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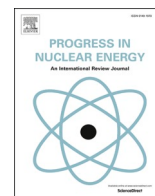
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Development of a new process for the radioactive ion exchange resins conditioning - HYPEX[®]

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ABSTRACT

A novel process, HYPEX[®], for the conditioning of radioactive ion-exchange resins (IEXs), has been developed and is presented here. The process involves the immobilization of radioactive IEXs into a geopolymer matrix after grounding down to a micrometer scale and a complete hydration. The studied geopolymers are based on metakaolin and activated by an alkali solution. The effects of ~ 90 different combinations of the structural atomic ratios in the geopolymer, such as silicon/aluminum (Si/Al) and water/aluminum (H₂O/Al), on macroscopic mechanical properties were examined, aiming at identifying the most suitable geopolymer for the conditioning of spent resins. Two geopolymer formulations were selected, both utilizing a fully sodium-based alkali solution and enriched with calcium hydroxide and siliceous inert filler to enhance their mechanical properties. One formulation involves the use of sodium silicate, while the other incorporates silica fume. Fractions of 20%wt and 30%wt of treated resin were added to the selected geopolymer matrices, and several tests were carried out in accordance with the Italian Safety Criteria for the Management of Radioactive Waste as far as resistance to compression, water immersion, thermal cycles, radiation, leachability, fire, and gas permeability are concerned. It is demonstrated here that HYPEX[®] satisfies the stringent Italian Criteria, even when 30%wt of resin is embedded.

Nomenclature

IEX(s)	Ion Exchange resin(s)
LLW	Low Level Waste
ILW	Intermediate Level Waste
IAEA	International Atomic Energy Agency
CRP	Coordinate Research Project
LWRs	Light Water Reactors
WAC	Waste Acceptance Criteria
GT33	Technical Guide 33
ICP-MS	Inductively Coupled Plasma-Mass Spectrometry
VRF	Volume Reduction Factor

1. Introduction

Ion exchange resins (IEXs) are widely used in the nuclear sector for various purposes, including purifying reactor primary water, cleaning spent fuel pools, removing radioactive contaminants from liquid waste, and controlling water chemistry (e.g., boron concentration) of the primary circuit (IAEA, 2002). Since spent IEXs constitute a substantial portion of Low or Intermediate Level Waste (LLW or ILW), the minimization of the final waste volume is an issue to be addressed.

Spent IEXs disposal is challenging due to their unique chemical and physical properties. Their swelling capacity and boron content can limit their integration into traditional Portland cement-based conditioning matrices, typically allowing only a low resin percentage (10% by weight (Matsuda et al., 1992)) to be embedded. This constraint results in a large waste volume, prompting the exploration of alternative treatments. Many of these methods involve high temperatures and pressures to reduce the waste volume (Wang and Wan, 2015), features which could increase risks to personnel and the environment.

An inorganic aluminosilicate-based geopolymer, characterized by an amorphous structure, has been selected here as the conditioning matrix for spent IEXs due to its superior compressive strength compared to cement, as well as its resistance to freeze-thaw cycles, fire, and leaching (Phillip et al., 2023; Vance and Perera, 2011). Additionally, boron can be easily incorporated into geopolymers, as it can substitute aluminum in the material molecular structure, due to their chemical similarity (Kim et al., 2021). The suitability of geopolymers as conditioning matrices for radioactive resins is not a novelty, as it has been extensively investigated by various researchers. For example (Lichvar et al., 2013), presented the SIAL[®] geopolymer, approved in both Slovakia and the Czech Republic as a matrix for sludge/resin mixtures. That geopolymer satisfies the compressive strength and leachability limits required for

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disposal in surface repositories in both countries, allowing the embedding of approximately 17.5%wt of radioactive waste (Lin et al., 2020). demonstrated that their metakaolin-based geopolymer can embed up to 12%wt of ion exchange resins while meeting Taiwan's Waste Acceptance Criteria for compressive strength, immersion tests, and leachability. Furthermore (Shin et al., 2023), reported that a geopolymer embedding 20%wt of spent resin satisfied South Korea's mandatory criteria for compressive strength, resistance to thermal cycles, radiation, leachability and immersion. Those results highlight the potential practical use of geopolymers as immobilization matrices for spent resins. However, a comparison between those studies is challenging, due to different national approaches to material suitability as conditioning matrices, as each country imposes distinct criteria. For instance, Slovakia requires compressive strength and leachability for acceptance into repositories, whereas South Korea also includes resistance to immersion, radiation, and thermal cycles.

The promising potential of geopolymers for waste management, coupled with the absence of a standardized protocol for their evaluation, has recently led the International Atomic Energy Agency (IAEA) to establish a Coordinated Research Project (CRP) to assess standard tests for geopolymers as conditioning matrices (IAEA, 2023).

