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Thermal evaluation of a Cs-loaded waste vitrification

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Abstract: Nuclear power generation has been increasing worldwide over the years, helping to avoid the emission of billions of tons of carbon dioxide (CO_2) compared to coal power generation, making it a reliable method for providing green energy. However, as a byproduct of nuclear reactors, as well as fuel processing plants, hospitals, and research institutes, radioactive waste is generated. These wastes pose a significant risk to human health and the environment due to the penetration of radioactivity into tissues, which damages DNA. Therefore, they need to be managed appropriately before long-term disposal in geological repositories. Among the many radionuclides found in high-activity waste, ^{137}Cs is of particular concern due to its high mobility in water systems, requiring special methods for its capture and immobilization in stable matrices. In this study, the immobilization of ^{137}Cs radionuclides in a borosilicate glass doped with niobium (Nb) was thermally evaluated through a vitrification process, using a synthetic type A zeolite saturated with ^{133}Cs (stable) as a simulated radioactive waste. The incorporation of 40.0 wt.% of this material into the glass composition resulted in a vitrified waste with good melting homogeneity and thermal stability. Several changes due to the incorporation were detected in thermal analysis (DTA), with events such as glass transition, initial crystallization, complete crystallization, and subsequent melting all shifting to higher temperatures. The compositional changes induced by vitrification moved the system to new locations in the ternary equilibrium phase diagrams of the subsystems, in different compatibility triangles, and closer to higher liquidus temperatures than those observed for the raw glass matrix. Through crystallization induced by heat treatment, crystalline phases were obtained, as indicated in the phase diagrams. Cs atoms previously immobilized in the glass network structure became components of pollucite crystals ($CsAlSi_2O_6$) during heating up to 800 °C. These results are promising for using this glass composition to immobilize waste containing ^{137}Cs, as Cs atoms showed excellent interaction with this system in both the glass and crystalline phases.

Keywords: cesium-137, nuclear waste vitrification, niobium-modified glass, zeolite A.

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Avaliação térmica da vitrificação de um rejeito saturado com Cs

Resumo: A geração de energia nuclear continua tem aumentado em todo o mundo ao longo dos anos, ajudando a evitar a emissão de bilhões de toneladas de dióxido de carbono (CO_2), quando comparada com a geração de energia à carvão, sendo um método confiável para o fornecimento de energia verde. No entanto, como subproduto dos reatores nucleares, bem como das fábricas de processamento de combustível, hospitais e institutos de pesquisa, são gerados rejeitos radioativos. Esses rejeitos representam alto risco à saúde humana e ao meio ambiente, devido à penetração da radioatividade nos tecidos causando danos ao DNA. Portanto, necessitam ser gerenciados adequadamente antes do descarte a longo prazo em repositórios geológicos. Entre os muitos radionuclídeos encontrados nos rejeitos de alta atividade, o ^{137}Cs é de particular preocupação, devido à sua elevada mobilidade através de sistemas hídricos, requerendo métodos especiais para a sua captura e imobilização em matrizes estáveis. Neste estudo, a imobilização de radionuclídeos ^{137}Cs em vidro borossilicato dopado com nióbio (Nb) foi avaliada termicamente através de um processo de vitrificação, utilizando uma zeólita sintética do tipo A saturada com ^{133}Cs (estável) como rejeito radioativo simulado. A incorporação de 40,0% em massa deste material na composição do vidro resultou em um rejeito vitrificado com boa homogeneidade de fusão e estabilidade térmica. Diversas alterações decorrentes da incorporação foram detectadas na análise térmica (DTA), com eventos como a transição vítrea, a cristalização inicial, a cristalização completa e a subsequente fusão todos deslocando para temperaturas mais altas. As alterações composicionais devido à vitrificação projetou o sistema para novas localizações nos diagramas ternários de equilíbrio de fases dos subsistemas, em diferentes triângulos de compatibilidade e próximos a temperaturas "liquidus" mais altas do que as observadas para a matriz de vidro bruto. Através da cristalização induzida por tratamento térmico, foram obtidas fases cristalinas, de acordo com a indicação nos diagramas de fases. Átomos de Cs previamente imobilizados na estrutura de rede do vidro tornaram-se componentes de cristais de polucita ($CsAlSi_2O_6$) durante o aquecimento até 800 ºC. Estes resultados são promissores para o uso desta composição de vidro para imobilizar rejeitos contendo ^{137}Cs, uma vez que os átomos de Cs apresentaram excelente interação com este sistema tanto na fase vítrea quanto na fase cristalina.

