



Article Hydrothermal Co-Processing of Coal Fly Ash Cenospheres and Soluble Sr(II) as Environmentally Sustainable Approach to Sr-90 Immobilization in a Mineral-like Form

Tatiana Vereshchagina ^{1,*}, Ekaterina Kutikhina ¹, Leonid Solovyov ¹, Sergei Vereshchagin ¹, Elena Mazurova ¹ and Alexander Anshits ^{1,2}

- ¹ Federal Research Center "Krasnoyarsk Science Center of Siberian Branch of the Russian Academy of Sciences", Institute of Chemistry and Chemical Technology, 50/24 Akademgorodok, 660036 Krasnoyarsk, Russia; ekaterina_kutikhina@mail.ru (E.K.); leosol@icct.ru (L.S.); snv@icct.ru (S.V.); len.mazurowa@yandex.ru (E.M.); anshits@icct.ru (A.A.)
- ² Department of Chemistry, Siberian Federal University, Svobodny Av. 79, 660041 Krasnoyarsk, Russia
- Correspondence: tatiana@icct.ru or vereschagina.ta@icct.krasn.ru

Abstract: Co-processing of radioactive effluents with coal fly ash-derived materials is recognized as a resource-saving approach for efficient stabilization/solidification of radioactive components of wastewater. In this context, the paper is focused on the hydrothermal synthesis of Sr^{2+} -bearing aluminosilicate/silicate phases as analogs of a mineral-like ⁹⁰Sr waste form using hollow glasscrystalline aluminosilicate microspheres from coal fly ash (cenospheres) as a glassy source of Si and Al (SiO₂-Al₂O₃)_{glass}) and Sr(NO₃)₂ solutions as ⁹⁰Sr simulant wastewater. The direct conversion of cenosphere glass in the Sr(NO₃)₂-NaOH-H₂O-(SiO₂-Al₂O₃)_{glass} system as well as Sr²⁺ sorption on cenosphere-derived analcime (ANA) in the Sr(NO₃)₂-H₂O-ANA system were studied at 150–200 °C and autogenous pressure. The solid and liquid reaction products were characterized by SEM-EDS, PXRD, AAS and STA. In the Sr(NO₃)₂-NaOH-H₂O-(SiO₂-Al₂O₃)_{glass} system, the hydrothermal processing at 150–200 °C removes 99.99% of the added Sr²⁺ from the solution by forming Sr-tobermorite and Sr-plagioclase phases. In the Sr(NO₃)₂-H₂O-ANA system, Sr²⁺ sorption on analcime results in the formation of solid solutions $(Na_{1-n}Sr_{n/2})AlSi_2O_6 \cdot H_2O$ of the Na-analcime–Sr-wairakite series. The results can be considered as a basis for the development of environmentally sustainable technology for ⁹⁰Sr removal from wastewater and immobilization in a mineral-like form by co-processing waste from coal-fired and nuclear power plants.

Keywords: cenospheres; Sr-90; mineral-like phase; analcime; Sr-tobermorite; Sr-plagioclase

1. Introduction

The strategy for sustainable development of power production cannot be realized without solving the environmental problems caused by the formation and accumulation of huge amounts of solid and liquid waste [1]. In particular, coal fly ash (CFA) [2–4] and liquid radioactive waste [5] have arisen from the operation of coal-fired and nuclear power plants, respectively. Co-processing of radioactive effluents with CFA-derived materials is recognized as a resource-saving and cost-effective approach for CFA minimization and the efficient removal and stabilization/solidification of radioactive components of wastewater [6–8]. In most cases, as-produced multicomponent fly ashes of appropriate bulk chemical composition are used as cementitious materials to produce Portland cement- [9] and geopolymer-based [3,10,11] concrete waste forms or as source materials to synthesize zeolites entrapping radionuclides from wastewater due to their efficient ion exchange properties [12–15].

The environmentally safe management of high-level radioactive waste of all types is oriented at concentrating and confining the most hazardous radionuclides (¹³⁷Cs, ⁹⁰Sr or long-lived actinides) in chemically, thermally and radiation-resistant solid matrices,



Citation: Vereshchagina, T.; Kutikhina, E.; Solovyov, L.; Vereshchagin, S.; Mazurova, E.; Anshits, A. Hydrothermal Co-Processing of Coal Fly Ash Cenospheres and Soluble Sr(II) as Environmentally Sustainable Approach to Sr-90 Immobilization in a Mineral-like Form. *Materials* **2021**, *14*, 5586. https://doi.org/10.3390/ ma14195586

Academic Editor: Wiesław Stręk

Received: 22 August 2021 Accepted: 18 September 2021 Published: 26 September 2021

Publisher's Note: MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.



Copyright: © 2021 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). such as crystalline and glass-crystalline ceramic materials, in which radioactive elements accommodate in host phases and are similar to naturally occurring minerals in their composition and structure [5,16,17]. This is the most preferred option for hazardous waste disposal compared to other immobilization technologies that use inorganic binders [9,11]. In the context of immobilizing radionuclide ¹³⁷Cs and ⁹⁰Sr, the largest contributors to nuclear waste activity, the mineral-like phases of Cs-feldspathoids (e.g., pollucite) and Sr-feldspars (e.g., plagioclase) types are of a great practical value [17,18]. Following the principles of industrial ecology, the tailoring of cesium or strontium aluminosilicate-based ceramics starting from the CFA-derived precursor of required chemical and mineral-phase composition can be considered a promising method of ¹³⁷Cs and ⁹⁰Sr stabilization and disposal.

