Investigating the Replicability of Geopolymer Formulations for Industrial-Scale HYPEX® Radioactive Waste Immobilization

WM2025 Conference, March 10 – 14, 2025, Phoenix, Arizona, USA

Investigating the Replicability of Geopolymer Formulations for Industrial-Scale HYPEX® Radioactive Waste Immobilization– 25513

Marino Corrado[12,], Francesca Crivelli[1,2], Silvio Cao[1], Claudio Mascialino[1], Laura Savoldi[2]
[1]green-land s.r.l. Brescia (Italy)
[2]MAHTEP Group, Dipartimento Energia "Galileo Ferraris", Politecnico di Torino (Italy)

ABSTRACT

This research presents a comprehensive investigation of the factors influencing geopolymer quality, offering a pathway to standardize and optimize geopolymer production for industrial applications, particularly when used as conditioning matrices for Low Level Waste (LLW) and Intermediate Level Waste (ILW) for instance in the HYPEX® process. The focus here is on the chemical and mechanical characterization of commercially available metakaolins with the goal of establishing standards for industrial replication. The chemical characterization was performed estimating the concentrations of oxides such as Si, Al, Na, K, and Ca in metakaolin using techniques like X-Ray Fluorescence. The mechanical characterization was performed analysing the specific surface area of each metakaolin powder using the BET method. The specific surface area resulted a key factor in the dissolution process of metakaolin in alkaline solutions. A lower specific surface area slows down the dissolution process, while an excessively high surface area requires a large amount of water, which can be detrimental to the geopolymer formation and its final properties. Furthermore, the thermal profile of the geopolymer during the first 24 hours of formation under adiabatic conditions was studied, varying the batch of metakaolin, fundamental atomic ratios, and water content. The results showed that metakaolins developing different temperature profiles tend to produce geopolymers with different mechanical characteristics. This analysis helps identify the optimal temperature profile for geo-polymerization, that maximizes mechanical strength and minimizes leachability, while keeping the temperature below 95°C to prevent excessive water evaporation and ion volatility.

INTRODUCTION

The HYPEX® process consists in the incorporation of radioactive LLW and ILW in a new special geopolymer matrix [1]. A geopolymer, a non-organic aluminosilicate material that forms an amorphous network, is considered a promising conditioning matrix for radioactive waste due to its higher compression strength than cement, its lack of freeze-thaw problem, its fire and leaching resistance [2] ,[3] and its capacity to incorporate boron inside its chemical structure [4]. Recent studies suggest geopolymer is a better candidate then cement for the conditioning of spent Ion Exchange Resins (IEXs).

In-house studies suggest "high-performance" geopolymer are highly sensitive to the fundamental atomic ration and initial water content. To ensure a good characterization of the final geopolymer, the precursors powder (metakaolin), chemicals and the initial water content of the matrix must be carefully analysed, standardized and guaranteed over time. Unfortunately, metakaolin is not a synthetized products but rather a natural product affected by the local composition of the clay out of which it was extracted and by the calcination process it underwent; its purity is not guaranteed at priori. Therefore, only a commercial metakaolin with good mechanical and chemical properties, strictly constant over time, is the perfect candidate. For this reason, the mechanical (Brunauer–Emmett–Telle "BET" specific surface area) and chemical (X-Ray Fluorescence "XRF" composition) characteristics of different baches of the same commercial metakaolin have been analysed and compared with declared values to ensure or not reliability for an industrial-scale production of high-performance geopolymer.

It was already shown that the temperature profiles of the paste during its early-stage formation (first 24h) strongly influences final geopolymer mechanical properties and leachability [5]. The temperature during the reaction plays indeed a crucial role in forming atomic bonds and shaping the matrix structure, which greatly influences the mechanical strength and ion-leachability of the final product. Since the geo-polymerization is an exothermic reaction [6], the real temperature of industrial scale drums (D=1m, H=1,5m) tends to be spatially homogeneous and equal to adiabatic temperature of reaction, due to difficulty of external temperature control. Therefore, the temperature profile of the forming paste mostly depends on the metakaolin reactivity (dissolution energy) and the amount of water in the paste (heat capacity of the system). The water content must be carefully chosen depending on the reactivity of the initial powder, while maintaining a maximum adiabatic temperature below 95°C to minimize water evaporation and prevent ion volatility during geopolymer formation.