In this context, the Italian start-up company green-land s.r.l. has developed HYPEX®, an innovative process specifically designed for the treatment and conditioning of IEXs. The novelty of HYPEX® lies in its ability to incorporate over 20%wt of ground and wet radioactive resins into a geopolymer matrix, maintaining high mechanical properties, high resistance to leachability, and good performance under multiple stressors (immersion, radiation, thermal cycling, and fire). The key innovations of HYPEX® include the grinding of the resins to improve the homogeneity of the matrix, thus reducing internal stresses, and the identification of an optimized geopolymer formulation that can accommodate a high resin content without compromising structural integrity or long-term stability. By embedding higher quantities of resin, the process significantly reduces the final waste volume, offering a cost-effective solution for the safe conditioning of radioactive IEXs. Moreover, HYPEX® is conducted entirely at room temperature and atmospheric pressure, ensuring scalability and operational simplicity.

The nuclear power plant at Trino Vercellese, Italy, where approximately 100 m³ of radioactive IEXs still need proper conditioning (SOGIN, 2015), served as reference case study for the validation of the HYPEX® process. Even though Trino reactor was shut down over thirty years ago, the use of ion exchange resins in LWRs remains as relevant today as in the past (Gong et al., 2024) making it a pertinent reference case study. For this Italian application, the test results were compared with Waste Acceptance Criteria (WAC) specified by the Italian Inspectorate for Nuclear Safety and Radiation Protection in Technical Guide 33 (GT33) (ISIN, 2022). Note that the WAC typically differ across nations. For instance, in the UK the threshold value for compressive strength is 0.4 MPa (Maclachlan et al., 2024), whereas in Italy and in Slovakia it is set at 10 MPa, thus resulting in much stringent requirements on the manufacts.

2. Methodology

The development of the HYPEX® process was carried out in two phases. The first phase aimed at identifying the optimal geopolymer formulation to be used as a conditioning matrix for the radioactive IEX and at refining the resin treatment (hydration, grinding) to achieve the highest quality final product. The second phase focused on ascertaining the performance of the selected geopolymer-resin product in accordance with the Italian Radioactive Waste Management Criteria. In all cases, to manufacture the final geopolymer-resin paste, the resin was grinded, hydrated, saturated with ions and finally mixed with the geopolymer's alkali solution to achieve homogeneity, then the geopolymer precursor powder was inserted.

2.1. Phase 1. performance assessment of geopolymer matrix and resin treatment

Phase 1 targeted first the study on many alkali-based aluminosilicate geopolymers, to develop a geopolymer suitable for a conditioning matrix of a suitably hydrated and grounded IEX.

Geopolymers form through the activation of the precursor powder, such as metakaolin or fly ash, with an alkali solution. Aluminosilicate sources derived from coal industry, such as fly ash, cannot, however, guarantee specific and constant characteristics overtime since their composition depends on the industrial processes. On the contrary, metakaolin, which is derived from the specific thermal treatment of the natural kaolin (calcination), guarantees.

- a consistent chemical composition over time (if the clay furniture is preserved),
- excellent chemical reactivity, as Kaolin calcination at 800 °C increases the Aluminum reactivity and facilitates complete metakaolin dissolution, and
- constant mechanical reactivity, as standard granulometry and specific surface of the final powder is guaranteed by calcination process.

Based on these properties, metakaolin-based geopolymers were then chosen to develop the HYPEX® process. An alkaline solution based on Na/K hydroxide dissolved in water was chosen to activate the metakaolin, based on the following observations.

- Na and K hydroxides release monovalent cations Na⁺, K⁺, ideal for Al⁺³ balance in the Si⁺⁴-based geopolymer structure
- Na⁺, K⁺ are relatively small cations and, once bound to Al⁺³, do not alter strongly the tetrahedral symmetry of the Si-Al geopolymer structure
- NaOH, and KOH with low impurity are easily affordable also at the industrial scale (forecasting an industrial application of HYPEX® process).

The alkaline solution was left to rest for 24 h at room temperature (25 °C) to ensure a complete release of ions. The high OH⁻ ion concentration is able to dissolve the stable SiO₂ structure and form Si-based anions in the solution.

The hardening period and mechanical characteristics of geopolymers strongly depend on the fundamental molar ratio of the reactants involved in the process of geopolymerization, with the ratios of Silicon to Aluminum (Si/Al), Metal to Aluminum (M/Al), and Water to Aluminum (H₂O/Al) showing the largest impact on geopolymer performance.

As metakaolin was selected as the aluminosilicate source for the geopolymer, the workability of the paste and compressive strength of metakaolin-based geopolymers were analyzed with various Si/Al and H₂O/Al ratios, while keeping the M/Al ratio constant and equal to 1. The objective of this investigation was to identify a geopolymer that is pourable, easily pumpable (to facilitate emergency interventions at the plant), and with excellent compressive strength (to embed the maximum quantity of resin). Samples with different reactant ratios were first cured for 28 days at 25 °C and tested to assess their compressive strength. Subsequently, two geopolymer's formulations were selected, and their compressive strength was measured after 7 days of water immersion and after 24 h at 110 °C, in order to evaluate the optimal metal mix in the alkali solution. Each test was replicated three times for each sample.