Palavras-chave: césio-137, vitrificação de rejeitos radioativos, vidro modificado com nióbio, zeólita A.

1. INTRODUCTION

Nuclear power is one of the possible low-carbon electricity sources currently in use in thirty-two countries, with a total capacity of 390 GW [1]. However, radioactive wastes are generated, particularly from spent nuclear fuel reprocessing [2]. Of particular concern, most high-level waste (HLW) occurs in liquid form, containing several fission products and certain transuranic elements with half-lives that can last thousands of years. Among the many nuclides found in HLW, ^{137}Cs is especially dangerous due to its half-life of 30.2 years, high radioactivity (10^{15} Bq), and its ease of contamination through soil and rivers [3].

One solution to this problem is the capture of radionuclides from liquid effluents, which has been carried out using natural and synthetic adsorbents, such as zeolites. Zeolites are silico-aluminous microporous materials that present a high surface area. Their well-defined crystalline structure consists of interwoven SiO_4 and AlO_4^- tetrahedra, with alkaline and alkaline earth cations (e.g., Na^+, Ca^{2+}) balancing the residual negative charge on the AlO_4^-. These electrostatically bound ions can be replaced by other cations, such as Ti^{4+}, Fe^{3+}, and Cs^+, in liquid media. The ion exchange process depends on the so-called ion affinity, which includes zeolite characteristics like the number of exchangeable sites (Si/Al ratio), as well as factors such as acidity or basicity, and ionic properties like the cation-surface interaction and the hydrated ionic radius, among others [4,5]. Once loaded with radionuclides, these adsorbent materials can be subjected to densification processes, such as thermal treatments on compressed pellets or incorporation into matrices like geopolymers, cement blends, or glasses for subsequent disposal [4–6].

In this context, HLW vitrification is one of the most advantageous processes used to treat waste from nuclear power plants and nuclear activities [7]. In radiologically protected facilities, the general process begins with the calcination of HLW into a powder, which is then incorporated into glass additives for melting over a specified duration. The molten glass is then poured into stainless steel canisters, which are sealed and sent for disposal [8]. Some glass compositions have been used to vitrify nuclear waste for over 50 years. Borosilicate glasses are a viable choice for this application due to their ability to incorporate most radionuclides both in micro- and macro-structures, as well as their high resistance to thermal shock, radiation, hydrolytic attack, and other factors [8,9].

Although much research has been conducted on nuclear waste immobilization over the years, some problems still arise during the vitrification process, such as the undesired crystallization of Na- and Al-rich HLW in the melters [10]. Additionally, radioactive decay and radionuclide transmutations affect the vitrified waste forms during their long-term disposal in deep geological repositories. Their integrity can be compromised by crystallization, structural defects, bubbles, volume changes, and other issues [10–14]. For this reason, the search for new glass compositions that can help solve these problems is essential.

This study evaluates the thermal effects of Cs-loaded waste vitrification (simulated ^{137}Cs-rich waste) using ion-exchanged type A zeolite mixed with a borosilicate glass composition doped with Nb, which is suitable for this application. Changes in the thermal properties of the glass matrix after Cs-waste incorporation were observed due to the increase in SiO_2, Al_2O_3, Cs_2O, and Na_2O in the overall composition. Once incorporated into the glass network structure, Cs atoms follow the trend of crystallization upon heating, forming Pollucite ($CsAlSi_2O_6$) crystals, even in a network containing anions like Nb^{5+}, which are available to form crystalline phases. These findings are promising for the selective vitrification of ^{137}Cs from contaminated waters.