Numerous studies have shown that there are valuable microsphere products in multicomponent fly ashes [2,19], which have great potential as precursors of functional materials for various high-tech applications [20–22]. Among them, hollow aluminosilicate glasscrystalline microspheres, or cenospheres, are considered to be one of the most important value-added components of sialic CFAs [23–27]. Advanced utilization strategies require significant CFA cenosphere processing to extract the close-cut products with stabilized physical characteristics (size, density, magnetic properties, etc.), composition and globule structure. At present, the fine classification of cenospheres was realized [28–30], resulting in cenosphere fractions of the specific chemical, phase and granulometric composition with predictable high-tech properties [31–34].

The availability of close-cut cenosphere products with the $(SiO_2/Al_2O_3)_{wt.}$ ratios in the range of 1.2–3.5 was a key factor to use them as precursors for the synthesis of $^{137}Cs/^{90}Sr$ mineral-like host compounds (pollucite, Sr-feldspar). To achieve this, different approaches were used, such as (i) impregnation of loose cenospheres or cenospherebased open-cell porous materials with Cs⁺/Sr²⁺ salts followed by calcination of blends at 800–1100 °C [35,36], (ii) hydrothermal conversion of cenospheres into NaP zeolite followed by Cs⁺/Sr²⁺ sorption and heating of the Cs⁺/Sr²⁺ loaded zeolites up to 1100 °C [37] and (iii) direct synthesis of mineral-like aluminosilicate phases under hydrothermal conditions using cenospheres as a glassy Si and Al source [38,39].

The cenosphere-based hydrothermal synthesis seems to be the promising co-processing route to ¹³⁷Cs and ⁹⁰Sr immobilization in mineral-like forms because it can be implemented via the one-step mild thermobaric treatment of the Cs⁺/Sr²⁺-bearing alkaline solution-cenospheres mixture. As reported [38,39], in the Cs⁺-containing system, the pollucite–analcime solid solutions have been easily synthesized in a wide range of cesium concentrations at 150 °C using narrow cenosphere fractions with a high content of a glass phase (\geq 90 wt.%). Under applied hydrothermal conditions, the efficiency of trapping Cs⁺ from simulant solutions was up to 96%. At the same time, the hydrothermal co-processing of Sr²⁺-bearing solutions and cenospheres has not been studied yet in detail.

The paper presents the results of studying the hydrothermal conversion of cenospheres of stabilized composition and cenosphere-derived material into the Sr^{2+} -bearing mineral-like phases using a strontium stable isotope as an imitator of ⁹⁰Sr. Two experimental approaches were applied, (i) a one-step hydrothermal crystallization of Sr^{2+} -bearing phases in the $Sr(NO_3)_2$ -NaOH-H₂O-(SiO₂-Al₂O₃)_{glass} system at temperatures not higher than 200 °C and (ii) a two-step process based on the hydrothermal conversion of cenospheres into analcime followed by the Sr^{2+} sorption on the cenosphere-derived analcime under hydrothermal conditions at elevated temperatures. This methodology was expected to provide both Sr^{2+} removal from the reaction solution and incorporation in crystalline silicate and/or aluminosilicate phases as solid precursors of final ceramic waste forms suitable for ultimate safe disposal.

2. Materials and Methods

2.1. Chemicals and Materials

Sodium hydroxide ("p.a.", Vekton, Russia) and strontium nitrate ("puriss.", LenReactive, Russia) were used for the preparation of non-radioactive Sr²⁺-bearing solutions.

The cenosphere fraction with ~95 wt.% glass phase of $(SiO_2/Al_2O_3)_{wt.} = 3.1$ (marked as $(SiO_2-Al_2O_3)_{glass}$) was the product of the separation of a CFA cenosphere concentrate resulting from the combustion of Kuznetsk coal (Russia) according to the reported procedures [28–30]. Chemical and phase compositions (wt.%) of the initial cenosphere fraction were as follows [40]: SiO_2-67.6, Al_2O_3-21.0, Fe_2O_3-3.2, CaO + MgO + Na_2O + K_2O-7.7; quartz-3.4, mullite-0.8, calcite-0.5, glass phase-95.4; (SiO_2/Al_2O_3)_{glass}-3.1. Micrographs of the cenosphere globules are given in Figure 1a.



Figure 1. SEM images of (**a**) initial cenosphere material and (**b**) analcime-bearing globules; BSE micrographs and associated EDX spectra for local parts of (**c**,**e**) cenosphere surface and (**d**,**f**) analcime layer.

