



DuraLith geopolymer waste form for Hanford secondary waste: Correlating setting behavior to hydration heat evolution



Hui Xu, Weiliang Gong*, Larry Syltebo, Werner Lutze, Ian L. Pegg

Vitreous State Laboratory, The Catholic University of America, 620 Michigan Avenue NE, Washington, DC 20064, USA

HIGHLIGHTS

- Quantitative correlations firstly established for cementitious waste forms.
- Quantitative correlations firstly established for geopolymeric materials.
- Ternary DuraLith geopolymer waste forms for Hanford radioactive wastes.
- Extended setting times which improve workability for geopolymer waste forms.
- Reduced hydration heat release from DuraLith geopolymer waste forms.

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ABSTRACT

The binary furnace slag-metakaolin DuraLith geopolymer waste form, which has been considered as one of the candidate waste forms for immobilization of certain Hanford secondary wastes (HSW) from the vitrification of nuclear wastes at the Hanford Site, Washington, was extended to a ternary fly ash-furnace slag-metakaolin system to improve workability, reduce hydration heat, and evaluate high HSW waste loading. A concentrated HSW simulant, consisting of more than 20 chemicals with a sodium concentration of 5 mol/L, was employed to prepare the alkaline activating solution. Fly ash was incorporated at up to 60 wt% into the binder materials, whereas metakaolin was kept constant at 26 wt%. The fresh waste form pastes were subjected to isothermal calorimetry and setting time measurement, and the cured samples were further characterized by compressive strength and TCLP leach tests. This study has firstly established quantitative linear relationships between both initial and final setting times and hydration heat, which were never discovered in scientific literature for any cementitious waste form or geopolymeric material. The successful establishment of the correlations between setting times and hydration heat may make it possible to efficiently design and optimize cementitious waste forms and industrial wastes based geopolymers using limited testing results.

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1. Introduction

The most hazardous radioactive wastes, generated in large quantities during 1943–1989 from extracting plutonium from dissolved spent nuclear fuel in support of the US defense program, are currently stored in 177 underground tanks at the Hanford Site in Washington State [1,2]. For long-term safe stabilization and disposal of these wastes, the US Department of Energy (DOE) is constructing the Hanford Tank Waste Treatment and Immobilization Plant (WTP), which will convert these wastes into stable glass via vitrification. Processing of the tank wastes in the WTP will

generate solid and liquid secondary wastes. The liquid Hanford secondary waste (HSW), which may include process condensate and liquid effluents from off-gas treatment systems, will be sent to the Effluent Treatment Facility (ETF), a Resource Conservation and Recovery Act (RCRA)-permitted multi-waste treatment and storage unit for low-level and mixed-waste water. Since treatment of the HSW stream from the WTP is expected to involve solidification, a testing program was initiated to support the evaluation and selection of suitable waste forms [3,4]. The candidate waste forms included Cast Stone (a cementitious composite) [5], DuraLith (a geopolymer) [6], a fluidized-bed steam reformer (FBSR) granular product encapsulated in a geopolymer matrix [7], and Ceramicrete (a phosphate bonded ceramic) [8]. Further testing was performed on Cast Stone, DuraLith, and Ceramicrete to assess the viability of each candidate [9]. The test results showed that DuraLith

* Corresponding author. Tel.: +1 202 319 5393; fax: +1 202 319 4469.
E-mail address: gongw@vsl.cua.edu (W. Gong).

geopolymer waste form continued to be promising. However, further study is needed to assess the potential for improvements in performance of the waste form.

Geopolymers, first proposed by Davidovits in the late 1970s, are a class of alkaline-activated aluminosilicate binder materials featuring a predominantly X-ray amorphous nature [10–12]. The fundamental structure of geopolymers is an aluminosilicate gel network consisting of tetrahedral coordination of Si and Al atoms linked by oxygen bridges, with alkali metal cations (typically Na^+ and/or K^+) associated as charge balancers for AlO_4^- [13,14]. Geopolymeric materials have been investigated as waste forms for solidification/stabilization of chemically hazardous and/or radioactive wastes as well as durable green construction materials [15–18]. Specifically, the resistance of geopolymers to attack of chemicals such as sulfuric, nitric, hydrochloric and organic acids, is far better than that of ordinary Portland cement (OPC) [19,20], making geopolymer waste forms a promising alternative for immobilization of various hazardous wastes.