The study aims first to verify the quality and the reliability over time of commercial metakaolin powder to produce geopolymer matrixes suited for conditioning LLW and ILW. Secondly, chemical and mechanical proprieties of industrial size geopolymer are extrapolated by laboratory scale tests. The first 24 h curing of industrial size geopolymer has been simulated with laboratory scale geopolymer samples cured in almost adiabatic environment. By preserving curing temperature profile during the scaling down from industrial to laboratory scale, samples give realistic information on chemical and mechanical proprieties of an industrial size drum. More specifically, two batches (B3, B4) of the same commercial metakaolin have been analysed and used for the formation of geopolymers with different water content. The early-stage temperature (0-24h) during the formation of the geopolymer, the resistance to compression, the leachability of the Strontium ion and the water permeability of the matrixes are analysed.

METHODOLOGY

The samples analyzed are aluminosilicate geopolymers produced by the dissolution of a commercial metakaolin powder (B) in alkali solution, containing sodium and silicates ions (SiO_2=27.5 %wt., Na_2O=8 %wt, H2O=64.5 %wt.). Chemical composition of two different batches (B3 and B4) of the commercial metakaolin have been analyzed by X-Ray Fluorescence (XRF), while the specific surface has been analyzed by BET (Brunauer–Emmett–Telle) technology [7].

Four geopolymer formulations with different water/solid ratios were analyzed (water/solid: F1=**0.48**; F2= **0.54**; F3= **0.59** and F4= **0.65**). The lower water/solid ratio refers to the minimum amount of water needed to have a satisfactory hand workability of the paste. For all samples, the fundamental atomic ration Si/Al varies between 1.42-1.71, Na/Al is kept fixed to 1.00 and H2O/Al varies between 4.60-6.85. The geopolymer paste, after being vigorously mixed for 5 minutes until macroscopic homogeneity is reached, was poured into plastic cylinder (Diameter = 100 mm, Height = 100 mm) which was placed in a closed polystyrene structure, with a thickness of 50mm on all sides. The insulating structure guaranteed a spatially uniform temperature, equal to the adiabatic one during the early-stage formation. Since the samples were almost hermetically closed, the humidity during the curing was high.

The resistance to compression, the leachability, the water permeability and the temperature during the early-stage (0-24h) were measured according to the procedure described below:

1. Resistance to compression: compression strength measured according to UNI EN 12390-3 [8]. Two samples for each formulation were tested by Tecno-Piemonte S.p.A. (an authorized Italian company for cement certification).
2. Resistance to leachability: a leaching test for the Strontium cation (Sr^{2+}) was conducted by analyzing water samples from two different immersion periods: one lasting 7 hours and the other 89 hours. The analysis was performed using ICP-MS (inductively coupled plasma-mass

spectrometry [9]) following a simplified short-term procedure based on ANSI/ANS-16.1-1986 guidelines [10], as only 2 water samples and not 6 have been considered. This approach was chosen due to the lack of significant variations in diffusion coefficients observed in earlier rigorous and exploratory tests involving six different water samples immersed over 96 hours as legislation required. For these samples, a few grams of $SrCl_2$-$6H_2O$ are inserted into the alkali solution before the insertion of the metakaolin powder.

3. Water permeability: the samples, after 21 days of curing at 25°C in a dry environment, were immersed in water at 25°C and atmospheric pressure. The amount of water which gradually permeates inside the matrix was measured by monitoring the weight of the sample over time, until a plateau was reached.
4. Early-stage temperature profile: a probe recorded temperature into the center point of the sample from the casting until complete solidification of the geopolymer.

RESULTS

Metakolin composition

The XRF analysis reveals that the two baches of the same commercial metakaolin have similar chemical composition. The specific surface of both baches were analyzed by BET technology, and the two specific areas (13610 m^2/g for B3 and 14100 for B4) turned out to be similar to the declared ones (14000 m^2/g).

Table 1 "Chemical composition, by XRF analysis, of B3 and B3 batches, value refers to % in weight"

[% wt.]	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	Na_2O	K_2O	P_2O_5	MgO	LOI
B3	48.58	49.41	0.28	1.04	6E-2	0	0	0.35	0	0.28
B4	48.43	49.36	0.32	1.09	6.4E-3	0	0	0.396	0	0.33

Temperature profile during geo-polymerization

The study aimed to simulate the temperature of an industrial-size 200-liter drums during the geopolymer formation. The bigger the sample is, the higher is the volume/surface ratio (volume scale with L^3 while surface with L^2) and the lower the specific thermal dissipation is. For samples approaching the real size drums, thermal dissipations are negligible compared to the thermal energy produced from the slightly exothermic reaction of geo-polymerization, and the real temperature of formations tends to the adiabatic temperature of the reaction. The temperature during early-stage formation of the geopolymer (0-24h) is crucial for the formation of atomical bonds and, if carefully calibrated, also a small geopolymer can precisely simulate industrial scale geopolymer blocks.

