Measuring geopolymer set times under ionizing radiation - advances in instruments and procedures

Luka Rubinjoni, Srboljub Stanković, Aco Janićijević

***Abstract*— Geopolymers are a class of alkali activated binders, and present a viable alternative to Portland cement. Utilization of geopolymers is a way to reduce greenhouse gas emissions and utilize secondary materials.Geopolymers are becoming a material of choice in radioactive waste conditioning, for grouting and encapsulation. Binder set times are a key parameter in determining the workability of grouts, mortars and concrete. While studying the effects of ionizing radiation on geopolymer set times, we were constrained by the configuration of the irradiation device and field, so we developed a modified Vicat apparatus, sample case/phantom, and temperature/humidity monitor. The modified procedure has allowed for a better temporal resolution of the measurements, with continuous monitoring of the experimental conditions. Fly-ash geopolymer set times under Co-60 gamma radiation are presented.**

***Index Terms*— gamma radiation; geopolymer; set time; Vicat apparatus.**

I. Introduction

Geopolymers are a class of alkali activated binders. When fine aluminosilicate powder is mixed with a strong alkaline solution, it partially dissolves and forms a gel that solidifies into an amorphous binder with some crystallization. For example, the activation of fly ash by water glass produces a binder held together by sodium-aluminium-silicate-hydrate gel (NASH gel).[1] Interest in alkali activated binders in general, and geopolymers in particular, is growing because they present a viable alternative to Portland cement in many applications. Production of binders based on secondary materials (that would otherwise have to be managed as waste) enables the reduction of both total greenhouse gas emissions, and reduction of unutilized solid waste.[2] Geopolymer formulations are more resistant to high temperatures, compared to Portland cement, and often excel in terms of mechanical strength.

Geopolymers are becoming a material of choice in radioactive waste conditioning, suitable for different operations. Geopolymers can be used as sorbents to bind radionuclides from solutions and reduce the volume of waste, as grouts for the solidification of sludge and other non-solids, or for encapsulation of solids such as compressed waste drums.[3] The common approach in this field is to first test and optimize the mixture using radiostable ("cold") waste simulants, followed by confirmation with the use of actual radioactive ("hot") waste.

Binder set times are a key parameter in determining the workability of grouts, mortars and concrete, and their measurement is standardized for Portland cement in construction and civil engineering applications.[4] Initial set time indicates the beginning of the solidification of the binder, and final set time indicates the end of practical workability.[5] Vicat apparatus and a time piece are used to determine the set times. Vicat apparatus consists of a weighted needle on a frame guide – the penetration of the needle into the sample is measured at regular intervals.

We have based our research on the encapsulation use case: the flowing grout is poured in a vessel containing compressed waste drums, thus the binder is exposed to gamma radiation, but is not directly mixed with the waste. We have investigated the effect of gamma irradiation on fly ash geopolymer set times by irradiating freshly prepared binder paste during setting. Adopting to the constraints imposed by the configuration of the irradiation field at our disposure, we have devised and fabricated a number of devices that improved the temporal resolution of our measurements.

II. Materials and Methods

In our previous work, we have irradiated fly ash geopolymer paste we have prepared on site.[6] The humidity of the paste was maintained by keeping the molds in plastic bags during setting. We have taken further precaution not to contaminate the room with the radioactive source by putting the irradiated sample mold into a plastic container. The procedure required removing the container with the sample from the irradiation room, removing the sample from both the container and the plastic bag, measuring the penetration of the Vicat needle, returning the sample into both the plastic bag and the container, and repositioning the container in the irradiation room. The control sample was kept outside the irradiation room, inside a plastic bag to prevent evaporation, and had to be removed and returned to the bag for every measurement. We have modified the procedure as following: the irradiated and control sample are placed above water in a

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closed case. A modified Vicat apparatus is used to measure penetration without moving the cases, or removing the sample from the case. Temperature and relative humidity are continuously monitored both within the cases and in the laboratory and the irradiation room.

A. Sample case/phantom

A pair of cases was constructed from cast 1cm thick polymethyl methacrylate (PMMA, Plexiglass), dimensions 32x32x21 cm, with four 4x4x3 cm stands on the bottom corners. Polystyrene foam lids were used to close the cases. Case dimensions match the commonly used water phantoms, and can be used that way. For this experiment, the cases were partially filled with water, so that the samples remained above the water line. The phantom with the bridge is depicted in Figure 1.

B. Mold and mold stan

Conical plastic molds Ø 70/80x40 mm high, following EN, NF specifications (Matest S.p.A, Italy) were used. Instead of glass base plates, plexiglass stands were constructed. The plates were made from 5 mm thick extruded plexiglass pane, a 90x90 mm square supported by five 40x40 mm squares for a total height of 45 mm.