Based on geopolymer chemistry, DuraLith waste forms can be adjusted and optimized for specific requirements of radioactive waste stabilization, specific ingredients employed, and specific additives used to enhance the immobilization of hazardous elements and radionuclides such as ^{99}Tc and ^{129}I [6,21]. The binary furnace slag-metakaolin DuraLith waste form investigated for HSW has demonstrated superior mechanical strength and comparable chemical durability to those of the other waste form candidates [9]. However, the initial binary DuraLith formulations showed relatively rapid setting behavior [6] and larger margins to allow for process upsets would be desirable. Besides, although geopolymer waste forms have been attracting increasing interests for immobilization of radioactive and chemically hazardous wastes [22–24], their hydration heat evolutions for high loading of complex waste like HSW remained uninvestigated. Moreover, to the authors' best knowledge, no quantitative relationship has ever been established between setting times and hydration heat for any cementitious waste form or geopolymeric material.

Thus, this study aimed at improving the setting behavior of the DuraLith geopolymer waste form without significantly degrading the chemical durability. For this purpose, a Class F fly ash was introduced into the binary furnace slag-metakaolin DuraLith system at up to 60 wt% of the composite binder material. Early stage hydration heat releases from the ternary DuraLith waste form pastes were investigated by isothermal calorimetry. An attempt

Table 2

Composition of baseline Hanford secondary waste stream simulant HSW S1-1X containing 1 mol/L of sodium.

Constituent	Concentration (mol/L)
Na	1
$\text{Al}(\text{OH})_3$	9.39E–02
Si	1.88E–03
K	5.82E–04
OH^-	3.98E–01
NO_3^-	3.28E–01
CO_3^{2-}	2.28E–02
Cl^-	2.25E–02
NO_2^-	1.20E–02
PO_4^{3-}	6.87E–03
SO_4^{2-}	4.41E–03
F^-	5.57E–04
Cr	2.03E–04
Ag	6.27E–06
As	3.48E–05
Cd	1.57E–06
Pb	8.99E–06
Tc	1.81E–05
I	4.62E–06
TOC^a	9.39E–02

^a Total organic carbon.

was made to quantitatively relate both initial and final setting times to the calorimetric data. Chemical durability and mechanical strength were determined on cured ternary DuraLith waste form samples by the Toxicity Characteristic Leaching Procedure (TCLP) [25] and compressive strength tests, respectively.

2. Materials and methods

2.1. Raw materials

The three composite binder materials used in this study are Class F fly ash (FFA) from SEFA Group, ground blast furnace slag (BFS) from Lafarge North America, and metakaolin (MK) from Thiele Kaolin Company. Silica fume from Norchem Incorporation and dry sand were employed as reactive filler and fine aggregate, respectively. The chemical compositions of the raw materials, except for sand, were analyzed by X-ray fluorescence (XRF), and the results are shown in Table 1.

2.2. HSW simulants and activating solution

The composition of the HSW simulant S1 is shown in Table 2. This simulant S1 is representative of the composition of a projected waste stream from the off-gas treatment system in the Hanford WTP nuclear waste vitrification system. More specifically, it represents the immobilized low-activity waste off-gas caustic scrubber effluent downstream of the high-efficiency particulate air (HEPA) filters [4,6,9]. The sodium concentration in the simulant is 1 mol/L and thus the identification for the simulant is HSW S1-1X. In this study, the sodium concentration was increased from the baseline of 1 to 5 mol/L based on the assumption that the stream could be concentrated by evaporation in order to increase the loading into the solidified waste form. Accordingly, the concentrated simulant containing 5 mol/L of sodium was identified as HSW S1-5X.