The temperature of all samples was measured during the first 24h. The thermal dissipation during formation was minimized by covering the samples with a 50mm thick layer of polystyrene, to keep the temperature as close as possible to the adiabatic temperature of the reaction during first hours of geo-polymerization. Figure 2 and Figure 3 show temperature behavior of geopolymer different water/solid ratios for the two different batches B3 and B4. The temperature profile shows three consecutive phases during geo-polymerization where different phenomena occur (Phase I, Phase II and Phase III). More in depth:

- ***Phase I***: During geo-polymerization, strong-alkali solution dissolves metakaolin powder. In this phase, OH^- anions of the solution break atomic structural bonds of SiO_2 and Al_2O_3 of the

metakaolin. The dissolution of the metakaolin rates depends on the basicity of the solution (easily measurable by a pH-meter and controllable by pH adjustment), the initial temperature and the reactivity of the powder (hard to measure). Phase I (dissolution of the metakaolin) is therefore characterized by a sudden increase of the temperature in a small amount of time, due to the exothermicity of the dissolution process and it can give excellent experimental information on the metakaolin powder reactivity. The temperature rise is proportional to the energy released in the dissolution while the duration gives us information on metakaolin dissolution rate.

- ***Phase II***: After being dissolved, aluminosilicate atoms relocate spatially forming a geopolymer network. During this process the stability of the structure is increased (ions rearrange to form lower energy and therefore more stable structure), energy is released, and the temperature of the paste gradually increases over time (atoms relocation is a long process compared to metakaolin dissolution) until maximum temperature is reached. High temperature increases the ions' mobility and allows them to easily reach stable structures. The rate at which the temperature increases over time depends mostly on the heat capacity of the system and, therefore, on the water content of the geopolymer. In ideal adiabatic conditions, the maximum temperature coincides with the adiabatic temperature of the geo-polymerization, which depends solely on the reactivity of the metakaolin and the water content. In real case, the temperature rise is slightly dampened by thermal dissipation phenomena and the maximum temperature is lower than the adiabatic temperature (Figure *1*).
- ***Phase III***: After reaching the maximum temperature, thermal dissipation phenomena become predominant, and the temperature slowly decreases until it returns to ambient conditions (25°C). During the cool down no convection phenomena take place inside the forming geopolymer because of the high viscosity of the materials, and heat is therefore transferred out only by conductive phenomena. The decreases rate depends on the spatial scale of the sample (L): the bigger the sample, the slower the temperature decreases (Figure *1*) and vice versa. In industrial 200-liter drums, the temperature slowly decreases, and Phase III can last several days. For a small-size sample, if it is significantly isolated from outside, Phase III is similar to real case drum, and it can simulate the geopolymer formation of the real case (Figure *1*).

Correlations between laboratory and industrial scale samples have been achieved by an in-house lumped parameter transient model for the temperature evolution of the sample, considering a single-reaction model. A [m²] is the surface area of the sample, while T and T_0 are respectively the temperatures of the sample surface and the surrounding environment. K_1 [W/(m²·K)] is the overall heat transfer coefficient of the system. $K_2\, e^{-ct}$ [J/(kg·s)] is the specific constant of the geopolymerization reaction, which quantifies the power released per unit mass of metakaolin. The coefficient c [1/s] is a macroscopic parameter that quantifies the reaction rate of the geo-polymerization. $c_{p.w}$ [J/kg/K]is the heat capacity of the initial water solution. m_{tot} is the total mass of the sample. φ is defined as the weight ratio between the solution mass and the metakaolin powder mass.