C. Bridge / Vicat holder

A bridge for positioning the Vicat probe was constructed from 10 mm thick extruded plexiglass pane. The bridge is positioned on top of the sample case during measurement, and keeps the probe vertical, perpendicular to the sample surface. The probe is joined to the bridge by a clamp, and secured in position by teflon screws. The final penetration depth can be finely adjusted by a screw on top of the probe holder. Another screw holds the weighted needle in place during positioning, and is used to release the needle during measurement. 3D model of the bridge and Vicat holder are depicted in Figure 2.

D. Temperature and humidity monitor

Four DHT22 capacitative digital temperature and relative humidity sensors were connected, using 10 m of cable each, to a common Arduino Nano board with LCD screen. Temperature and relative humidity were monitored on the LCD screen, and on the computer terminal connected via a USB cable. Cables were led from the laboratory to the irradiation room via the existing cable port, not interfering with the safety features of the lab. Four measurement points enabled the monitoring both in the sample cases, and in the surrounding rooms.

E. Geopolymer preparation

Coal fly ash from TENT B thermoelectric power plant (Obrenovac, Serbia) was mechanically activated by vibrational mill. At the beginning of the experiment, the ash was mixed with water glass activator (Galenika Magmasil, Serbia) of modulus s=1,5 and NaO%mass=10%, with powder/activator ratio of 0.8, and thoroughly mixed using an electric mixer. The time of the mixing of the powder and the activator was noted. The molds and stands were coated in machine oil, and filled with fresh binder paste. The molds were tapped by hand to eliminate air and ensure uniform fill.

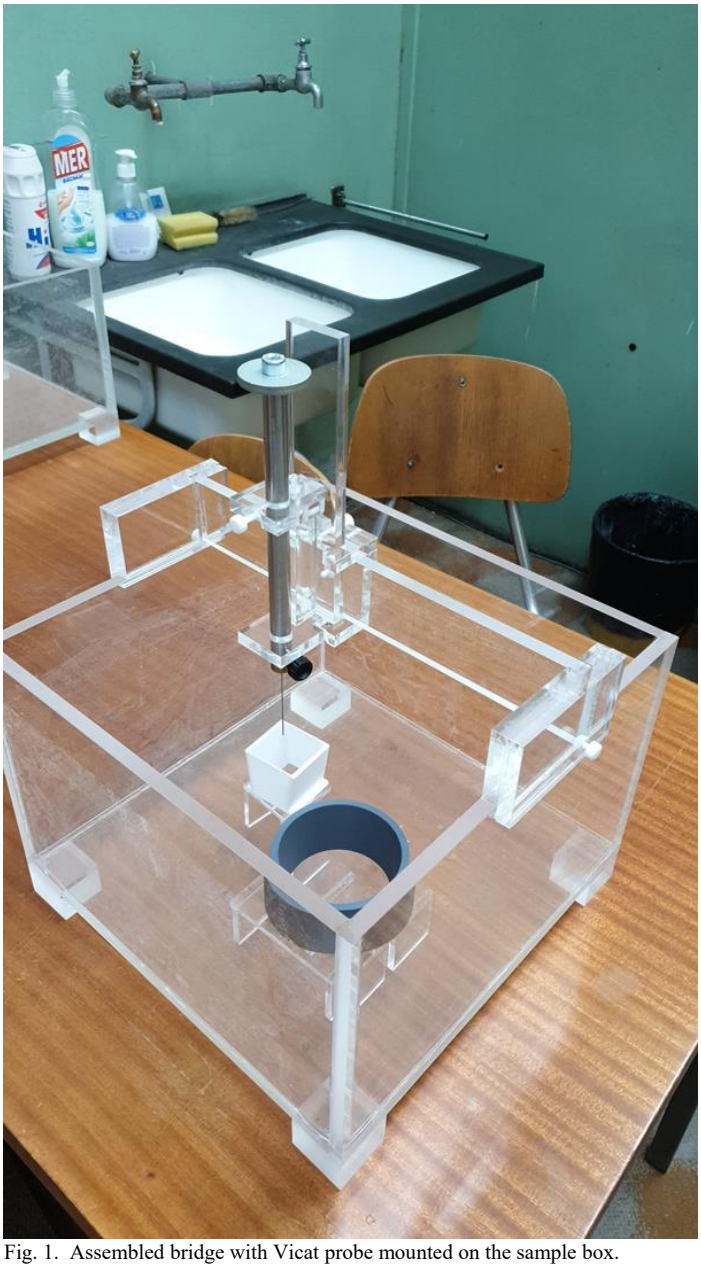

Fig. 1. Assembled bridge with Vicat probe mounted on the sample box.