Based on these results obtained during this first screening campaign, the two most promising geopolymer recipes were selected. Then, the formulations were studied and optimized with the addition of additives (Ca(OH)₂ and sand) to best meet the necessary requirements for suitability as radioactive waste conditioning matrices.

The IEX selected for conducting the experiments was AmberLite 150 H/OH (DuPont), a mixed-bed resin. The resin hydration before the

mixing to the matrix were investigated, aiming at limiting the swelling capacity of the resin and enhance the mechanical performance of the final product. Incorporating dry resin mitigates in fact the issue of drying out during matrix curing since the resin has no water to vaporize. However, this leads to significant water absorption during the immersion test, causing the resin to expand and generate massive tensile stress at the interface between the wet resin and the surrounding geopolymer. Conversely, incorporating fully hydrated resin into the geopolymer can prevent water intrusion during immersion and improve the matrix's resistance to immersion. During drying, the resin particle volume decreases due to water loss, creating interstitial voids between the resin and geopolymer. The resin easily detaches from the surrounding geopolymer, as no strong chemical bonds form between the organic and inorganic molecules, and this detachment introduces voids but does not lead to additional stresses on the geopolymer. However, when the matrix absorbs water, the resin re-expands to its initial volume, reducing structural voids, without further stressing the surrounding geopolymer. The resin was ground from 650 μm to 50 μm to enhance the homogeneity of the final matrix (by preventing precipitation).

According to explanations above, fully hydrated ground resin was

$$D = \frac{A_{\text{Cs-134}} \sum_{i=1}^9 (P_{\text{Cs-134}}^i E_{\text{Cs-134}}^i) + A_{\text{Bi-208}} \sum_{i=1}^5 (P_{\text{Bi-208}}^i E_{\text{Bi-208}}^i) + A_{\text{Cs-137}} E_{\text{Cs-137}} + A_{\text{Co-60}} \sum_{i=1}^2 (P_{\text{Co-60}}^i E_{\text{Co-60}}^i)}{M_{\text{tot}}} \quad (1)$$

selected for immobilization using the HYPEX® process. For all the experiments involving the resin, the commercial bead resin underwent the following four consecutive steps.

1. Drying in an oven for 24 h at 110 °C to ensure complete water loss.
2. Grinding to a micrometric scale using a laboratory ball mill.
3. Hydration of the ground resin and full chemical saturation by introducing Fe, Cr, Ni and Cs salts, Na, K, Li hydroxides, and boric acid. Resin was saturated with non-radioactive isotopes matching those found in a PWR reactor's primary circuit.

In particular, the anionic portion of the mixed-bed resin, which represents 50% of the total resin, was fully saturated with boric acid, resulting in a maximum Boron/Aluminum molar ratio of 0.013 in the final product. This calculation considers the highest resin incorporation tested, which was 30%wt. This ratio is well below the threshold of 0.15 reported by (Rožek et al., 2021) who experimentally demonstrated that aluminosilicate geopolymers with a Boron/Aluminum molar ratio of up to 0.15 maintain good mechanical properties. Therefore, based on both the literature and our experimental conditions, the presence of boron in the geopolymer matrix does not raise any concern regarding its mechanical integrity or performance.

2.2. Phase 2. performance assessment of geopolymers with resin

Phase 2 aimed at validating the two geopolymer formulations for the final conditioning matrix used in the HYPEX® process. Each geopolymer with different weight percentages of ground and wet IEXs (20%wt and 30%wt) underwent tests for compression resistance, thermal cycling, radiation resistance, water immersion, leachability, fire resistance, and gaseous permeability. These tests were conducted on cylindrical samples (26.9 mm in diameter and 27 mm in height) that were cured for 28 days at 25 °C in a plastic-sealed environment. The test were performed and evaluated in agreement with the standards imposed by the Italian Inspectorate for Nuclear Safety and Radiation Protection in Technical Guide 33 (GT33). Each of the following test has been replicated on 3 different samples, to ensure the reproducibility of the results.