The concentrated simulant HSW S1-5X was employed to make the activating solution. Solid NaOH and KOH were added slowly into the simulant under mechanical stirring and silica fume was then added. Stirring was continued overnight to obtain a homogeneous liquid. No additional water was used for preparation of the activating solution from the concentrated HSW simulant. Since the radionuclide ^{99}Tc is assumed to occur in the HSW stream in its most soluble form of pertechnetate TcO_4^- , Re as NaReO_4 was

Table 1
Chemical compositions of composite binder materials and reactive filler (wt%).

Oxide	Furnace slag	Metakaolin	Fly ash	Silica fume
Al_2O_3	9.97	42.42	28.91	0.34
BaO	0.11	0.01	0.20	0.00
CaO	40.72	0.03	1.66	0.86
Cr_2O_3	0.00	0.03	0.03	0.00
CuO	0.00	0.01	0.03	0.01
Fe_2O_3	0.48	0.52	6.81	0.73
K_2O	0.44	0.17	2.73	0.73
MgO	8.22	0.00	0.94	0.45
MnO	0.40	0.00	0.027	0.09
Na_2O	0.20	0.23	0.51	0.00
P_2O_5	0.21	0.26	0.52	0.13
PbO	0.00	0.00	0.01	0.00
SO_3	1.12	0.08	0.51	0.24
SiO_2	37.10	53.29	53.27	94.87
SrO	0.05	0.00	0.13	0.00
TiO_2	0.49	2.05	1.47	0.00
V_2O_5	0.03	0.03	0.00	0.00
ZnO	0.00	0.00	0.02	0.04
ZrO_2	0.02	0.00	0.06	0.00
LOI ^a	0.43	0.82	2.08	1.39

^a Loss on ignition.

Table 3

Recipe for 20 liters of Hanford secondary waste stream simulant HSW S1-5X containing 5 mol/L of sodium.

Order of addition	Analyte	Target mol/L	Reagent	Assay	Target mass (g)
1	Ag	3.10E–5	AgNO ₃	0.999	0.107
1	As	1.74E–4	Na ₂ HAsO ₄ ·7H ₂ O	1.000	1.086
1	Al	4.70E–1	Al(OH) ₃	0.990	957.456
1	Cd	7.85E–6	Cd(NO ₃) ₂ ·4H ₂ O	0.985	0.049
1	CO ₃ ^{2–}	1.14E–1	Na ₂ CO ₃	1.000	241.702
1	Cr	1.02E–3	Na ₂ Cr ₂ O ₇ ·2H ₂ O	0.990	6.110
1	PO ₄ ^{3–}	3.44E–2	Na ₂ HPO ₄ ·7H ₂ O	0.990	185.963
1	Si	9.40E–3	Na ₂ SiO ₃	0.980	23.416
1	SO ₄ ^{2–}	2.21E–2	Na ₂ SO ₄	0.990	63.271
1	NO ₃ [–]	1.64	NaNO ₃	0.980	2839.233
1	NO ₂ [–]	6.00E–2	NaNO ₂	0.980	84.484
1	Cl	1.13E–1	NaCl	0.980	134.180
1	F	2.79E–3	NaF	0.990	2.274
1	K	2.92E–3	KNO ₃	0.990	5.954
1	Pb	4.50E–5	Pb(NO ₃) ₂	0.990	0.301
1	TOC ^a	4.16E–1	Na ₂ C ₂ O ₄	0.980	1137.524
1	TOC ^a	5.35E–2	C ₂ H ₂ O ₄ ·2H ₂ O	0.980	137.751
2	H ₂ O		H ₂ O	1.000	16,824.010
3	OH [–]	1.99	NaOH	0.987	1614.191
4	Tc	5.37E–4	HReO ₄	0.562	3.561
Total					24,265.381

^a Total organic carbon.**Table 4**

Recipe for 15 kg of activator solution prepared from concentrated Hanford secondary waste simulant HSW S1-5X.

