THE EFFECT OF ^{60}Co GAMMA IRRADIATION ON COAL FLY-ASH GEOPOLYMER PASTE SETTING TIME

by

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Cementation is the baseline technology for conditioning of low to intermediate level radioactive waste. Geopolymers, a class of alkali activated binders, are a promising new material for radioactive waste treatment. Coal fly-ash based geopolymers are a low-cost, low greenhouse gas footprint alternative to metakaolin based materials. Both the grouting of sludge/powders/liquids and encapsulation of solids/compacted waste rely on the grout maintaining optimal flow (rheological properties) during the mixing and pouring operations, and achieving a set leading to proper long term solidification (mechanical properties). The initial and final setting time for fly-ash geopolymer paste, based on the SRPS EN 196-3 standard, has been measured upon irradiation by gamma rays in a ^{60}Co reference field positioned with a kerma air rate of 3.42 mGys^{-1}. The binder paste was prepared using fly-ash from the TENT B power plant's electrostatic filters without further sieving, activated by water glass with module 1.5 and mixed with distilled water until a satisfactory flow was obtained, and poured into the sample and control molds. The initial and final setting times for the irradiated sample and non-irradiated control were determined by the Vicat apparatus. The irradiated sample demonstrated an 11 % shorter initial setting time, and 16 % shorter final setting time, compared to the control.

Key words: geopolymer, setting time, gamma irradiation, alkali-activated binder

INTRODUCTION

Inorganic binders have numerous applications in radioactive waste management, ranging from use as construction or shielding materials, to the solidifying of non-solid waste [1]. Materials based on a Portland cement binder (mortars, grouts and concretes) are essential in modern construction work. National and international standards, knowledge and experience from construction and civil engineering, and commercial availability of Portland cement have made it the material of choice for radioactive waste conditioning, with cementation being the baseline technology for conditioning of low level and intermediate level waste [2, 3]. Several challenges have been identified in such applications, such as the long term (a timescale of hundreds of years) stability of Portland cement materials due to the complex chemical reactions among the components of the material matrix, and interaction between environmental factors and the material. Several alternatives to Portland cement based materials have been considered, studied and used in practice, with varying results [4]. Geopolymers are a promising class of materials that exceed Portland cement in terms of compressive strength, fire resistance and retention of radionuclides upon leaching [5, 6]. Geopolymers are made by mixing fine aluminosilicate powder with an alkali activator solution. Upon activation (most frequently by sodium hydroxide or sodium silicate), aluminosilicates partially dissolve, forming an alkaline aluminosilicate hydrate gel (N-A-S-H) that solidifies by cross-linking into an amorphous solid with some zeolite crystallization [7]. The reference base material in geopolymer synthesis is metakaolin, but a wide array of powders, including industrial byproducts and wastes, can be used for production of materials with desirable properties [8]. There is a growing interest in the use of fly-ash from coal burning thermoelectric power plants in geopolymer applications [9]. Several studies have investigated the behavior of geopolymer materials under ionizing radiation, and indicated satisfactory properties for the immobilization of low to intermediate level radioactive waste [10, 11]. A special challenge in radioactive waste con-

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ditioning is the radiolysis of water leading to the release of hydrogen gas [12, 13]. One of the benefits of a geopolymer as the conditioning matrix is that, upon curing, the pore water can be removed by thermal treatment [5].

Both the grouting of sludge/powders/liquids and encapsulation of solids/compacted waste rely on the grout maintaining optimal flow (rheological properties) during the mixing and pouring operations, and achieving a set leading to proper long term solidification (mechanical properties). The binder setting time is the measurement of time needed for the phase change of binder paste [14]. The initial setting time indicates the beginning of the solidification of the gel, and the final setting time marks the end of the workability period of the binder, with the paste completely losing its plasticity. To the authors' knowledge, the experiments on geopolymer irradiation reported in the literature have been performed after setting, during the curing or aging phase – the materials have already solidified before irradiation. In the experiments and practical applications of radionuclide cementation, mechanical properties have been tested after the set and cure – the effect of radiation on the setting time has not been reported. In this study, we explored the effect of gamma irradiation on the initial and final setting time of the fly-ash geopolymer paste.

MATERIALS AND METHODS

Fly-ash from the TENT B thermoelectric coal plant (Obrenovac, Serbia) was activated with water glass (SiO_2/Na_2O = 1.5). Unfractionated fly-ash was used. The chemical composition and loss on ignition of the fly-ash used was reported by Komljenović *et al*., the data are presented in tab. 1 [15]. The binder paste was mixed by a manually operated power drill with a mixing attachment. Deionized water was incrementally added until satisfactory consistency of the binder was obtained. In total, 900 g of ash, 541 g of water glass, and 400 ml of water was used.