2. MATERIALS AND METHODS

Incorporating radioactive elements into glass matrices is a complex task, and several important aspects must be considered, such as the physical and chemical characteristics of the waste elements, the melting temperature required for vitrification, and the volatilization temperature of the radionuclide(s). Depending on its physical state, the waste may need to be pretreated. Liquid radioactive wastes must be calcined, as previously mentioned, while solid radioactive wastes must be ground, both prior to mixing with glass precursors or glass frits. The vitrification process used in this work was first studied and developed in our recently published study [15], utilizing a very specific glass composition. This composition shows notably low leaching rates for Cs (1×10^{-3} g/m^2) after 7 days under the Product Consistency Test (PCT-B) and high thermal stability (up to ~650 °C), enhanced by up to 8.0 mol% Nb additions [15,16]. However, a focused analysis of vitrification aspects, such as phase concentration and comparison with raw glass matrices, was still lacking. For this work, a glass matrix (G3), with the nominal composition shown in Table 1, was produced according to the procedure described in our previous studies [15,16]. The glass system belongs to the borosilicate family but contains considerable amounts of sodium and calcium, which were carefully introduced in previous formulations [17] to obtain a wide-open network structure, capable of accepting different-sized and different-valence waste cations, such as those found in solid galvanic wastes. The medium wasteform composition is also shown in Table 1.

Table 1: Nominal composition of G3 glass matrix (X-ray Fluorescence, XRF) [16] and medium composition for the wasteform (G3 + Cs-loaded waste) [15].

	Oxide	**SiO2**	**B2O3**	**Na2O**	**CaO**	**K2O**	**Al2O3**	**Nb2O5**	**Cs2O**
G3	wt. %	40.68	7.96	25.37	19.80	0.99	1.99	3.21	-
G3 + Cs-loaded waste	wt. %	34 - 37	4.5 -5	13 - 15	11 - 14	0.2 – 0.5	10 - 15	1 – 1.3	4.5 – 5.5

The simulated 137Cs-loaded waste was obtained through an adsorption experiment adapted from reference [18], in which ash-derived synthetic type A zeolite was added to a CsCl aqueous solution (0.5 L, 1:1 zeolite/salt ratio). The mixture was stirred for 24 hours, filtered, and then dried at 105 ºC for 16 hours. To produce the vitrified simulated waste (G3 + Cs-loaded waste), the raw materials SiO_2, NaOH, CaO, K_2CO_3, H_3BO_3, Al_2O_3, and Nb (metallic, 99.999%) were mixed with the Cs-loaded zeolite A (3:2 glass/waste wt. ratio), homogenized, and transferred to an alumina crucible for melting in an electrical furnace at 1280 ºC for 1.5 hours. The molten mixture was then cast onto a metallic plate for rapid cooling and solidification. The crystallization of the glass specimens was carried out through a thermal treatment in air at 800 ºC for 2 hours, followed by slow cooling inside the furnace.