1. **Compression Resistance:** Measured according to UNI EN 12390-3 (UNI, 2019).
2. **Thermal Cycle Resistance:** Compression strength tested as in point 1 after 30 cycles (24 h each), with temperature ranging from -30 °C to $+40$ °C and a thermal gradient exceeding 10 °C/h. Relative humidity was maintained at 90%.
3. **Radiation Resistance:** Compression strength was tested, as in point 1, after irradiating samples up to 10^6 Gy at a qualified external laboratory of ENEA, located in Casaccia, Rome, Italy. The irradiation was conducted using a gamma-ray Co-60 source, with a dose intensity of 1836 Gy/h. The Italian Technical guide GT33 imposes tests on MLW irradiated to 10^7 Gy, which can drop to 10^6 Gy if the artifact is proved to not exceed a 10^6 Gy dose in 300 years. This is the case for the IEX resins at the Italian Nuclear Plant Enrico Fermi (Trino Vercellese), as an in-house conservative estimate suggest that an artifact, containing 40%wt of the most activated resin (Table 1) there, reaches a total dose $D < 10^5$ Gy in 300 years (Fig. 1a). The estimate, based on Eq. (1), conservatively assumes that each artifact absorbs all its own gamma radiation.

in (1), A_j is the total activity of the j -th element in the artifact, P_j^i is the j -th element probability of decaying with a E^i energy photon (see Fig. 1b), and M_{tot} is the total mass of the artifact. The reduction in time of the activity of the j -th element is described in Eq. (2), where $t^{1/2}$ is the half lifetime of the element, reported in Table 1, and $A_{j,0}$ is the activity of the j -th element at time $t = 0$.

$$A_j(t) = A_{j,0} e^{-\ln(2) \frac{t}{t^{1/2}}} \quad (2)$$

4. **Water Immersion Resistance:** Compression strength measured as in point 1 after 30 days of immersion.
5. **Leachability Resistance:** A leaching test for the Cesium cation (Cs^+) was performed by analyzing water samples from two immersion periods: 7 h and 89 h. The analysis used inductively coupled plasma-mass spectrometry (ICP-MS (Wilschefski and Baxter, 2019)) following a simplified short-term procedure based on ANSI/ANS-16.1-1986 guidelines (American Nuclear Society, 2019), which allows considering only 2 leaching water samples instead of 6. This approach (analysis of 2 instead of 6 water samples) was chosen due to consistent and constant diffusion coefficients observed in previous comprehensive tests involving six samples over 96 h, as required by legislation, see also below.
6. **Fire Resistance:** The tests involved subjecting the sample to an open flame produced by a Bunsen burner. As specified in (ASTM

Table 1

Radiological specific characterization of the most activated resin of Trino Vercellese at the January 01, 2012, 25 years later the reactor's shut down (the unit mass is referred to the dry resin) (SOGIN, 2012).

	Cs-134	Cs-137	Co-60	Bi-208
Specific gamma activity [Bq/kg]	3.5×10^{10}	1.1×10^5	3.9×10^6	2.9×10^8
Half lifetime ($t^{1/2}$) [year]	2.065	30.17	5.27	3.68×10^5

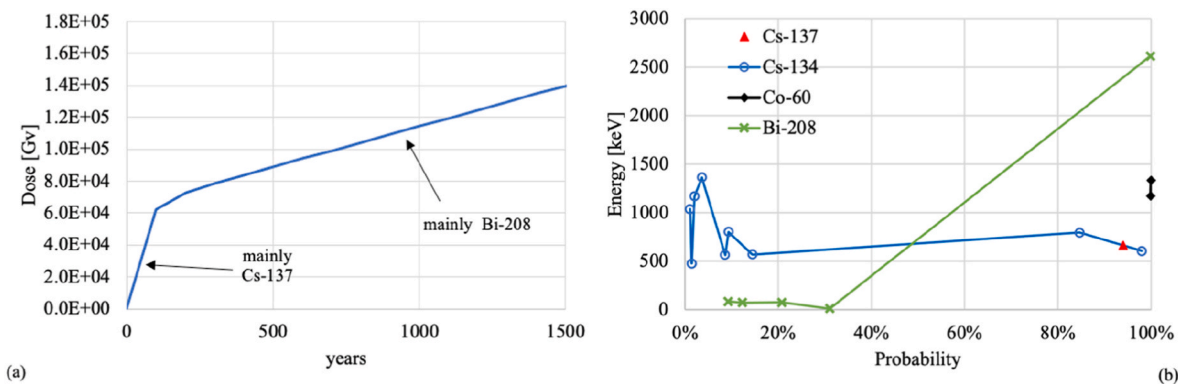


Fig. 1. (a) Photon energy of Cs-134, Cs-137, Co-60 and Bi-208 decay as function of its probability; (b) evolution over time of the total gamma-induced dose of artifact embedding 40%wt of resin.

International, 2022), the flame was oriented at a 45° angle to the sample, which was positioned with its main axis horizontal. The self-extinguishing or non-flammability was proved by visual inspection.

- 7. Gaseous Permeability:** The porosity of the samples was determined using a gas pycnometer (Micromeritics AccuPyc II 1340). Robust statistical significance was achieved by conducting six measurements for each sample. Helium-5 (He-5) was used as an inert gas to estimate the void volume within the samples, while the apparent volume was calculated based on geometrical measurements. The void percentage represents the cumulative volume of all interconnected voids in the sample. Due to its low reactivity and high permeability, He-5 can effectively infiltrate even micro-pores, thereby exposing voids down to the structural scale.

