali-activated samples reveals high porosity with vitreous nature that points to an intensive chemical interaction with NaOH, but non-uniform elsewhere in the volume of the sample. Some oval or angular quartz residues are established.

According to these results it can be seen that alkali activation in combination with high temperature curing leads to the transformation or decomposition of majority of existing minerals, and the formation of some new crystalline phases and amorphous matter. The highest degree of alkaline activation seems to be achieved with the Chelopech materials, where the only crystalline phase existed in the primary material, is quartz. The rest of minerals are transformed either into high temperature phases as nepheline or cristobalite or into amorphous matter. The high content of hematite is the result of the presence of pyrite which is widespread in the initial material. The formation of nosean is favored by the presence of sulfur in the material, but also strongly dependent on Na/Al ratio.

The results point out that the application of alkaline activation and high temperature curing on mining waste materials is a possibility to obtain new stable materials both to develop new approach for minimizing the negative environmental impact of tailing ponds and turn tailings into usable industrial product.

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