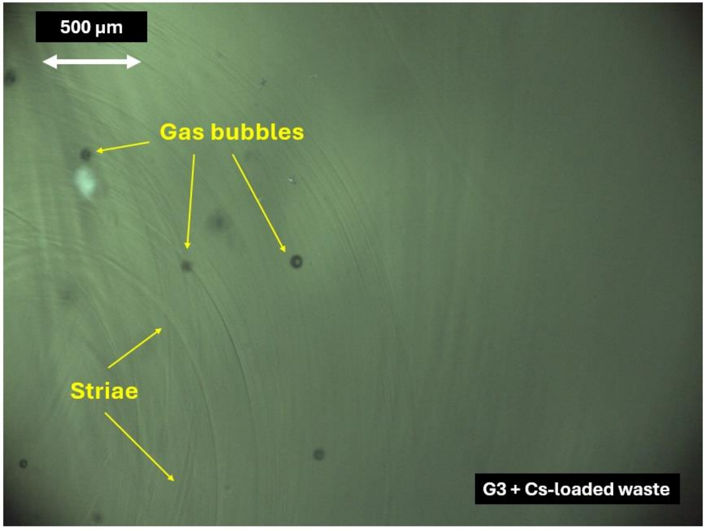
2.1. Characterization

Differential Thermal Analysis (DTA) was performed using a DSC/DTA instrument in synthetic air, at a heating rate of 10 ºC/min up to 1300 ºC. X-ray diffractometry was conducted on powder samples in Bragg-Brentano configuration, using a multichannel detector diffractometer operating with Cu-α radiation (1.15 Å) at a scan rate of 2.7 º/s. Rietveld refinement was performed on the obtained XRD pattern using crystallographic information files (CIF) with the following numbers: 5910011 ($NaNbO_3$), 9001797 ($CsAlSi_2O_6$), 9007720 ($Na_2Ca_2Si_3O_9$), and 9010480 ($NaAlSiO_4$), obtained from the Crystallographic Open Database (COD).

3. RESULTS AND DISCUSSIONS

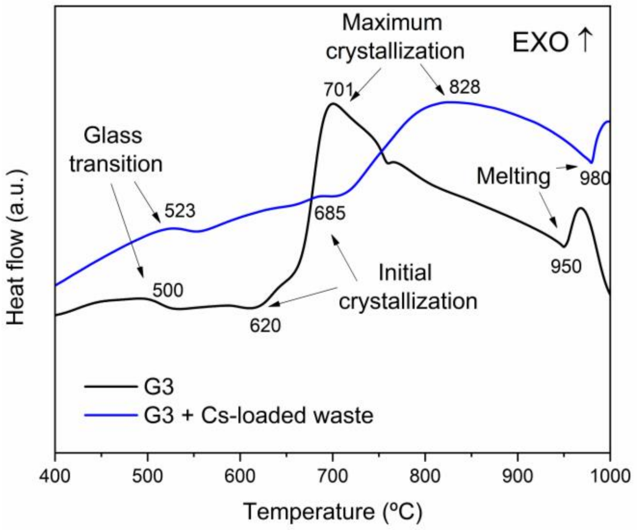
Figure 1 shows an image of the glass wasteform sample, obtained using a transmitted light microscope. A "liquid-like" appearance is observed with striae, suggesting local phase fluctuations, and a few bubbles are seen throughout the glass macrostructure. These bubbles are attributed to the high melt viscosity, which hinders the release of gases from the chemical reactions. Nevertheless, melting occurred appropriately for the applied temperature and duration, resulting in a homogeneous vitreous wasteform.

Figure 1: Transmitted light microscope image showing the good homogeneity of vitreous wasteform.



The thermograms of the glass matrix before and after the incorporation of Cs-loaded waste are shown in Figure 2. The first thermal event during heating, indicated by a curve deviation in the endothermic direction, corresponds to the glass transition (Tg), representing the loosening of the network structure. The Tg increases from 500 °C (G3) to 523 °C (G3 + Cs-loaded waste), a 4.6% increase, suggesting that the vitrified waste glass exhibits greater network strength compared to G3. The second event is another endothermic deviation that indicates the growth of the first crystals, i.e., the initial crystallization temperature range. This temperature increases from 621 °C (G3) to 669 °C (G3 + Cs-loaded waste), a 7.7% increase. The next thermal event is an exothermic peak, corresponding to complete crystallization. This event shifts from 700 °C (G3) to around 828 °C (G3 + Cs-loaded waste), representing an 18% increase. The increase in the interval from Tg to the initial crystallization temperature indicates that the wasteform sample (G3 + Cs-loaded waste) exhibits higher thermal stability than G3. The last important event is endothermic and indicates the melting of the crystals grown during the crystallization process. This melting occurs at 950 °C for G3 and 980 °C for the vitrified waste glass (G3 + Cs-loaded waste), a 3.2% increase, showing its higher overall thermal stability compared to G3.