The threshold values for waste acceptability at the Italian National Repository correspond to compressive strength, resistance to immersion, thermal cycles, and radiation meeting a minimum of 10 MPa, while the leachability index for cesium must exceed 7. Regarding fire resistance, the waste must demonstrate to be non-combustible or self-extinguishing. The mandatory gas permeability test currently does not yet provide a limit value for waste acceptability.

3. Results

3.1. Phase 1. geopolymers' analysis

The compressive strength test results for 89 unique combinations of fundamental molar ratios are presented in Fig. 2. Each combination was tested on three samples to ensure the repeatability of the results.

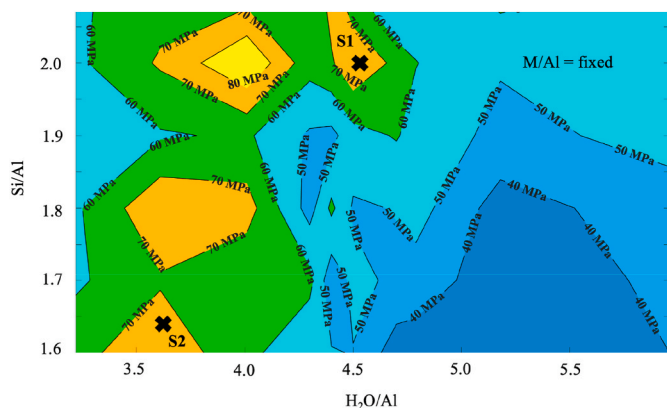


Fig. 2. Compressive strength of geopolymers cured 28-days at 25 °C as a function of their Si/Al and H₂O/Al ratios, for a fixed ratio M/Al.

To vary the quantities of silicon and aluminum ions, as well as H₂O, in the geopolymer formulations, the same metakaolin powder was mixed with different activating solutions: sodium metasilicate, a blend of sodium metasilicate and silica fume, and a combination of silica fume and distilled water. These activating solutions provided sources of SiO₂ and H₂O. In highly basic alkali solutions (pH = 15), silica fume dissolves, generating silicate ions comparable to those from liquid metasilicate. Sodium metasilicate limits the Si/Al and H₂O/Al ratios due to its fixed formulation, whereas silica fume allows for greater flexibility, enabling independent variation of SiO₂ and H₂O. The use of all these activating mixtures facilitated precise control of Si/Al and H₂O/Al ratios, making the systematic investigation of the 89 combinations possible.

The main outcome from Fig. 2 is that higher water content results in lower compression strength of the geopolymer. For an H₂O/Al ratio ≤ 4.0, increasing the Si/Al ratio produces a more viscous paste that is difficult to pour. Two specific points, labeled S1 and S2, are highlighted on the graph as they correspond to the recipes selected for the development of HYPEX®. These recipes demonstrate compressive strengths exceeding 70 MPa and exhibit good workability. In the S2 recipe, a combination of low H₂O/Al and Si/Al ratios was chosen to ensure both workability and strength. Conversely, the reliability of the S1 recipe is attributed to its high Si/Al ratio and relatively high H₂O/Al ratio. Areas in Fig. 2 that exceed 70 MPa in compressive strength but are not labeled correspond to geopolymer pastes with poor workability. Specifically, geopolymers in the yellow region exhibit extremely high viscosity, making the mixture completely unworkable when resin was added to the paste.

Although S1 and S2 utilize different activating solutions (SiO₂ is sourced from silica fume powder in S1 and from liquid metasilicate in S2), they share the same metal mix in the alkali solution – 65% of Na⁺ and 35% of K⁺ – and use the same metakaolin powder as the geopolymer precursor. The alkali solution for S1 was prepared using sodium hydroxide, potassium hydroxide, demineralized water and silica fume (SiO₂ >95%, K₂O 1.1%, CaO 0.72%, Na₂O 0.18%, with an apparent density of 550 kg/m³, particle size distribution of 45 μm < 5% and a BET

Table 2

Compressive strength, resistance to immersion, and resistance to 110 °C for samples obtained using the S1 and S2 recipes. Different alkali metal mixes used to activated alluminosilicate powder are reported: 65% Na 35% K and 100% Na.

	65% Na 35% K		100% Na	
	S1	S2	S1	S2
Resistance to compression [MPa]	67.5 ± 6.8	67.7 ± 3.2	36.3 ± 4.7	44.4 ± 3.0
Resistance to immersion [MPa]	0 ± 0	0 ± 0	30.4 ± 4.6	41.7 ± 2.2
Resistance to 110 °C [MPa]	0 ± 0	0 ± 0	31.3 ± 4.2	36.2 ± 0.4

specific surface area of 23 m²/g). In contrast the alkali solution for S2 consisted of sodium silicate (SiO₂ 27%, Na₂O 8%, H₂O 65%), sodium hydroxide, and potassium hydroxide.