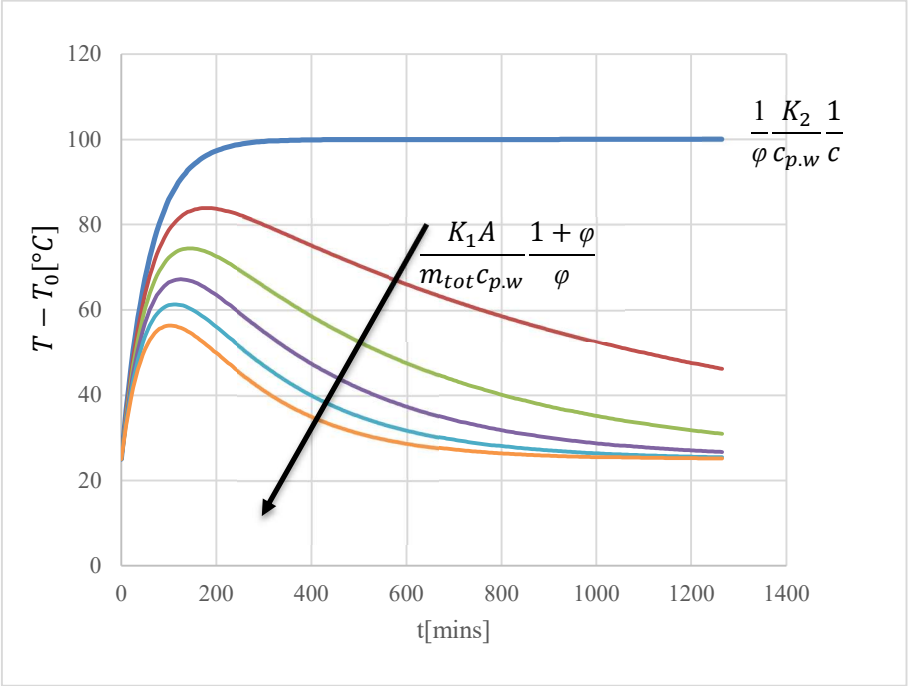

Figure 1 " Temperature evolution of the sample over time, according to the in-house model"

For both the B3 and B4 batches, Phase I last about 5 minutes, showing both batches have similar dissolution velocities. Only for geopolymer with water/solid ratio equal to 0.48, the Phase I is not visible from the temperature profile (Figure 2 & Figure 3). In this case the phases I and II overlap, and there is a sudden increase of the temperature until reaching the maximum temperature (99.3°C for B3 and 99.8°C for B4). The peak temperature is reached instantly (less than a minute) for both B3 and B4. In this case atoms do not have time to properly relocate and form stable gel structures. For this reason, most of the water molecules meant to become structural[a] water (water needed to keep an equilibrium between Na^+ cations dissolved in water and Na^+ cations bonded to Al^{+3}) are still free when the paste reached 100°C after a minute. The temperature does not exceed 100°C because further energy is used to evaporate the free water of the mixture. Unfortunately, excessive evaporation of free water during early-stage geo-polymerization can be harmful for the matrix because future structured water cannot form and the ionic balance in the geopolymer structure is not guaranteed.

For both the B3 and B4 batches, the geopolymer with water/solid ratio equal to 0.54 overcome 100°C during the formation. The sample B3 reaches 106.5°C after 61 minutes while B4 reaches 103°C after 41 minutes. B3 remains over 100°C for 42mins while B4 for only 22mins. After about 40 minutes, the part of the free water (needed for structural purpose) has reached equilibrium with the Na+ cations, becoming structural water. Because it is chemically bound, it does not evaporate even for temperatures higher than 100°C, on the contrary free water evaporate is not bound evaporate in a 100°C environment. The fact that the matrix exceeds 100°C proves that most water has already become structural.

[a] Free water refers to water molecules, not chemically bounded. For this reason, they tend to spontaneously evaporate in a 100°C environment. On the contrary structural water refers to water molecules chemical bounded to structural atoms. More specifically, structed water keep an equilibrium between Na^+ cations dissolved in water and Na^+ cations bonded to Al^{+3}, providing charge stability to the structure.

Furthermore, by comparing temperature curves during phase II of the geopolymer with w/s 0.65, it is visible that B4 is a slightly more reactive metakaolin than B3 because the maximum temperature is higher (75.6°C for B4 and 64.7°C for B3) and reached sooner (~270mins for B4 and ~390 mins for B3).