2.2. Hydrothermal Procedures

2.2.1. Hydrothermal Crystallization

Reaction mixtures with a liquid-to-solid (L/S) ratio of about 7/1 (v/v) were prepared by the addition of cenospheres (~5.0 g) and Sr(NO₃)₂ to 1.5 M NaOH resulting in two Sr(NO₃)₂-NaOH-H₂O-(SiO₂-Al₂O₃)_{glass} systems with different molar compositions and Sr/Si ratios (Table 1). The reaction mixture was transferred into a Teflon-lined stainlesssteel autoclave ("Beluga", Premex AG, Switzerland) which was tightly closed without preliminary evacuation. The syntheses were carried out at 150, 180 and 200 °C with autogenous pressure for 24 h under stirring at a rate of 50 rpm. The solid products were separated by filtration, washed with distilled water several times until neutral reaction of a supernatant occurred and isolated by centrifuging the suspension. The sediments were dried at 80 °C in air and the filtrates were analyzed for Sr²⁺ content. The products thus prepared are denoted as xSr-T hereafter, where x is a Sr/Si atomic ratio in the initial mix and T is temperature of treatment.

Table 1. Molar composition of reaction mixtures and efficacy of the Sr^{2+} trapping from reaction solutions of $Sr(NO_3)_2$ -NaOH-H₂O-(SiO₂-Al₂O₃)_{glass} systems.

System	Sample	T, °C	E, %
$5.5SiO_2/1.0Al_2O_3/1.0SrO/3.65Na_2O/270H_2O$ (Sr/Si) _{at.} = 0.18	0.18Sr-150 0.18Sr-180 0.18Sr-200	150 180 200	99.99 99.99 99.99
$5.5SiO_2/1.0Al_2O_3/2.0SrO/3.65Na_2O/270H_2O$ (Sr/Si) _{at.} = 0.36	0.36Sr-150 0.36Sr-180 0.36Sr-200	150 180 200	>99.99 >99.99 99.99

2.2.2. Hydrothermal Sorption

Analcime was synthesized at 150 °C from the cenosphere fraction according to the reported procedure [38] and used as a sorbent (ANA). Part of the analcime material was hydrothermally treated at 200 °C for 24 h in order to follow possible structure alterations. The typical sorption experiment was as follows. About 1 g ANA was contacted with a 100 mL Sr(NO₃)₂ solution of a given Sr²⁺ concentration, such as 500 and 1000 mg/L, at 25, 150 and 200 °C for 24 h in the autoclave under stirring at a rate of 50 rpm. Then the sorbent was separated by filtration, washed with distilled water and dried at 80 °C in air. The products are denoted as xSr/ANA-T, where x is Sr²⁺ concentration in the initial Sr(NO₃)₂ solution and T is temperature of treatment (Table 2). Micrographs of the analcime-bearing globules are shown in Figure 1b.

Table 2. Composition, lattice parameters for Na,Sr-ANA phases, Sr^{2+} sorption and efficacy of Sr^{2+} extraction from solutions, TG data for the product.

Sample	Composition	Lattice Parameter, Å	Sr ²⁺ Sorption, mg/g	E, %	Δm ³ , % (40–150 °C)	T _m , ⁴ °C
ANA	NaAlSi ₂ O ₆ ·H ₂ O ¹	13.7332 (1)	-	-	7.77 (0.65)	302
1000Sr/ANA-25	NaAlSi ₂ O ₆ ·H ₂ O ¹	13.7337 (8)	15.9	22.7	7.89 (0.84)	299
500Sr/ANA-25	NaAlSi ₂ O ₆ ·H ₂ O ¹	13.7339 (8)	15.4	31.7	7.80 (0.79)	300
1000Sr/ANA-150	Na _{0.82} Sr _{0.09} AlSi ₂ O ₆ ·H ₂ O ²	13.7288 (6)	47.0	47.7	7.81 (0.68)	295
500Sr/ANA-150	Na _{0.86} Sr _{0.07} AlSi ₂ O ₆ ·H ₂ O ²	13.7298 (5)	37.1	72.7	7.74 (0.67)	303
1000Sr/ANA-200	Na _{0.58} Sr _{0.21} AlSi ₂ O ₆ ·H ₂ O ²	13.7168 (9)	79.3	80.0	7.77 (0.55)	291
500Sr/ANA-200	Na _{0.76} Sr _{0.12} AlSi ₂ O ₆ ·H ₂ O ²	13.7241 (8)	46.2	91.7	7.78 (0.54)	305

¹ ICDD 01-070-1575. ² By data of the full-profile crystal structure refinement. ³ Mass loss under heating at 10° /min in the range of 150–600 °C. ⁴ Temperature of mass loss at a maximal rate (according to the DTG curve).

2.3. Characterization Techniques

Powder X-ray diffraction (PXRD) data were collected on DRON-3 (IC "Bourevestnik", St. Petersburg, Russia) and X'Pert PRO (PANalytical, Almelo, Netherlands) diffractometers equipped with a solid-state detector PIXcel using Cu K α radiation (2 θ range 12–120°). The samples were prepared by grinding with octane in an agate mortar and packed into a flat sample holder for the PXRD measurements in Bragg–Brentano geometry. The full-profile crystal structure analysis was performed using the Rietveld method [41] with derivative difference minimization (DDM) [42] refinement. The Na/Sr ratio was estimated from the refined occupancy of respective atomic sites in the analcime lattice taking into account the substitution of two Na⁺ ions by one Sr²⁺. An accurate crystal structure model of analcime obtained in [43] was utilized in the DDM refinement. The crystallographic database of the Joint Committee on Powder Diffraction-International Centre for Diffraction Data (JCPDS-ICDD, now known as the ICDD) JCPDS-ICDD PDF-2 Release 2004 and software PhasanX 2.0 were used to process PXRD patterns.