Chemical	Weight (g)	Order of addition
HSW S1-5X	9992.7	1
KOH	2148.2	2
NaOH	183.9	2
Silica fume	2680.4	3

spiked into the waste to simulate the ⁹⁹Tc. The recipes for preparing HSW simulant S1-5X and the activator solution are presented in Tables 3 and 4, respectively.

2.3. Sample preparation

DuraLith geopolymers waste form samples were prepared with 0, 15, 30, 45 and 60 wt% of FFA in the composite binder material as a substitute for BFS. The MK content was kept constant at 26 wt%. The enhancers, i.e., Ag-zeolite, Na₂S, and copper slag used in the binary DuraLith waste forms [6], were not included for simplicity. The water/binder ratio was fixed at 0.371 and the concentration of (K + Na) was 8.75 mol/L. The solids were weighed and transferred into a 5-gal bucket and mixed with a hand-held mixer (UNITEC Mixer EHR 23/1.3R) for about 2 min. Then, the activator solution was poured into the solids and the mixing was continued for a few minutes to obtain a pourable geopolymer paste. The fresh paste was immediately transferred into 2 inch × 4 inch cylindrical plastic molds, followed by vibration on a vibrating table to remove air bubbles. Finally, the prepared samples were sealed with lids and cured at room temperature. The mix designs for the ternary DuraLith geopolymer waste forms are presented in Table 5.

Table 5

Mix designs for ternary fly ash-furnace slag-metakaolin DuraLith geopolymer waste forms.

Sample ID	Mass (g)					
	Fly ash	Furnace slag	Metakaolin	Sand	Silica fume	Activator solution
6XA	0.0	1473.3	511.6	938.3	49.4	2000.7
6XB	294.7	1178.7	511.6	938.3	49.4	2000.7
6XC	589.3	884.0	511.6	938.3	49.4	2000.7
6XD	884.0	589.3	511.6	938.3	49.4	2000.7
6XE	1178.7	294.7	511.6	938.3	49.4	2000.7

2.4. Methods of analyses

Initial and final setting times were measured on two Vicatronic E044N automatic Vicat needle penetration instruments (Matest, Italy). Early stage hydration heat evolutions of fresh DuraLith geopolymer waste form pastes were recorded on an eight-channel TAM Air isothermal calorimeter (TA Instruments, USA) at 25 °C, and compressive strength of cured DuraLith geopolymer waste form samples was measured on a CM-4000-SD instrument (Test Mark Industries, USA) following the ASTM C39 standard [25]. The chemical durability of the ternary DuraLith geopolymer waste forms was determined using the TCLP leach test [26].

3. Results and discussion

3.1. Setting times

The initial and final setting times of the DuraLith geopolymer waste form samples were measured following the method for automatic Vicat needles described in the ASTM C191 standard [27]. However, the time interval between two penetrations was modified to 36 min to accommodate the longer setting times of ternary DuraLith geopolymer waste forms. It should be noted that the reading of the Vicatronic apparatus is the balance of 40 minus the penetration height in mm. The initial setting times were calculated to the nearest 1 min as follows

$$\frac{H-E}{C-D} \times (15-D) + E \quad (1)$$

where H = time in minutes of the first reading greater than 15 mm, E = time in minutes of the last reading smaller than 15 mm, C = reading at time H , and D = reading at time E . The determined

Table 6

Initial and final setting times of ternary fly ash-furnace slag-metakaolin DuraLith geopolymer waste forms.

Sample ID	Initial setting (min)	Final setting (min)
6XA	378	468
6XB	462	576
6XC	554	684
6XD	631	828
6XE	921	1116

initial and final setting times are presented in Table 6. It is evident that both the initial and final setting times increased with the increase of FFA content in the waste form. The initial setting times are in the range of 378–921 min, far longer than the typical 150 min observed for the binary DuraLith waste forms [6] as intended.

It is known that geopolymerization of low-calcium Class F fly ash may be very slow at ambient temperatures [28–30], and that the relatively low reactivity of the fly ash usually leads to slow setting of the fresh paste and poor compressive strength of the hardened material [31–33]. Therefore, the incorporation of FFA into the binder materials is believed to be responsible for the increase of the setting times. Besides, elevated curing temperatures of 40–85 °C may accelerate the geopolymerization of fly ash [34–36]. Thus the reduced hydration heat, as observed from calorimetry measurements in Section 3.2, may also contribute to the extended setting times.