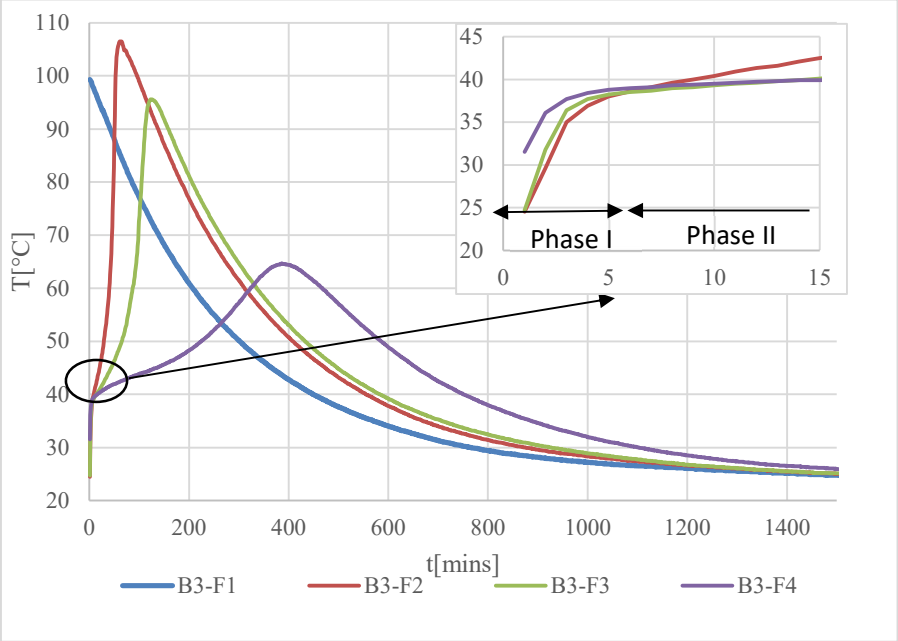

Figure 2. "Temperature behavior during early stage (0-24h) geo-polymerization of cylindrical samples (D=100mm, H=100mm), covered by a 5mm thick polyethylene layer. The B3 stands for the metakaolin batch used as precursor powder. F1, F2, F3 and F4 stand for water/solid ratios."

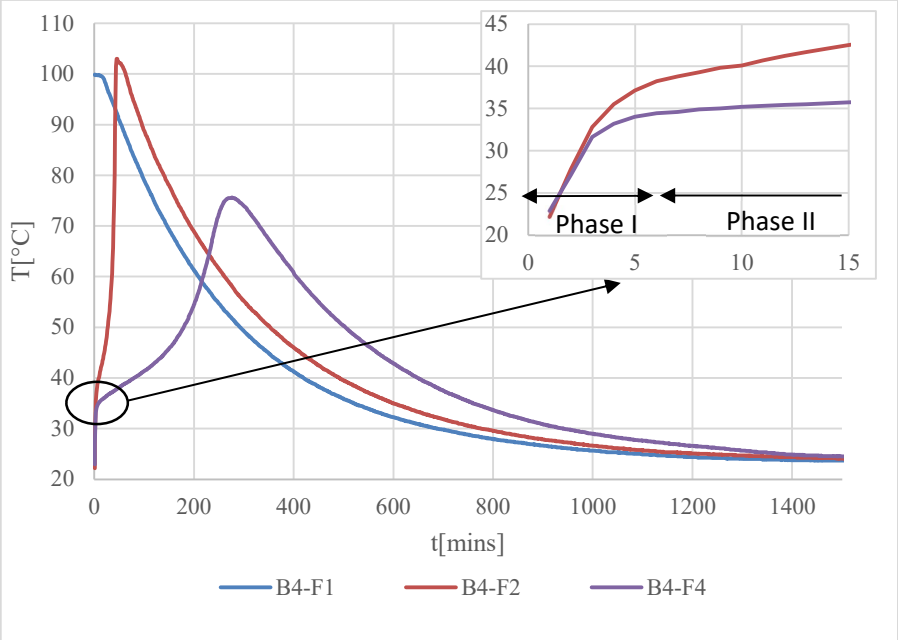

Figure 3. "Temperature behavior during early stage (0-24h) geo-polymerization of cylindrical samples (D=100mm, H=100mm), covered by a 5mm thick polyethylene layer. The B4 stands for the metakaolin batch used as precursor powder. F1, F2, F3 and F4 stand for water/solid ratios."