Morphologies of product particles were studied by scanning electron microscopy (SEM) using TM-1000, TM-3000 and TM-4000 (Hitachi, Tokyo, Japan) instruments. To study the elemental composition of surfaces of product particles, energy-dispersive X-ray spectroscopy (EDS, EDX) examination was performed using TM-3000 and TM-4000 microscopes equipped with the microanalysis system (Bruker, Billerica, MA, USA) including an energy-dispersive X-ray spectrometer with an XFlash 430 H detector and QUANTAX 70 software.

Simultaneous thermal analysis (STA) was performed on a TG-DSC NETZSCH STA 449C (Selb, Germany) analyzer equipped with an Aeolos QMS 403C mass spectrometer. The measurements were carried out under dynamic 20% O₂-Ar atmosphere at ambient pressure on heating in the range of 40–600 °C in Pt crucibles with perforated lids (a sample mass 10–12 mg; $\beta = 10^{\circ}$ /min). The qualitative composition of the gas phase was determined by on-line QMS in the Multiple Ion Detection mode from the intensity of ions m/z = 18 (H₂O), 32 (O₂) and 44 (CO₂).

The Sr²⁺ concentration in the post-synthesis solutions was determined by the atomic absorption analysis at an AAS-30 spectrophotometer (Carl Zeiss, Jena, Germany).

The sorbed Sr^{2+} specific quantity in the solid phase (Q_s, mg/g) was determined as $Q_s = (C_o - C) \cdot v/m$, where C_o and C are Sr^{2+} concentrations (mg/L) in the initial liquid phase and post-synthesis liquor, accordingly; V (L) is the volume of solution; and m (g) is mass of the specimen.

The efficacy of Sr^{2+} trapping from the reaction solutions (E, %) was calculated according to the equation E = $[(m_o - m)/m_o] \times 100\%$, where m_o and m are the Sr^{2+} quantities (mg) in the initial and post-synthesis solutions, respectively.

3. Results and Discussion

3.1. Hydrothermal Crystallization

As seen from Table 1, the hydrothermal processing of all the $Sr(NO_3)_2$ -NaOH-H₂O- $(SiO_2$ -Al₂O₃)_{glass} systems provides the near quantitative, no less than 99.99%, Sr^{2+} trapping from reaction solutions into solid products.

Figure 2 shows PXRD patterns of products resulted from crystallization of cenosphere glass at different temperatures in the presence of a varied strontium amount. By the PXRD data, phases of cubic analcime, NaAlSi₂O₆·H₂O (ANA, ICDD 01-070-1575), orthorhombic or triclinic tobermorite, Ca_{2.25}Si₃O_{7.5}(OH)_{1.5}·H₂O (ICDD 04-011-0271; 04-014-8455) and feldspar, such as plagioclase, Na_{0.499}Ca_{0.499}K_{0.031}Al_{1.488}Si_{2.506}O₈ (WWW-Mincryst, 3714) or Ca_{0.65}Na_{0.35}Al_{1.65}Si_{2.35}O₈ (ICDD 01-083-1369), were identified. The definite identification of tobermorite and plagioclase phases is rather complicated in the polyphase system because of overlapping low-intensive peaks. Cubic analcime was the dominant phase among the crystal phases formed. The temperature rise and the Sr content increase in the reaction mixtures resulted in an intensity increase of the PXRD peaks related to tobermorite and plagioclase (Figure 2a,b). This observation makes it obvious that strontium is involved in the formation of these phases. A slight shift in the position of the PXRD peaks compared to the reference phases not containing strontium also gives reason to propose the formation of (Sr,Ca)-bearing tobermorite and plagioclase with participation of calcium being part of cenosphere glass and added strontium (Figures 3e–h and 4e–h).



Figure 2. PXRD patterns of products resulting from hydrothermal crystallization in the Sr(NO₃)₂-NaOH-H₂O-(SiO₂-Al₂O₃)_{glass} systems at (**a**) 150 °C and (**b**) 200 °C: A—analcime; T—tobermorite; P—plagioclase.



Figure 3. SEM images of product particles resulting from (**a**–**d**) hydrothermal crystallization in the $Sr(NO_3)_2$ -NaOH-H₂O-(SiO₂-Al₂O₃)_{glass} systems at 150 °C; (**e**–**h**) BSE micrographs and associated EDX spectra for local parts of the particles.



Figure 4. SEM images of (**a**–**d**) product particles resulting from hydrothermal crystallization in the Sr(NO₃)₂-NaOH-H₂O-(SiO₂-Al₂O₃)_{glass} systems at 200 °C; (**e**,**f**) BSE micrographs and (**g**,**h**) associated EDX spectra for local parts of the particles.