3.2. Isothermal calorimetry

The normalized heat flows and normalized heats of DuraLith geopolymer waste form samples, as measured by isothermal calorimetry at 25 °C, are shown in Figs. 1 and 2. Since an equilibration time is needed after placing the samples into the calorimeter, any minor dissolution peaks, which typically occur immediately after the addition of activating solution to the binder materials [37], were not captured. The reaction time in Figs. 1 and 2 has been adjusted for each sample starting from the beginning of the wet mixing. As shown in Fig. 1, all the heat flow peaks center at around 148 min, which may be determined by the highly reactive MK and BFS in the composite binder materials. The height and sharpness of the peaks, however, is affected by the FFA content. Fig. 2 shows that the total hydration heat release decreased with the increase of the FFA content.

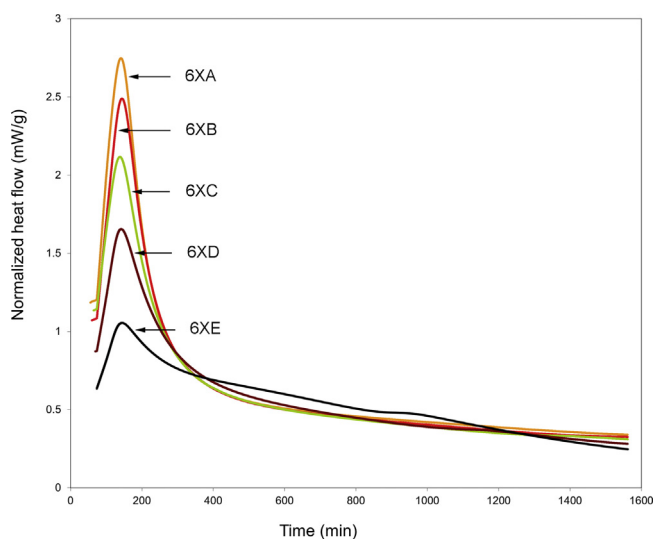


Fig. 1. Normalized heat flows of DuraLith geopolymer waste forms.

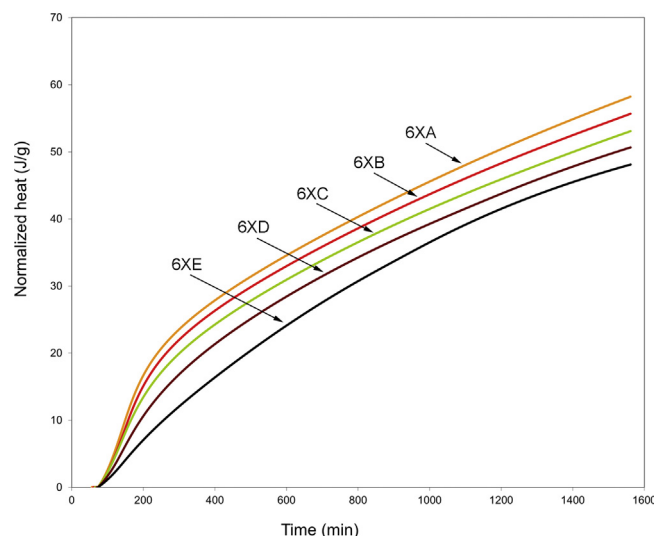


Fig. 2. Normalized heats of DuraLith geopolymer waste forms.

3.3. Correlating setting times to hydration heat

It is reasonable to expect that the setting behaviors of cementitious waste forms have a direct relationship to the kinetics of their hydration reactions. De Schutter and Taerwe [37] employed the degree of reaction as a means of determining the hydration degree for Portland and blast furnace slag cements. They defined the degree of reaction at time t as the fraction of the total heat of hydration that has been released up to that time, as shown in Eq. (2)

$$R(t) = \frac{Q(t)}{Q_{\max}} = \frac{1}{Q_{\max}} \int_0^t q(t) dt \quad (2)$$

where $R(t)$ is the reaction degree at time t ; $Q(t)$, the accumulated heat released at time t ; $Q_{\max}$, the total heat released; and $q(t)$, the measured heat flow as a function of time.