Geopolymer density

During the curing period, the volume of the samples remained the same (no visible shrinkage phenomena or cracks occurred). The density of the samples progressively decreased during the first 21 days because of evaporation of still existing free water in the matrix (Figure 4 and Figure 5). Initial density is obviously dependent on the initial water content (ranging from 1.64 to 1.77g/cm^3): the higher the water content, the lower the density and vice versa. For samples with fixed volume, the density decrease is directly connected with a mass loss. Surprisingly, the samples with lower initial water content are the ones which lose more water during the settlement of the geopolymer (Table 2). Among the ones studied, the B3 and B4 batches behave similarly and geopolymers with w/s equal to 0.59 minimize the water loss during first 21 hours curing.

Table 2. "Increase in density of geopolymer from B3 and B4 batches. 4 water/solid ratios are analyzed".

$\lvert\Delta\rho[g/cm3]\rvert$	w/s: 0.48	w/s: 0.54	w/s: 0.59	w/s: 0.65
B3	0.20	0.12	No data	0.10
B4	0.24	0.14	6.5E-2	0.12

After immersion in water, density of all samples for both batches increases because water permeates inside the matrix. Results show that in less than 4 days water penetration is complete.

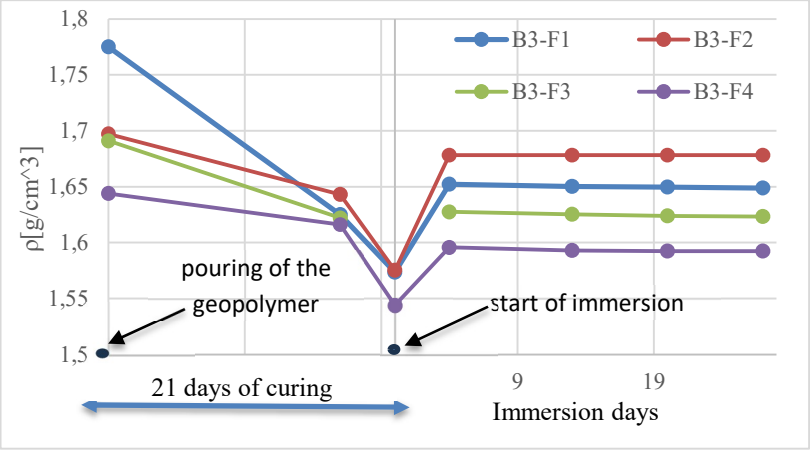

Figure 4. "Density variation of B3 geopolymers, during 21 days curing period and during a successive 28 day immersion. The B3 stands for the metakaolin batch used as precursor powder. F1, F2, F3 and F4 stand for water/solid ratios"

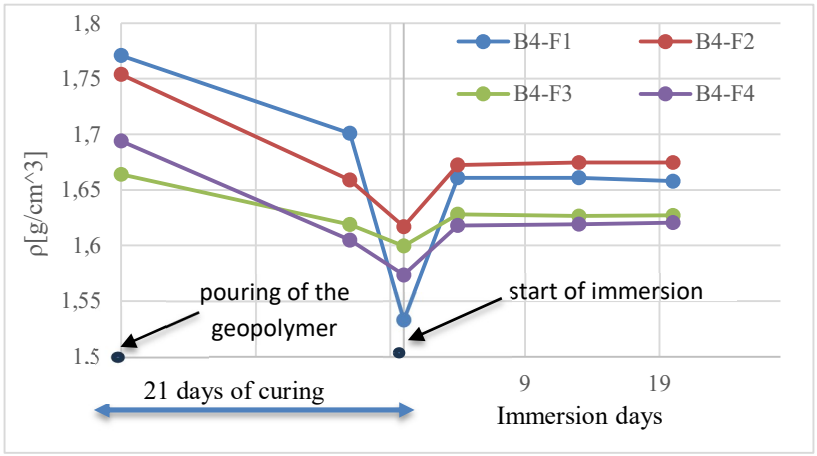

Figure 5."Density variation of B4 geopolymers, during 21 days curing period and during successive 28 day immersion. The B4 stands for the metakaolin batch used as precursor powder. F1, F2, F3 and F4 stand for water/solid ratios "