Microstructures of the product particles with a visible amount of tobermorite and plagioclase phases synthesized at 150 and 200 °C are presented in Figures 3 and 4 by SEM data. It can be seen that the products consist of devitrified hollow microspheres, and their chips and particles have an irregular shape with inhomogeneous composition and structure. Typically, the majority of microspheres have a multilayered composite shell with compact or loose analcime [44] covering (Figures 3a,b,d and 4a,d) and underlying Sr-bearing matters (Figure 3b–h). Analcime crystals can be found also in the internal void of microsphere globules. The strontium content in analcime is insignificant and amounts to 3.0-5.0 wt.% corresponding to the range of Sr/Si molar ratio of 0.04-0.08. Analcime crystals are supported by porous matter enriched with strontium (Sr/Si = 0.3-0.5) and composed of fine-needle and hair-like formations as well as residues of unconverted glass (Figure 3).

Individual Sr enriched (Sr/Si ~0.7) globules not coated by analcime were also revealed among the product particles (Figure 4b). In addition, the prismatic elongated crystals of 8–10 µm in length being typical for feldspars [45] and containing about 42 wt.% Sr were disseminated in the product matter (Figures 3c and 4d,f,h). There are radial aggregates (Sr/Si = 0.4) with a needle-shaped habit of crystals in the voids of broken globules, which is characteristic of tobermorite (Figure 4c,e) [46]. According to SEM-EDS data, the needle-like tobermorite crystals contain 30–35 wt.% Sr and 3–6 wt.% Ca (Figure 4g) confirming the formation of Ca,Sr-bearing solid solutions (Ca,Sr)_{2,25}Si₃O_{7,5}(OH)_{1,5}·H₂O.

Thus, based on the PXRD, SEM-EDS and AAS characterizations of solid products and post-synthetic solutions, it was established that the hydrothermal treatment of the $Sr(NO_3)_2$ -NaOH-H₂O-(SiO₂-Al₂O₃)_{glass} systems at 150–200 °C removes 99.99% of added strontium from the solution by forming Sr enriched mineral-like phases, such as (Sr,Ca)-tobermorite and (Sr,Ca)-plagioclase.

3.2. Hydrothermal Sorption

As demonstrated above, the direct hydrothermal co-processing of $Sr(NO_3)_2$ solutions and cenospheres in an alkaline medium resulted in the crystallization of Sr-bearing silicate phases, such as analcime, (Sr,Ca)-tobermorite and (Sr,Ca)-plagioclase, among which the analcime phase incorporates a negligible Sr amount in all range of Sr^{2+} content in the systems. At the same time, pollucite–analcime solid solutions $(Na_nCs_{1-n})AlSi_2O_6 \cdot nH_2O$ were easily crystallized as the main host phases for cesium in the similar co-processing route [38,39]. Moreover, Komarneni et al. [47] reported about the formation of analcimebased Sr-wairakite, $SrAl_2Si_4O_{12} \cdot 2H_2O$, when $Sr(OH)_2$ interacts with clinoptilolite and clay under more prolonged thermobaric treatment at 200 °C and 30 MPa. With this connection noted, it was of interest to obtain the Sr^{2+} -enriched analcime-based phases under milder conditions (25–200 °C, autogenous pressure). The sorption approach was applied to incorporate Sr^{2+} in the analcime lattice by means of ion exchange at elevated temperatures and pressures with the use of sodium-bearing analcime (Figure 1b) displaying poor Sr^{2+} capacity at 25 °C [48] but capable of trapping Sr^{2+} under hydrothermal conditions at 250–300 °C [49].

Table 2 shows the Sr²⁺ sorption value and efficacy of Sr²⁺ removal upon contacting the analcime-based sorbent with Sr(NO₃)₂ solutions at 25, 150 and 200 °C. It is evident that the degree of Sr²⁺ removal increases markedly as temperature rise but does not exceed ~92% for the lower Sr²⁺ concentration (500 mg/L). In turn, the Sr²⁺ sorption capacity is appropriately greater at the higher Sr²⁺ concentration (1000 mg/L) in all the temperature ranges.

The SEM-EDS data for hydrothermally treated analcime in Figure 5 point to the fact that the formation of Sr^{2+} silicate compounds attached to the analcime surface (Figure 5a,b—area b-1,e,f—area f-1) and Sr^{2+} enrichment of the analcime phase area (Figure 5b—area b-2,f—area f-2) take place.

In other words, Sr^{2+} cations are trapped from the solution by two ways, (i) Na⁺ exchange for Sr^{2+} in the analcime structure and (ii) interaction of Sr^{2+} cations with silicate species occurring in the porous structure of the analcime-bearing material as a result of its preliminary synthesis from aluminosilicate glass with $(SiO_2/Al_2O_3)_{glass} > (SiO_2/Al_2O_3)_{ANA}$ (Figure 1c-f) [38].

As revealed, the Sr²⁺ content in the analcime phase of the sorbent material increases regularly as the temperature rises up to 150 °C and 200 °C for the same initial Sr²⁺ concentration in the liquid phase. The EDX spectra for local parts of the analcime layer after contacting with strontium nitrate solutions at 25 °C (500Sr/ANA-25) and 200 °C (1000Sr/ANA-200) are presented in Figure 5d,h, respectively. Compositions of Na,Sr-ANA phases calculated by SEM-EDS data satisfy the conode NaAlSi₂O₆–Sr_{0.5}AlSi₂O₆ in a ternary diagram Na-Sr-Al (Figure 6) that corresponds to the formation of solid solutions (Na_{1-n}Sr_{n/2})AlSi₂O₆·H₂O of the Na-analcime–Sr-wairakite series. Based on



the data obtained, one can assume that, because of sorption runs, the solid solutions $(Na_{1-n}Sr_{n/2})AlSi_2O_6 \cdot H_2O$ being part of the Na-analcime–Sr-wairakite series are formed.