Similar to the case of cementation, geopolymerization is known to be an exothermic process [6,10]. Therefore, we introduced Eq. (2) to the calorimetric data obtained for the ternary DuraLith waste forms. This may allow us to calculate the reaction degrees at the initial and final setting time points for each sample. However, it should be noted that the reaction in geopolymerization process is different from that of cement, although both are exothermic. An attempt was further made to correlate the reaction degrees calculated from hydration heat to the initial and final setting times. As a result, near-perfect linear relationships between hydration heat and both initial and final setting times were obtained, as presented in Fig. 3. As the fly ash content increased, a progressively larger fraction of the total heat had been released before either initial setting or final setting occurred.

3.4. Compressive strength

Compressive strength tests were conducted on DuraLith geopolymer waste form samples after curing ages of 7, 14, and 28 days. As shown in Fig. 4, the replacement of BFS by FFA in DuraLith geopolymer waste forms led to lower compressive strength and the strength decreased with increasing FFA content. After curing for 28 days, sample 6XE with 60 wt% of FFA in the composite binder materials developed a compressive strength of 57.5 MPa, which is 47.3% less than the 121.7 MPa of the control sample 6XA, i.e., the sample without FFA. However, all of the ternary DuraLith waste form samples easily meet the 3.54 MPa (500 psi) acceptance

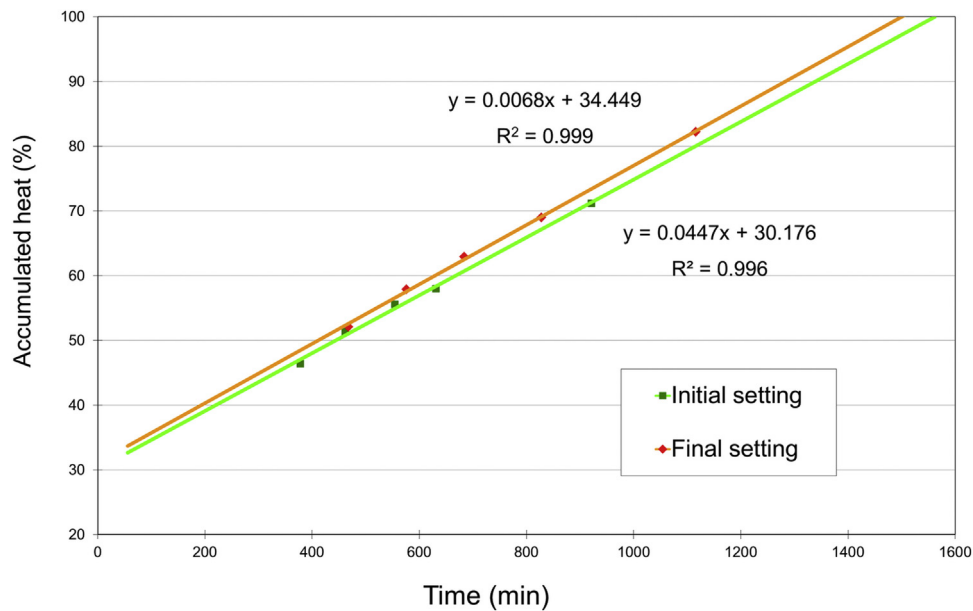


Fig. 3. Correlating initial and final setting times to hydration heats for DuraLith geopolymer waste form samples.

Table 7

TCLP leach test results for ternary fly ash-furnace slag-metakaolin DuraLith geopolymer waste forms.