Following the compressive strength tests, the selected geopolymers were further assessed for their resistance to water immersion and exposure to 110 °C. Since the goal is to develop a conditioning matrix for radioactive waste, the material must demonstrate good resistance to water immersion. Although not mandatory, resistance to 110 °C is used as an additional criterion for evaluating the matrix's suitability: failure in this test indicates inadequacy as a cementitious material. Despite their excellent compressive strength (see Table 2), both S1 and S2 recipes, formulated with 65% sodium and 35% potassium, failed these tests, showing a complete loss of compressive strength. Consequently, the metal mix in HYPEX® was adjusted to 100% sodium, yielding positive results: sodium-based geopolymers show reduced compressive strength but exhibit good resistance to both water immersion and thermal conditions (see Table 2). The superior water immersion resistance of the Na-based geopolymer, as shown in Table 2, is attributed to the behavior of potassium in the K-based geopolymer. When exposed to water, potassium forms hygroscopic salts that absorb moisture, expand, and potentially disrupt the internal structure. Moreover, the smaller ionic radius of potassium compared to sodium results in greater mobility, which allows potassium to leach out more easily from the geopolymer. This leaching leads to charge instability within the material, weakening its overall structure.

Based on the results presented in Table 2 and the previous discussion, geopolymers S1 and S2, activated with a fully sodium-based alkaline solution, were selected for the development of the HYPEX® process. These formulations were then further improved with the following two additions.

- To further enhance the compressive strength of the selected geopolymer recipes while maintaining a good workability of the paste, 2%wt calcium hydroxide was added to both formulations as suggested by (Kim et al., 2022). The beneficial effect of Ca⁺² cation, produced by the dissolution of Ca(OH)₂, lies in its ability to form an additional ionic bond compared to Na⁺. This extra bond strengthens the geopolymer matrix, enhancing its overall structural integrity. As a result, the compressive strength increased by approximately 15% compared to values presented in Table 2.
- Additionally, 30 wt% sand from the Alpine crystalline massifs was incorporated as an inert filler in both S1 and S2 recipes, which were previously presented in Table 2 without sand. This addition aims to reduce the geopolymer's drying shrinkage and subsequent cracking (Künzel, 2013). The particle size of the sand ranged from 0.3 to 0.6 mm and its grain density is 2.62 g/cm³. Literature commonly suggests sand-to-precursor (metakaolin in this study) ratios of 1:1, 1:2, and 1:3 (Maaze and Shrivastava, 2023). Since the geopolymers under development are intended as matrices for radioactive waste, which itself acts as an inert filler, the lowest recommended ratio was chosen to ensure that the mass of the inert material does not exceed that of the binder.

3.2. Phase 2. performance assessment on selected geopolymer with resin

The S1 and S2 geopolymer recipe, enriched with 2%wt of Ca(OH)₂ and 30%wt of sand as explained above, were tested respectively with 20%wt and 30%wt of ground and hydrated IEXs.

Fig. 3 presents the results of various mandatory tests required for the Italian approval of a product as a conditioning matrix for radioactive waste. Generally, lower resin content results in better test outcomes. This holds true except for gamma radiation resistance of recipe S2, embedding 20%wt of resin, a result that does not align with the other outcomes. This topic requires further research. It is noteworthy that both S1 and S2 recipes meet the Italian Waste Acceptance Criteria (Italian WAC) when 30%wt resin is included. The S2 recipe, which does not

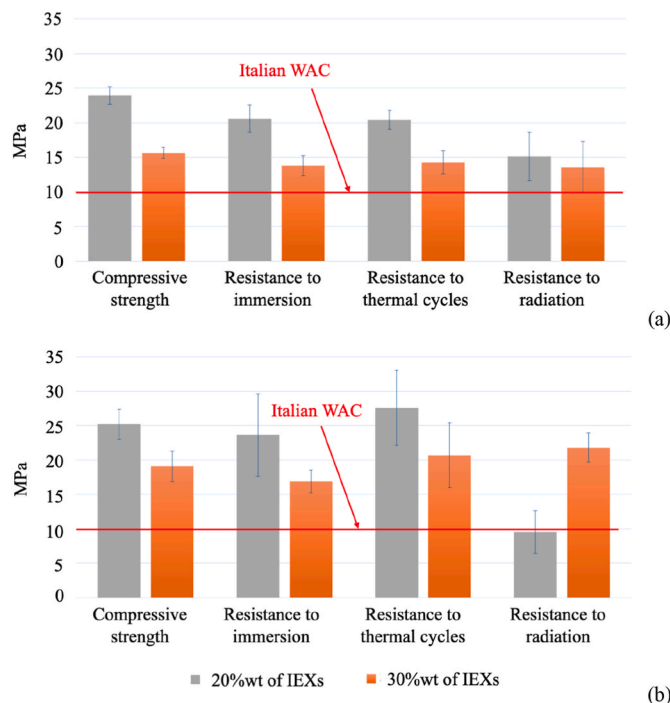


Fig. 3. Compressive strength and resistance to immersion, thermal cycles and radiation results of S1 (a) and S2 (b) geopolymers with respectively 20%wt of resin (grey bars) and 30%wt (orange bars). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

Table 3

Total porosity of samples made with S1 and S2 recipe with resin content equal to 20%wt and 30%wt.