Figure 5. SEM images of product particles resulted from hydrothermal treatment of the $Sr(NO_3)_2$ -H₂O-ANA systems at (**a**) 25 °C and (**e**) 200 °C; (**b**,**f**) BSE micrographs and associated EDX spectra for local parts of the particles: (**c**,**d**)—for points b-1 and b-2, accordingly; (**g**,**h**)—for points f-1 and f-2, accordingly.



Figure 6. Composition of solid solutions $(Na_{1-n}Sr_{n/2})AlSi_2O_6 \cdot H_2O$ in Na-Sr-Al coordinates (at.%) by SEM-EDS data.

The PXRD analysis with DDM refinement was used to monitor the variation of the analcime lattice parameter, which is sensitive to the substitution of Na⁺ ions by Sr²⁺ in the lattice, and to estimate the composition of Na,Sr-ANA phases. Observed and calculated PXRD patterns after the DDM refinement for samples ANA and 1000Sr/ANA-200 are presented, as an example, in Figure 7.



Figure 7. Observed (top, black), calculated (mid, red) and difference (bottom, blue) PXRD profiles after DDM crystal structure refinement for samples (**a**) ANA and (**b**) 1000Sr/ANA-200.

Table 2 summarizes the composition and cubic (*Ia-3d*) lattice parameters for initial ANA phases and Na,Sr-ANA phases obtained from both the ICDD database and full-profile structure analysis. As seen from Table 2, the Sr^{2+} sorption at 25 °C does not cause statistically significant changes in values of the lattice parameters compared to the untreated analcime. Due to these facts, the assumption was made that the Sr^{2+} sorption on analcime at 25 °C was negligibly low, and detection of strontium in the analcime phase by SEM-EDS was likely to be caused by the Sr^{2+} sorption on alternative sorption sites of the inhomogeneous analcime-bearing material, for example, residues of unreacted glass supporting the analcime crystals (Figure 1b,d) [38]. As seen in Figure 5, a significant part of sorbed Sr^{2+} can be localized in the Sr-enriched compounds providing the observed degree of Sr^{2+} removal from the liquid phase at 25 °C (Table 2). The marked changes of the lattice parameters are observed only for analcime phases exposed to the hydrothermal treatment

in the presence of Sr²⁺ at 150 °C and 200 °C. The full-profile crystal structure refinement for the Na,Sr-analcime phases resulted from Sr²⁺ sorption at elevated temperatures allowed the composition of solid solutions (Na_{1-n}Sr_{n/2})AlSi₂O₆·H₂O formed at these temperatures (Table 2). As shown in Figure 8, the Sr²⁺ content in the Na,Sr-ANA solid solutions calculated from the PXRD data (Q_{xrd}) correlates with the sorbed Sr²⁺ quantity (Q_s) in the specimen determined by the AAS data of filtrate solutions. The linear dependence does not go through a zero point at the *x*-axis and intercepts the segment at ~16 mg/g. That is in agreement with the existence of at least two forms of the Sr²⁺ binding upon contacting analcime with Sr(NO₃)₂ solutions, and the formation of the Sr compound is responsible for the shift of the linear correlation.



Figure 8. The dependence of the Sr^{2+} content in analcime by XRD data (Q_{xrd}) on the sorbed Sr^{2+} quantity (Q_s) in the specimen by the AAS data of filtrate solutions.

Additional indication of formation of solid solutions $(Na_{1-n}Sr_{n/2})AlSi_2O_6 \cdot H_2O$ is the result of simultaneous thermal analysis. It is known that when Na⁺ cations are substituted for Sr²⁺, the Sr²⁺ ions are placed in the same position as the analcime lattice [44]. In this case, the water content in its structure would not be changed, but the binding energy of water molecules with the aluminosilicate framework can lessen due to the decrease of the number of two-charged cations. To estimate the water state in the analcime structure, thermogravimetric analysis (TG/DTG) is sufficiently informative.

The heating of all samples in the range of 40–600 °C was accompanied by continuous mass loss up to temperatures of about 450 °C. By the MS analysis of off-gases, this loss is caused by the water evolving which occurred as two slightly resolved steps at 40–150 °C and 150–450 °C. The analcime samples, before and after hydrothermal treatment in the presence of strontium salt, showed similar behavior in heating with the water content being approximately equal (Table 2). At the same time, the increase in Sr content in analcime resulted in narrowing peaks and shifting the peak maxima to low temperatures. This observation points to a reduction of the binding energy of water molecules and a more uniform distribution by dehydration enthalpy. The effect becomes the most apparent for samples after sorption at 200 °C, which are characterized by the highest degree of substitution of Na⁺ for Sr²⁺ cations (Table 2).

Thus, as a result of the implementation of the sorption approach, including the Sr²⁺ sorption on analcime under hydrothermal conditions at 150–200 °C, the formation of solid solutions (Na_{1-n}Sr_{n/2})AlSi₂O₆·H₂O of the Na-analcime–Sr-wairakite series was demonstrated. The elevated temperatures favor the Sr²⁺ incorporation in the analcime-based phases with the simultaneous increase of the Sr²⁺ removal efficiency from Sr²⁺ containing solutions.