Sample ID	Concentration in TCLP extract (mg/L)										
	Ag	As	Ba	Cd	Cr	Ni	Pb	Re	Se	Zn	Zr
Blank	<0.07	<0.20	0.00	<0.03	<0.01	<0.04	<0.10	<0.25	<0.90	0.10	<0.02
6XA	<0.07	<0.20	1.01	<0.03	0.15	0.05	0.72	0.65	<0.90	0.15	<0.02
6XB	<0.07	<0.20	0.92	<0.03	0.13	0.05	0.64	0.78	<0.90	0.16	<0.02
6XC	<0.07	<0.20	1.00	<0.03	0.11	0.04	0.53	0.93	<0.90	0.17	<0.02
6XD	<0.07	<0.20	1.22	<0.03	0.08	<0.04	0.34	1.11	<0.90	0.23	<0.02
6XE	<0.07	<0.20	0.92	<0.03	0.09	<0.04	0.26	1.23	<0.90	0.24	<0.02
EPA regulatory limit	5.00	5.00	100.00	1.00	5.00	N/A ^a	5.00	N/A ^a	1.00	N/A ^a	N/A ^a

^a N/A, not available.

criteria for the HSW waste form [3,38]. The optimized mix designs, the presence of reactive silica fume filler, and the coexistence of calcium-silicate-hydrate (C-S-H) and geopolymer gels are believed to be responsible for the high compressive strength developed [6,39,40]. Since the compressive strengths of the binary DuraLith

geopolymer waste forms so far exceed the requirement for immobilized HSW [4,6], some sacrifice in compressive strength was acceptable to improve other properties, such as extending the setting times, which was accomplished in this study.

3.5. TCLP leach test

The TCLP leach test was conducted on samples cured for 180 days. As shown in Table 7, all of the regulated metals in the TCLP extract meet the EPA limits. However, the average concentration of Re is about three times higher than that found for the binary furnace slag-metakaolin DuraLith geopolymer waste form [6], most likely due to the absence of the enhancers for fixation of Re in the samples investigated in this study.

4. Conclusions

The incorporation of Class F fly ash (FFA) into the raw binder materials has greatly extended the setting times and reduced the hydration heat release for DuraLith geopolymer waste forms. With the increase of the FFA content, both the initial and final setting times increased whereas the total hydration heat release decreased. The compressive strengths of the ternary fly ash-furnace slag-metakaolin DuraLith geopolymer waste forms still far exceed the requirement for immobilized Hanford secondary wastes (HSW). Based on the results of the TCLP leach test, chemical durabilities of the ternary DuraLith geopolymer waste forms are in general comparable to those of the binary DuraLith system.

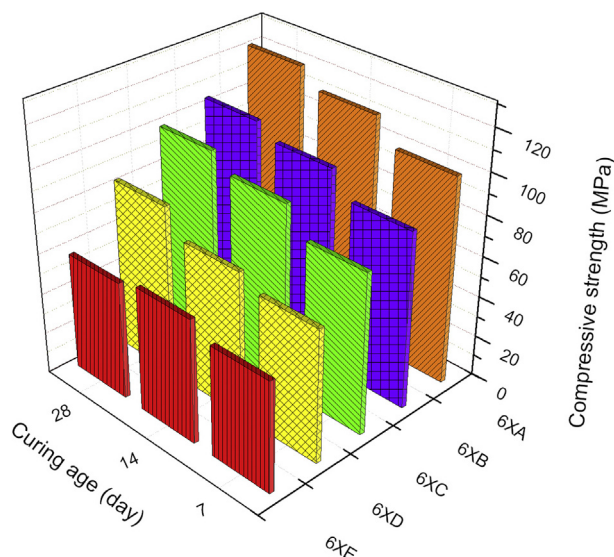


Fig. 4. Compressive strength development of DuraLith geopolymer waste forms.

This paper has firstly established near-perfect quantitative relationships between both initial and final setting times and hydration heat release for cementitious geopolymer waste forms, which were never discovered in the scientific literature for any cementitious waste form or geopolymeric material. The successful establishment of the correlations between setting times and hydration heat may make it possible to efficiently design and optimize cementitious waste forms as well as industrial wastes based geopolymers on the basis of limited testing results.

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