The paste was transferred to cylindrical plastic molds with glass bottoms, in accordance with the SRPS EN 196-3 standard[14]. Both the test and control sample were cast from the same batch of the binder. The samples were covered with plastic bags to prevent evaporation of water; then placed in transparent, thin walled plastic containers, in order to minimize the risk of ecological contamination of the irradiation room. The molds were oiled using synthetic motor oil for ease of separation after setting. The control sample was left to set in the work space shielded from the radiation, outside the irradiation room. The test sample was manually positioned in the irradiation area, and irradiated by lifting the source from the containment remotely, after clearing the room. The temperature of both the work and the irradiation area was in the 20 2 °C range during the experiment.

The sample was irradiated in the ^{60}Co reference field – IRPIK B device at the Secondary Standard Dosimetry Laboratory (SSDL), Vinča Institute of Nuclear Sciences. The sample was positioned in the field, and exposed to a kerma air rate of 12.32 Gyh^{-1}. The exposure times and absorbed dose in air are presented in tab. 2.

The Vicat apparatus was used to determine the initial and final setting time of the samples, by testing the set at regular intervals. The piston and needle weighed 300 g. For the initial set, a stainless steel needle with 1 mm diameter was used, and a penetration of less than 6 mm was used as the criteria for the set. After the initial set, the glass bottoms of the molds were slid off, and the molds with the paste were placed bottom up on the glass for determination of the final set. For the final set, a 1 mm diameter needle with a limiter/indicator disc was used, and penetration of less than 1 mm was used as the criteria for the set.

RESULTS AND DISCUSSION

The observed initial setting times were 3 hours 25 minute for the irradiated sample, and 3 hours 50 minute for the control sample. The observed final setting times were 4 hours 5 minute for the irradiated sample, and 4 hours 50 minute for the control sample. The comparison is given in fig. 1.

The irradiated sample had an 11.5 % shorter initial setting time, and 16.8 % shorter final setting time, compared to the control sample. The time from the initial to final set was 40 for the irradiated sample, and 60 for the control sample, indicating a 40 % faster setting for the irradiated sample.

Table 1. Chemical composition and loss on ignition, as a mass percentage of the fly-ash, as reported in [15]

Sample ID:	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO^3	LOI at 1000 °C
TENT B	54.26	24.90	6.50	6.34	1.89	2.51	2.06

Table 2. Irradiation times and reference values for the absorbed dose in air at the position where the experimental sample was placed during irradiation

Irradiaton sequence ID	Irradiation time interval Δt [h]	Increment of kerma air during the irradiation time interval, K_{air} [Gy]	Referred to the absorbed dose in air, $D_{air,tot}$ [Gy]
1	0.5	6.16	6.15
2	0.5	6.16	12.30
3	0.5	6.16	18.44
4	0.25	3.08	21.52
5	0.25	3.08	24.59
6	0.25	3.08	27.66
7	0.25	3.08	30.02

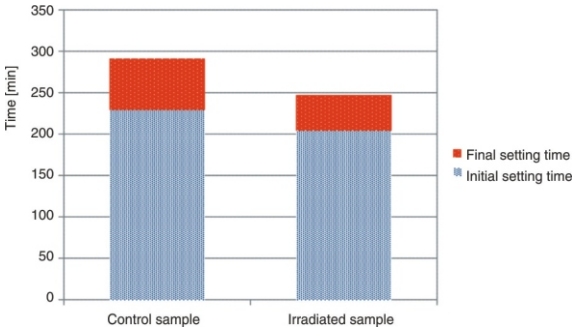

Figure 1. Initial and final setting times

During setting, some separation of water was observed at the contact of the plastic mold and glass bottom, and a small amount of unburnt coal particulates was observed on the surface of the paste, indicating excess water in the mixture. Since the binder was saturated with water during the setting, water loss through radiolysis did not lead to any observable exsiccation.

CONCLUSION

Irradiation by gamma rays of ^{60}Co accelerates the set of the fly-ash geopolymer binder paste. Exposure to a kerma air rate 12.32 Gyh^{-1} and absorbed dose in air of 30 Gy did not lead to flash setting, nor delayed setting. The observed effect is not detrimental to the potential practical application of the fly-ash geopolymer in radioactive waste conditioning. Further research is needed to explore the functional relation of the irradiation field and dose characteristics and geopolymer setting times. These insights into the effects of gamma ionizing radiation on the kinetics of chemical reactions in alkali activated binders shall aid in the optimization of geopolymer formulations and preparation procedures for specific applications in radioactive waste management and radiation protection.

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AUTHORS' CONTRIBUTIONS

All measurements were performed by S. J. Stanković and L. Z. Rubinjoni. The manuscript was prepared by L. Z. Rubinjoni, and reviewed by B. B. Lončar and S. J. Stanković. All authors developed the concept of the experiment, analyzed the data and discussed the results.