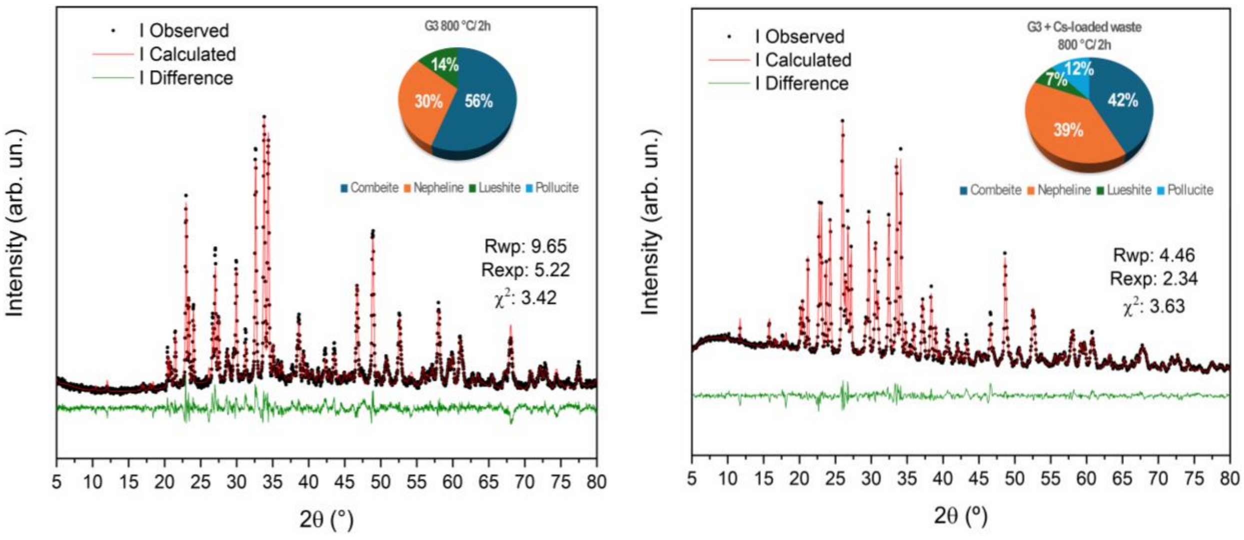
Figure 2: Differential thermal analysis (DTA) before (G3) and after (G3 + Cs-loaded waste) the Cs-waste incorporation (40 wt.%) through vitrification.



Using the intrinsic glass property of crystallization, the G3 glass matrix and wasteform specimens were analyzed by X-ray diffractometry after thermal treatment at 800 °C for 2 hours. The Rietveld analysis, which includes the devitrified phases, is shown in Figure 3. The four crystalline phases detected were Combeite ($Na_2Ca_2Si_3O_9$), Nepheline ($NaAlSiO_4$), Pollucite ($CsAlSi_2O_6$), and Lueshite ($NaNbO_3$). These phases represent stable atomic structures that naturally form due to the glass's metastability, although at a very slow rate of kinetics.

Figure 3: Rietveld analysis on the XRD patterns after a heat treatment at 800 ºC during 2h: (a) G3 glass matrix and (b) wasteform (G3 + Cs-loaded waste).