F. Irradiation and measurement of set times

The experiment was performed at Vinča Institute of Nuclear Sciences. The sample was irradiated in the 60Co reference field – IRPIK B device at the Secondary Standard Dosimetry Laboratory (SSDL), at kerma air rate of 9.528 Gyh–1. In preparation for the irradiation, laboratory and irradiation room were cooled to 20° C. Sample cases were partially filled with water, closed, and left to equalize with the room temperature. Sensor wires were safely positioned, and sensors were positioned in place using strong adhesive tape. An empty mold was used to precisely position the irradiated sample case. Geopolymer samples were placed in the irradiation and control cases, and the field was activated by rising the 60Co source. The irradiation was interrupted at intervals in order to perform the penetration measurements by opening the sample case, positioning the bridge on top, positioning and releasing the Vicat needle and noting the time

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and penetration into the sample (without moving the sample). Upon measurement, the bridge was removed, case lid repositioned, the researcher safely left the irradiation room, and field was reactivated. The control sample was measured in the same way, as close as possible to the time of the irradiation sample.

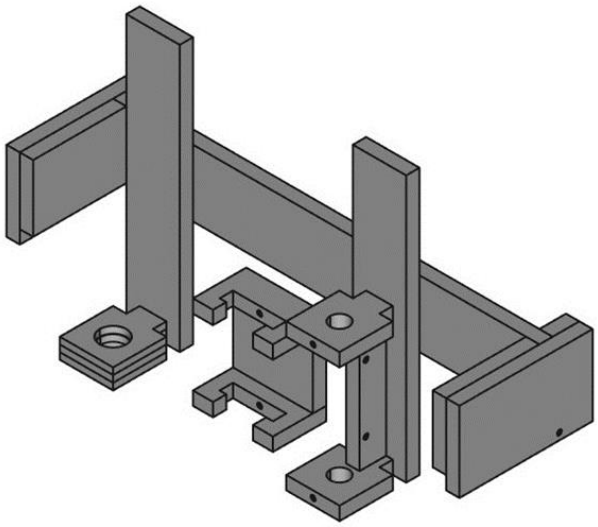

Fig. 2 Bridge, clamp, and two probe holders (Vicat holder on the right).

III. Results

Total duration of the irradiation was 2h 35min. Initial set time for both pastes was at 3h 37min. Final set time for irradiated paste was at 4h, and 4h 20min for the control paste. The timeline of the experiment is given in Table 1.

The laboratory and the irradiation room were kept at 20° C using the HVAC system, which proved sufficient to maintain the temperature of 20° C in the sample cases. Relative humidity in the sample boxes was over 90% while they were closed, would drop to about 75% during opening and measurement, and rise to over 90% within minutes of the repositioning of the lids.

The only issue with the sensors was the strength of the adhesive tape: common, thin and transparent tape would detach because of humidity, so strong tape had to be used.

IV. Conclusion

With improved procedure and devices, we have managed to repeatedly and consistently measure the penetration of the Vicat needle in irradiated and control samples within two minutes. Simultaneous measurement would require an automatic Vicat apparatus, which is not practical for irradiation experiments. The dose rate 9.528 Gyh–1 showed no effect on initial set times, and the observed reduction of final set time for the irradiated paste does not pose a problem for practical applications, such as encapsulation of waste.

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TABLE I
Experiment timeline

Time	Irradiated sample	Control sample
16:40	Paste mixed, beginning	Paste mixed, beginning
16:56	First dose start, 1h	
18:57	First dose stop	
18:59	Penetration 40 mm	Penetration 40 mm
19:00	Second dose start, 1h	
19:58		Penetration 12-18 mm
20:00	Second dose stop, further irradiation duration is 5 minutes each	
20:01	Penetration 4-15 mm	
20:07		Penentration <6 mm, initial set time
20:08	Penentration <6 mm, initial set time	
20:11	Pen. >1 mm	
20:12		Pen. >1 mm
20:17	Pen. >1 mm	
20:18		Pen. >1 mm
20:22	Pen. >1 mm	
20:23		Pen. >1 mm
20:29	Pen. >1 mm	
20:30		Pen. >1 mm
20:35	Pen. >1 mm	
20:36		Pen. >1 mm
20:41	Penetration >1 mm, final set time, end of irradiation	
20:42		Pen. >1 mm
20:47		Pen. >1 mm
20:55		Pen. >1 mm
21:00		Penetration >1 mm, final set time, end of experiment

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