4. Conclusions

The hydrothermal treatment of strontium-bearing solutions in the presence of coal fly ash cenospheres and cenosphere-derived zeolite material was demonstrated as a model for sustainable co-processing of wastes generated by coal-fired and nuclear power plants in order to remove the radioactive contaminant from wastewater and fabricate a mineral-like waste form for its final disposal. Two experimental approaches were implemented, (i) the direct hydrothermal synthesis of Sr-bearing mineral-like phases (Sr-tobermorite, Sr-plagioclase) in an alkaline medium using cenospheres as a glassy source of Si and Al at temperatures not higher than 200 °C and (ii) the Sr²⁺ sorption on cenosphere-derived analcime under the same hydrothermal conditions resulting in solid solutions (Na_{1-n}Sr_{n/2})AlSi₂O₆·H₂O of the Na-analcime–Sr-wairakite series. Among these two methods, hydrothermal synthesis seems to be more efficient because it has the highest degree (>99.99%) of strontium removal from solutions. The fabrication of Sr-bearing matrix materials is carried out in a hermetically sealed autoclave and characterized by both low temperature (no more than 200 °C) and low emission.

The results were obtained jointly with the ability of cenospheres to bind cesium (I) in the structure of pollucite–analcime solid solutions even at 150 °C which can be considered as original data for the development of resource-saving and energy-efficient hydrothermal technology for ¹³⁷Cs and ⁹⁰Sr removal from wastewater and immobilization in a mineral-like form. A wide variety of ¹³⁷Cs and ⁹⁰Sr-bearing aqueous radioactive wastes can be the object of its application including high sodium acid and alkaline radioactive wastes resulting from spent nuclear fuel processing and fast neutron reactors decommissioning, accordingly.

Another potential of cenospheres and cenosphere-based analcime in relation to the problem of radioactive waste disposal can be connected with the possibility to use the materials in underground nuclear waste repositories as a sorptive barrier for migrating radionuclides. Elevated temperatures, up to 250–300 °C, in a near surrounding field create suitable conditions for the hydrothermal processing of soluble ¹³⁷Cs and/or ⁹⁰Sr leached from the nuclear waste form with underground water.

Author Contributions: Conceptualization, A.A.; data curation, E.K.; formal analysis, L.S.; investigation, E.K., L.S., S.V. and E.M.; methodology, T.V.; project administration, T.V.; supervision, A.A.; writing—original draft, T.V. and S.V.; writing—review and editing, T.V. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by Russian Foundation of Basic Research (Grant No. 19-03-00448) and Ministry of Science and Higher Education of the Russian Federation (Budget Project No. 0287-2021-00-13 for the Institute of Chemistry and Chemical Technology SB RAS).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Acknowledgments: The reported study was conducted by using the equipment of Krasnoyarsk Regional Research Equipment Centre of SB RAS for SEM-EDS, XRD, AAS analyses and Siberian Federal University for STA and full-profile crystal structure refinement. The authors acknowledge O.A. Levitskaya and V.R. Kuzik for AAS measurements, as well as G.N. Bondarenko for performance of PXRD analysis.

Conflicts of Interest: The authors declare no conflict of interest.

References

- 1. Ye, J.; Zubair, M.; Wang, S.; Cai, Y.; Zhang, P. Power production waste. Water Environ. 2019, 91, 1091–1096. [CrossRef]
- Harris, D.; Heidrich, C.; Feuerborn, J. Global Aspects on Coal Combustion Products. Available online: https://www.coaltrans. com/insights/article/global-aspects-on-coal-combustion-products (accessed on 5 August 2021).
- Gollakota, A.R.K.; Volli, V.; Shu, C.-M. Progressive utilisation prospects of coal fly ash: A review. *Sci. Total Environ.* 2019, 672, 951–989. [CrossRef]