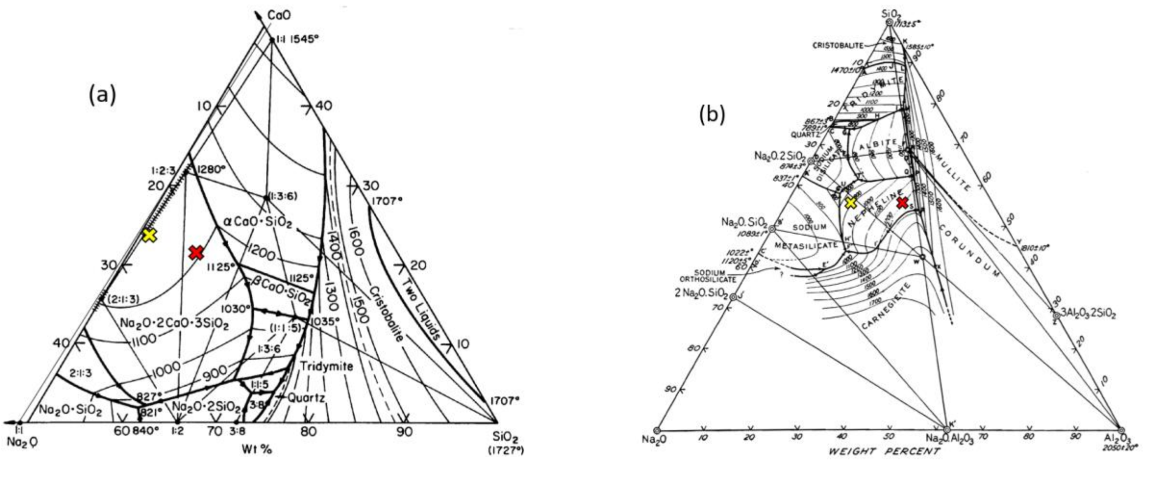
(a) (b)

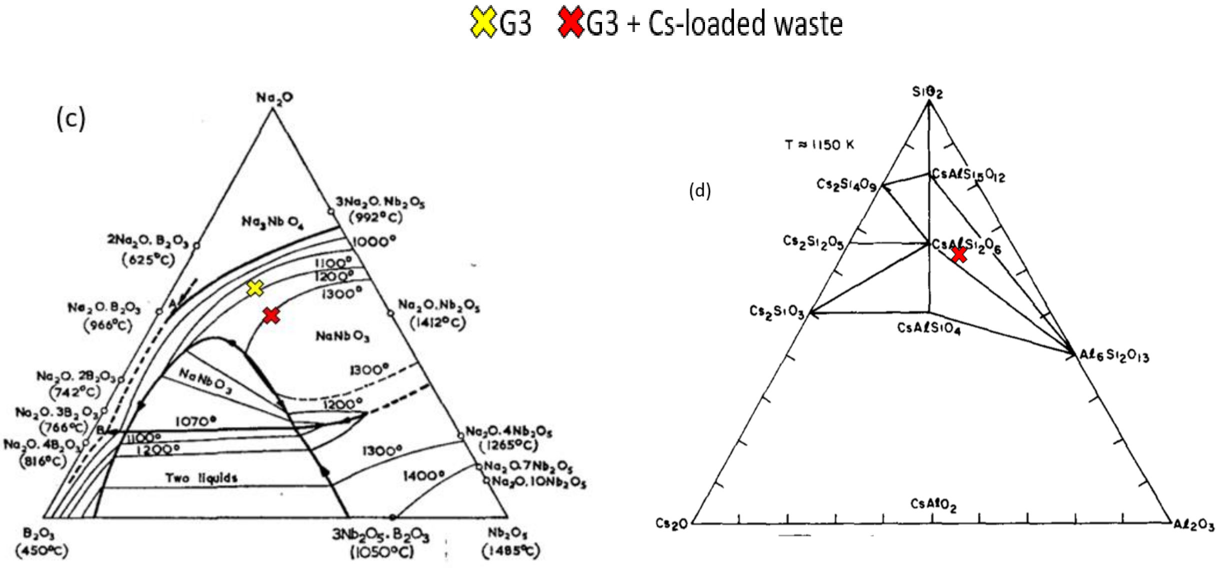


When comparing the phase concentrations of the G3 glass (Figure 3-a) with those of the wasteform (Figure 3-b), decreases were observed for Combeite (-14%) and Lueshite (-7%), while an increase was seen for Nepheline (+9%). Since the global composition changed for the wasteform compared to G3 (see Table 1), the availability of each component for phase growth also changed. The Pollucite concentration aligns with expectations and suggests no loss of Cs during thermal treatment up to 800 °C. Once Cs^+ cations are immobilized into the glass network structure as modifier agents, their stable state will be a crystalline phase. Pollucite, induced by the heat treatment, is the only phase involving Cs, even with the availability of Nb^{5+} anions to interact in this system. Such results are promising for 137Cs vitrification using this glass composition, as Cs is immobilized in both stable glassy and crystalline phases.