Resistance to compression

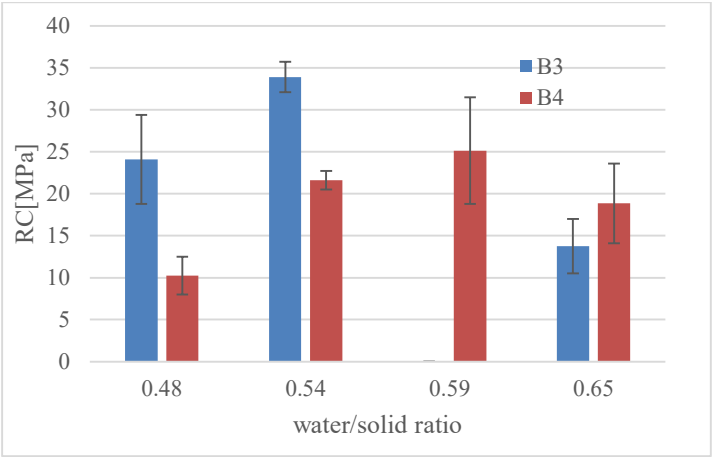

Figure 6. "Resistance to compression of geopolymer from B3 and B4 metakaolin batches. Four different water /solid ratios are analyzed"

The sample resistance of compression was tested after 21 days curing (1 day in adiabatic condition and 20 days at 25°C), and the results are reported in Figure 6. The relative humidity on the first day was high (H.R: =90%), while for the following 20 days it was 70%. The batches 3 and 4 behave differently, even if the same curing conditions were applied. This strong mechanical difference suggests that the chemical composition of the initial powder is not the only determining parameter for good replicability of geopolymer. Other characteristics, such as the effectiveness of the calcination process of the metakaolin, must be analyzed. The results showed that the samples cured in adiabatic conditions perform worse than the samples cured at ambient temperature (25°C) [1]. A high temperature curing gives to the final matrix worse mechanical proprieties than curing at ambient temperature. In the latter case, low temperature delays chemical reactions: Si and Al ions relocate slowly after the powder dissolution and atomics bonds of the geo-polymerization matrix are formed later but stronger. Alternatively, the superior resistance to

compression of geopolymers cured at room temperature [1] may derived from the presence of sand as an aggregate in the receipt (not present in receipt of this case study), which enhances the structural solidity of the matrix.

Leachability

Short term leachability index of the matrix for the Strontium has been analyzed. Figure 7 shows the matrix has excellent retention capacity for the Sr^{2+} ion. The Leachability index seems weakly dependent on the initial water content and no clear trend is visible. Excellent Strontium retention index can make metakaolin based geopolymer a good candidate for conditioning spent nuclear fuel.

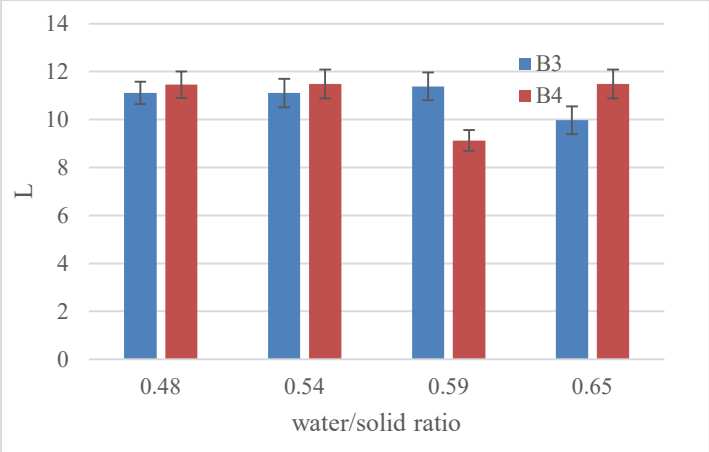

Figure 7. "Leachability index of geopolymer from B3 and B4 metakaolin batches, for the Strontium ion. Four different water /solid rations are analyzed."

DISCUSSION AND CONCLUSION

This study investigated the technical feasibility and the reproducibility of implementing HYPEX® geopolymer on an industrial scale for the conditioning of LLW and ILW.

The results of this study demonstrate that both tested metakaolin batches exhibit similar chemical compositions (SiO2 ~ 48%, Al2O3 ~ 49%) and mechanical proprieties (BET ~14000 m^2/g), which indicate consistency in the material properties. However, differences were observed in the temperature profiles during geopolymer formation, suggesting that B4 is more reactive than B3. For geopolymer with water/solid ratio equal to 0.65, the higher reactivity of B4 resulted in a quicker rise to maximum temperature, which could lead to faster formation of atomic bonds and stronger structural properties in the final geopolymer. This is consistent with the observed differences in resistance to compression, where B4 showed better compression resistance compared to B3 (for w/s equal to 0.65).