	20%wt of IEXs	30%wt of IEXs
S1	38.1 ± 0.2	44.8 ± 0.5
S2	36.7 ± 0.6	41.4 ± 0.8

include silica fume, performed better with 30%wt of IEXs, as it either doubles or nearly doubles the threshold imposed by GT33.

The enhanced resistance of S2 to immersion and thermal cycles compared to S1 can be attributed to their differing fundamental H₂O/Al molar ratios. S2, having a lower water content than S1, experiences less water evaporation during curing and consequently forms fewer voids, as evidenced by the gaseous permeability results presented in Table 3. During immersion, water infiltrates the matrix through these existing voids, which can lead to the dissolution and reorganization of the geopolymer structure. This may involve the migration of ions such as Na⁺ and destabilization of the silicate-aluminate network, potentially resulting in the formation of micro-cracks. Therefore, the reduced porosity of S2 lowers water permeability and mitigates these effects, thereby providing superior resistance to immersion. Furthermore, the lower H₂O/Al ratio of S2 indicates a reduced presence of interstitial water compared to S1. During thermal cycling, interstitial water undergoes freezing and thawing, which exerts stress on the matrix and contributes to its weakening. As a result, S2 experiences less stress from these thermal cycles due to its reduced interstitial water content.

Fig. 4 presents the results of the leachability tests, showing that the S1 formulation, which includes silica fume, outperformed S2, which does not include silica fume. However, both formulations meet the Italian Safety Criteria for the management of radioactive waste with up to 30%wt of resin.

The total void percentage (measured using a helium-based gas pycnometer Micromeritics AccuPyc II 1340) of the samples containing 20%

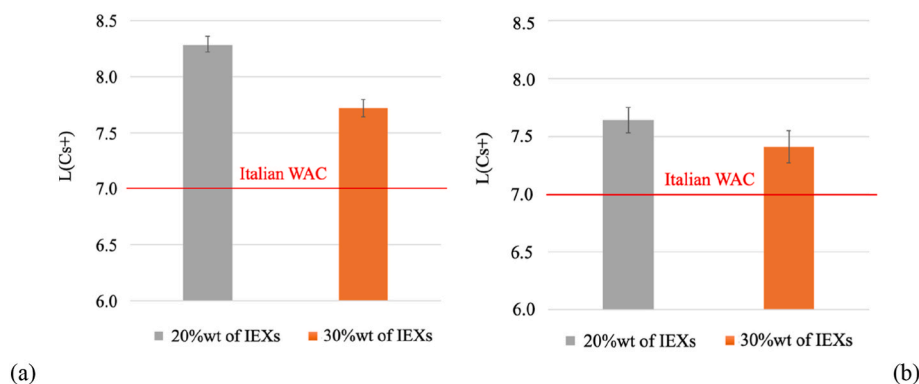


Fig. 4. Resistance to leachability of S1 (a) and S2 (b) recipes with respectively 20%wt of resin (grey bars) and 30%wt (orange bars). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

wt and 30%wt of resin is shown in Table 3. Each test was replicated six times. The geopolymer based on S2 exhibits a lower porosity than S1 as expected since it has a lower H_2O/Al ratio, implying that less water evaporates during curing and fewer voids are formed.

Fire resistance tests on S1 and S2 samples containing 20%wt and 30%wt of resin demonstrated that the samples are self-extinguishing (data not shown). The tests were visually evaluated and replicated three times. These findings confirm the inherent fire resistance properties of geopolymers.

4. Discussion and future perspective

4.1. Comparison between the two geopolymer's recipes selected

The S1 and S2 formulations have demonstrated to be best in the conditioning matrices for the immobilization of spent ion exchange resins, as both meet the Waste Acceptance Criteria for the management of radioactive waste in Italy with 30%wt of resin embedded.