REFERENCES

[1] Stanković, S. J., *et al*., Gamma Radiation Absorption Characteristics of Concrete with Components of Different Type Materials, Acta Physica Polonica, Series A: General Physics, Physics of Condensed Matter, Optics and Quantum Electronics, Atomic and Molecular Physics, *Applied Physics, 117* (2010), 5, pp. 812-816
[2] Glasser, F., Application of Inorganic Cements to the Conditioning and Immobilisation of Radioactive Wastes, in: *Handbook of Advanced Radioactive Waste Conditioning Technologies*, Woodhead Publishing, Sawston, UK, 2011, pp. 67-135
[3] Dimović, S. D., *et al*., Leaching Kinetics of Cs+ and Co^{2+} Under Dynamic Conditions, *Nucl Technol Radiat, 34* (2019), 3, pp. 243-248.
[4] Mobasher, N., *et al*., Gamma Irradiation Resistance of an Early Age Slag-Blended Cement Matrix for Nuclear Waste Encapsulation, *Journal of Materials Research, 30* (2015), 9, pp. 1563-1571
[5] Vance, E. R., Perera, D. S., Development of Geopolymers for Nuclear Waste Immobilisation, in: *Handbook of Advanced Radioactive Waste Conditioning Technologies,* Woodhead Publishing, Sawston, UK, 2011, pp. 207-229
[6] Cantarel, V., *et al*., Geopolymers and Their Potential Applications in the Nuclear Waste Management Field, A Bibliographical Study, Japan Atomic Energy Agency, Tokio, Japan, 2017
[7] Lichvar, P., *et al*., Behaviour of Aluminosilicate Inorganic Matrix Sial During and After Solidification of Radioactive Sludge and Radioactive Spent Resins and Their Mixtures, (2013), (No. IAEA-TECDOC-CD--1701 (COMPANION CD))
[8] Provis, J., Rees, C., Geopolymer Synthesis Kinetics, in: *Geopolymers*, Woodhead Publishing, Sawston, UK, 2009, pp. 118-136
[9] Komljenović, M., *et al*., Mechanical and Microstructural Properties of Alkali-Activated Fly Ash Geopolymers, *Journal of Hazardous Materials, 181* (2010), 1-3, pp. 35-42
[10] Leay, L., *et al*., Geopolymers from Fly Ash and Their Gamma Irradiation, *Materials Letters, 227* (2018), Sept., pp. 240-242
[11] Lambertin, D., *et al*., Influence of Gamma Ray Irradiation on Metakaolin Based Sodium Geopolymer, *Journal of Nuclear Materials, 443* (2013), 1-3, pp. 311-315
[12] Chupin, F., *et al*., Water content and Porosity Effect on Hydrogen Radiolytic Yields of Geopolymers, *Journal of Nuclear Materials, 494* (2017), Oct., pp. 138-146
[13] Cantarel, V., *et al*., On the Hydrogen Production of Geopolymer Wasteforms Under Irradiation, *Journal of the American Ceramic Society, 102* (2019), 12, pp. 7553-7563
[14] ***, SRPS EN 196-3:2017, Methods of Testing Cement-Part 3: Determination of Setting Times and Soundness, The Institute for Standardization of Serbia, 2017
[15] Komljenović, M., *et al*., Fly Ash as the Potential Raw Mixture Component for Portland Cement Clinker Synthesis, *J. Therm. Anal. Calorim., 96* (2009), 2, pp. 363-368

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ЕФЕКАТ ^{60}Co ГАМА ОЗРАЧИВАЊА НА ВРЕМЕ ВЕЗИВАЊА ГЕОПОЛИМЕРА – ПАСТЕ ЕЛЕКТРОФИЛТЕРСКОГ ПЕПЕЛА УГЉА

Цементирање је основна технологија за кондиционирање радиоактивног отпада ниске до средње активности. Геополимери, класа алкално активираних везива, су перспективни нови материјали за третман радиоактивног отпада. Геополимери на бази електрофилтерског пепела угља су економски повољна алтернатива материјалима на бази метакаолина, и доводе до укупно мање емисије гасова стаклене баште. И цементирање муљева/прашкастих материјала/течности, и енкапсулација чврстог или компактираног отпада се заснивају на томе да везиво задржи оптималну течљивост (реолошке особине) током операција мешања и изливања, и да оствари везивање које ће водити до доброг дугорочног очвршћавања (механичке особине). На основу стандарда SRPS EN 196-3, иницијално и финално време везивања за пасту геополимера од електрофилтерског пепела мерено је након озрачивања гама зрацима у референтном пољу ^{60}Co, на позицији са кермом у ваздуху од 3.42 mGys^{-1}. Везивна паста је припремљена употребом пепела из термоелектране ТЕНТ Б, сакупљеног са електростатичких филтера без даљег просејавања, активирана воденим стаклом модула 1.5, мешана уз додатак дестиловане воде до постизања задовољавајуће течљивости, и разливена у калупе за озрачивање и контролу. Иницијално и финално време везивања за озрачени узорак и неозрачену контролу утврђени су употребом Викат апарата. Озрачени узорак је показао 11 % краће иницијално време везивања, и 16 % краће финално време везивања, у поређењу са контролом.

Кључе речи: геополимер, време везивања, гама озрачивање, базом активирано везиво