The temperature behavior during early-stage geo-polymerization further highlighted the importance of carefully controlling the water/solid ratio. The results reveal that water/solid ratio less than 0.59 should be avoided to keep adiabatic temperature below 100°C. An excessive evaporation of free water occurs for T greater than 100°C, harmfully altering the structural water content of the final matrix. Moreover, in high temperature environment (close to 100°C), the volatility of ions (such as Sr^{2+}, Cs^{+}, Co^{2+} etc...) increases and radioactivity leaks from the matrix in air might occur, making geopolymer not suitable for LLW and ILM.

Results showed that geopolymers with a water/solid ratio of 0.59 exhibited minimal water loss and good mechanical strength. Furthermore, the leachability tests for Strontium indicated both B3 and B4 geopolymer cured at high temperature possess excellent retention capabilities ($9.12 < L_{Sr} < 11.1$), with minimal impact from varying water content. It suggests metakaolin-based geopolymers can be suitable for conditioning radioactive waste such as spent nuclear fuel.

Despite promising results, further work is needed to standardize characterization method for the initial metakaolin powder and to optimize water/solid ratio for industrial-scale production and ensure long-term stability. Future research should focus on the scalability of the geopolymer process, its thermal behavior in larger systems (e.g., 200-liter drums), and its performance under real-world conditions for radioactive waste disposal.

REFERENCES

[1] Crivelli, Corrado, and Savoldi, "HYPEX ® : A New Process for the Treatment and Conditioning of Radioactive Ion-Exchange Resins," Phoenix, Arizona (US): WMS24, Mar. 2024.

[2] E. Phillip, T. F. Choo, N. W. A. Khairuddin, and R. O. Abdel Rahman, "On the Sustainable Utilization of Geopolymers for Safe Management of Radioactive Waste: A Review," *Sustainability*, vol. 15, no. 2, 2023, doi: 10.3390/su15021117.

[3] E. R. Vance and D. S. Perera, "8 - Development of geopolymers for nuclear waste immobilisation," in *Handbook of Advanced Radioactive Waste Conditioning Technologies*, M. I. Ojovan, Ed., Woodhead Publishing, 2011, pp. 207–229. doi: https://doi.org/10.1533/9780857090959.2.207.

[4] B. Kim, J. Lee, J. Kang, and W. Um, "Development of geopolymer waste form for immobilization of radioactive borate waste," *J Hazard Mater*, vol. 419, p. 126402, 2021, doi: https://doi.org/10.1016/j.jhazmat.2021.126402.

[5] J. G. S. van Jaarsveld, J. S. J. van Deventer, and G. C. Lukey, "The effect of composition and temperature on the properties of fly ash- and kaolinite-based geopolymers," *Chemical Engineering Journal*, vol. 89, no. 1, pp. 63–73, 2002, doi: https://doi.org/10.1016/S1385-8947(02)00025-6.

[6] R. Mohamed, R. Abd Razak, M. Mustafa Al Bakri Abdullah, R. Khimi Shuib, N. Aida Mohd Mortar, and W. Wazien Ahmad Zailani, "Investigation of Heat Released during Geopolymerization with Fly Ash based Geopolymer," *IOP Conf Ser Mater Sci Eng*, vol. 551, no. 1, p. 012093, 2019, doi: 10.1088/1757-899X/551/1/012093.

[7] M. Jaroniec, M. Kruk, and A. Sayari, "Adsorption methods for characterization of surface and structural properties of mesoporous molecular sieves," in *Studies in Surface Science and Catalysis*, vol. 117, L. Bonneviot, F. Béland, C. Danumah, S. Giasson, and S. Kaliaguine, Eds., Elsevier, 1998, pp. 325–332. doi: https://doi.org/10.1016/S0167-2991(98)81008-2.

[8] "UNI EN 12390-3:2019 Testing hardened concrete - Part 3: Compressive strength of test specimens," 2019.

[9] Scott C Wilschefski and Matthew R Baxter, "Inductively Coupled Plasma Mass Spectrometry: Introduction to Analytical Aspects," *National Library of Medicine*, vol. 40, no. 3, pp. 115–113, Aug. 2019.

[10] ANSI/ANS-16.1, "Measurement of the Leachability of Solidified LowLevel Radioactive Wastes by a Short-Term Test Procedure," 2019.