The vitrification process was also assessed by plotting the composition of four subsystems in ternary phase diagrams: SiO_2:Na_2O:CaO, SiO_2:Al_2O_3:Na_2O, Na_2O:B_2O_3:Nb_2O_5 and SiO_2:Al_2O_3:Cs_2O before and after the incorporation of Cs-loaded waste. The results are shown in Figures 4 (a-d), and the compositions of the subsystems are listed in Table 2.

Figure 4: Ternary equilibrium phase diagrams of sub-systems: (a) SiO_2:Na_2O:CaO, (b) SiO_2:Al_2O_3:Na_2O, (c) Na_2O:B_2O_3:Nb_2O_5 and (d) SiO_2:Al_2O:Cs_2O, adapted from reference [19]





It is observed (Figures 4-a and 4-b) that for the SiO_2:Na_2O:CaO and SiO_2:Al_2O_3:Na_2O sub-systems, the Cs-loaded waste vitrification shifts the composition to different compatibility triangles, resulting in increased liquidus temperatures and different proportions of crystallized phases. For the Na_2O:B_2O_3:Nb_2O_5 sub-system (Figure 4-c), the new composition is projected to higher liquidus temperatures (1300 °C) compared to the G3 glass matrix (1200 °C); however, both compositions lie within the crystallization field of $NaNbO_3$. In the case of the SiO_2:Al_2O_3:Cs_2O system (Figure 4-d), the plotted composition falls within the crystallization field of Pollucite ($CsAlSi_2O_6$). In this case, Cs atoms acting as modifier cations compete with Na for charge stabilization on the AlO_4^- units [16]. All these phase projections to higher liquidus temperatures indicate an increase in thermal stability and are consistent with the results obtained from the thermal treatment of the glasses, as previously shown in Figure 3.

Table 2: Concentration (wt.%) of compounds in the sub-systems before and after the Cs-loaded waste vitrification.

***Sub-systems**	**(a)**			**(b)**			**(c)**			**(d)**		
Oxide	SiO_2	Na_2O	CaO	SiO_2	Na_2O	Al_2O_3	B_2O_3	Na_2O	Nb_2O_5	SiO_2	Al_2O_3	Cs_2O
G3	48.6	26.2	25.2	56.5	30.5	13.0	22.5	55.2	22.3	-	-	-
G3 + Cs-loaded waste	57.6	20.5	20.5	57.6	20.5	21.9	18.5	51.2	30.4	64.9	24.7	10.4

*The sub-systems were determined according to the chemical composition (Table 1).

4. CONCLUSIONS

The vitrification of the ^{137}Cs radionuclide was evaluated by incorporating Cs-loaded waste into a specific niobium-doped borosilicate glass composition, followed by thermal analysis and heat treatments. The wasteform (G3 + Cs-loaded waste) is suitable for the immobilization of ^{137}Cs-containing wastes due to its good homogeneity and improved thermal stability. These characteristics were achieved through compositional adjustments made by the simulated waste, as the ternary phase diagrams projected the vitrified compositions into different compatibility triangles and higher liquidus temperatures. The Cs atoms are immobilized in the glassy phase up to 680 °C, but also form Pollucite crystals upon heating (from 700 °C onward). These results are promising for the use of this glass composition to immobilize waste containing ^{137}Cs, as Cs atoms show excellent interaction with the system in both the glass and crystalline phases. Future work can focus on increasing the waste loading to evaluate its influence on the structure, homogeneity, and solubility in the glass matrix.

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CONFLICT OF INTEREST

All authors declare that they have no conflicts of interest.

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