The S2 recipe has silicate ions already dissolved in the alkali solution, while the S1 recipe obtains Si ions from silica fume powder. Silica fume is a byproduct of silicon or ferrosilicon alloy production, formed through the rapid cooling of silicon oxide vapors. This process generates microscopic particles with sizes ranging from 0.1 to 1 μm and a high specific surface area (up to 20 m^2/g). Unlike the stable formation of the quartz at high pressure and temperature, the rapid formation prevents the organization of Si and O atoms into a crystalline lattice, resulting in an amorphous and less stable structure with randomly distributed atoms. The low chemical stability and the high surface area make silica fume highly reactive. When exposed to the alkaline environment of geopolymer mortar, the bonds in the silica fume break and then reorganize, promoting the formation of metal silicates as well as geopolymer chains. Specifically, calcium hydroxide reacts rapidly with silica fume, leading to the formation of calcium silicate hydrates (C-S-H), as reported by (Wu and Young, 1984). These calcium silicates are highly hygroscopic and tend to swell when exposed to humidity, generating internal tensions within the geopolymer matrix. This behavior contributes to the lower resistance of S1 samples to immersion, as well as to compression, thermal cycles, and radiation, compared to S2. Furthermore, as highlighted by (Bar-Nes et al., 2008), the remaining unreacted silica fume can be subjected to hydrolysis, breaking Si-O-Si bonds and replacing them with Si-OH-Si bonds. This process may produce silica gel, which has the capability to absorb Cesium (Bascetin et al., 2003). This contributes to the immobilization of Cs within the geopolymer matrix, enhancing the S1 material's effectiveness in retaining the ion over time. This reaction accounts for the higher resistance to leachability observed in S1 samples compared to S2.

4.2. Volume Reduction Factor obtained with HYPEX® process

A relevant aspect that needs to be discussed for both formulations is the reduction of the waste final volume, if one of these kinds of geopolymer is selected for the IEXs immobilization. Considering as the Key Performance Indicator the Volume Reduction Factor (VRF), defined as in Eq. (3):

$$VRF = \frac{\text{wet resin volume}}{\text{conditioned resin volume}} \quad (3)$$

the VRF for HYPEX®, depending only on the %wt of resin, results to be 0.24. In Eq. (3), the wet resin volume refers to the volume occupied by the resin when fully hydrated according to its technical specifications (water retention capacity of 55% for H⁺ form and 60% for OH⁻ form).

The comparison of the HYPEX® VRF with other results in the literature is challenging due to the different Waste Acceptance Criteria imposed by various nations, as outlined in the Introduction. Notably, the most relevant comparison is with the SIAL geopolymer, which meets the Czech standards for compressive strength (≥ 10 MPa), aligned with Italian requirements. In this country and in Slovakia, the SIAL geopolymer has been qualified for conditioning a sludge/resin mixture (Lichvar et al., 2013). Since sludge and resin possess different chemical and physical properties, the comparison will focus solely on SIAL cases involving the conditioning of only spent resins. Specifically, this refers to the conditioning of 1.300 kg of spent resins from the A-1 NPP¹ during 2008–2009. In this instance, SIAL managed to achieve a VRF of 0.14, indicating that HYPEX® can further reduce the final waste volume to be disposed. Nevertheless, comparison remains difficult due to the lack of standard protocols for assessing the suitability of geopolymers as conditioning matrices, an issue that the CRP programmed by the IAEA aims to address (IAEA, 2023).

4.3. Future perspective

To further improve the Volume Reduction Factor, one of the future lines of optimization of HYPEX® includes increasing the resin content in the matrix. Preliminary tests on the S2 geopolymer with 35%wt of resin embedded show a compressive strength of 19.3 ± 1.1 MPa and a water immersion resistance of 16.5 ± 2.1 MPa. The goal is to enhance the mechanical properties characteristic of S2 samples while maintaining the high leachability resistance typical of S1 samples.

Future works will also address more specifically the characterization of initial raw powder (granular size distribution, specific surface,

¹ Nuclear Power Plant (NPP) in Jaslovské Bohunice; A1 refers to the HWGCR of the plant with a capacity equal to 143 MWe. This reactor operated from 1972 to 1977 (Stubna et al., 2002).

chemical reactivity) in order to assess how these variables influence the metakaolin powder dissolution in the alkali solution and the complete geopolymer formation.

5. Conclusion

The HYPEX® process is designed as conditioning method for the spent Ion Exchange Resins (IEXs) present in the nuclear power plant. It is an immobilization process performed at room temperature, utilizing a novel and special geopolymer as the conditioning matrix for grounded and hydrated IEXs. The tests results presented and discussed in the paper have demonstrated its capability to embed up to 30%wt of resin, in accordance with Italian Waste Acceptance Criteria, which is much stricter than that of other countries. Beside the possibility to operate at room temperature, the clear advantage offered by the proposed process is a reduction of the final waste volume to be disposed compared with the others immobilization-in-geopolymer processes.

CRedit authorship contribution statement

Francesca Crivelli: Writing – original draft, Visualization, Validation, Investigation, Formal analysis, Data curation, Conceptualization. **Silvio Cao:** Supervision, Resources, Project administration, Methodology. **Marino Corrado:** Writing – original draft, Visualization, Validation, Investigation, Formal analysis, Data curation, Conceptualization. **Claudio Mascialino:** Supervision, Funding acquisition. **Laura Savoldi:** Writing – review & editing, Supervision, Project administration, Funding acquisition. **Giancarlo Ventura:** Writing – review & editing, Supervision, Methodology, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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