- 4. Bhatt, A.; Priyadarshini, S.; Mohanakrishnan, A.A.; Abri, A.; Sattler, M.; Techapaphawit, S. Physical, chemical, and geotechnical properties of coal fly ash: A global review. *Case Stud. Constr. Mater.* **2019**, *11*, e00263. [CrossRef]
- Jantzen, C.M.; Lee, W.E.; Ojovan, M.I. Radioactive waste (RAW) conditioning, immobilization, and encapsulation processes and technologies: Overview and advances. In *Radioactive Waste Management and Contaminated Site Clean-Up. Processes, Technologies and International Experience*, 1st ed.; Lee, W.E., Ojovan, M.I., Jantzen, C.M., Eds.; Woodhead Published Limited: Oxford, UK; Woodhead Published Limited: Cambridge, UK; Woodhead Published Limited: Philadelphia, PA, USA; Woodhead Published Limited: New Delhi, India, 2013; Chapter 6; pp. 171–272.
- 6. Grutzeck, M.W.; Siemer, D.D. Zeolites synthesized from class F fly ash and sodium aluminate slurry. *J. Am. Ceram. Soc.* **1997**, *80*, 2449–2453. [CrossRef]
- Tian, Q.; Sasaki, K. Application of fly ash-based materials for stabilization/solidification of cesium and strontium. *Environ. Sci.* Pollut. Res. Int. 2019, 26, 23542–23554. [CrossRef]
- 8. Ogata, F.; Kobayashi, Y.; Uematsu, Y.; Nakamura, T.; Kawasaki, N. Zeolite produced from fly ash by thermal treatment in alkaline solution and its capability to adsorb Cs(I) and Sr(II) in aqueous solution. *Yakugaku Zasshi* **2020**, *140*, 729–737. [CrossRef]
- 9. Rahman, R.O.A.; Rakhimov, R.Z.; Rakhimova, N.L.; Ojovan, M.I. *Cementitious Materials for Nuclear Waste Immobilization*, 1st ed.; John Wiley & Son: Chichester, UK, 2015; pp. 67–68.
- Cozzi, A.D.; Bannochie, C.J.; Burket, P.R.; Crawford, C.L.; Jantzen, C.M. Immobilization of radioactive waste in fly ash based geopolymers. In Proceedings of the 2011 World of Coal Ash (WOCA) Conference, Denver, CO, USA, 9–12 May 2011. Available online: http://www.flyash.info/2011/190-Cozzi-2011.pdf (accessed on 5 August 2021).
- 11. Liu, X.; Ding, Y.; Lu, X. Immobilization of simulated radionuclide ⁹⁰Sr by fly ash-slag-metakaolin-based geopolymer. *Nucl. Technol.* **2017**, *198*, 64–69. [CrossRef]
- 12. Jha, B.; Singh, D.N. A review on synthesis, characterization and industrial application of fly ash zeolites. *J. Mater. Educ.* **2011**, *33*, 65–132.
- 13. Mimura, H.; Yokota, K.; Akiba, K.; Onodera, Y. Alkali hydrothermal synthesis of zeolites from coal fly ash and their uptake properties of cesium ion. *J. Nucl. Sci. Technol.* **2001**, *38*, 766–772. [CrossRef]
- Mishra, T.; Tiwari, S.K. Studies on sorption properties of zeolite derived from Indian fly ash. J. Hazard. Mater. 2006, B137, 299–303. [CrossRef]
- 15. Goni, S.; Bustos, A.M.G.; Lorenzo, M.P. Efficiency of fly ash belite cement and zeolite matrices for immobilizing cesium. *J. Hazard. Mater.* **2006**, *137*, 1608–1617. [CrossRef]
- 16. Donald, I.W. Waste Immobilization in Glass and Ceramic Based Hosts: Radioactive, Toxic and Hazardous Wastes, 1st ed.; John Wiley & Son: Chichester, UK, 2010; pp. 221–240.
- 17. Orlova, A.I.; Ojovan, M.I. Ceramic mineral waste-forms for nuclear waste immobilization. Materials 2019, 12, 2638. [CrossRef]
- Gatta, G.D.; Rinaldi, R.; McIntyre, G.J.; Nenert, G.; Bellatreccia, F.; Guastoni, A.; Ventura, G.D. On the crystal structure and crystal chemistry of pollucite, (Cs,Na)₁₆Al₁₆Si₃₂O₉₆·*n*H₂O: A natural microporous material of interest in nuclear technology. *Am. Miner.* 2009, *94*, 1560–1568. [CrossRef]
- 19. Blissett, R.S.; Rowson, N.A. A review of the multi-component utilisation of coal fly ash. *Fuel* **2012**, *97*, 1–23. [CrossRef]
- Fomenko, E.V.; Kondratenko, E.V.; Salanov, A.N.; Bajukov, O.A.; Talyshev, A.A.; Maksimov, N.G.; Nizov, V.A.; Anshits, A.G. Novel microdesign of oxidation catalysts. Part 1. Glass crystal microspheres as new catalysts for the oxidative conversion of methane. *Catal. Today* 1998, 42, 267–272. [CrossRef]
- 21. Koopman, M.; Chawla, K.K.; Ricci, W.; Carlisle, K.; Gladsyz, G.M.; Lalor, M.; Jones, M.L.; Kerr, K.; George, M.P.; Gouadec, G.; et al. Titania-coated glass microballoons and cenospheres for environmental applications. *J. Mater. Sci.* 2009, 44, 1435–1441. [CrossRef]
- 22. Hu, Y.; Zhang, H.; Li, F.; Cheng, X.; Chen, T. Investigation into electrical conductivity and electromagnetic interference shielding effectiveness of silicone rubber filled with Ag-coated cenosphere particles. *Polym. Test.* **2010**, *29*, 609–612. [CrossRef]
- 23. Vassilev, S.V.; Menendez, R.; Diaz-Somoano, M.; Martinez-Tarazona, M.R. Phase-mineral and chemical composition of coal fly ashes as a basis for their multicomponent utilization. 2. Characterization of ceramic cenosphere and salt concentrates. *Fuel* **2004**, *83*, 585–603. [CrossRef]
- 24. Fenelonov, V.B.; Mel'gunov, S.; Parmon, V.N. The properties of cenospheres and the mechanism of their formation during high-temperature coal combustion at thermal power plants. *Powder Part. J.* **2010**, *28*, 189–208. [CrossRef]
- 25. Hirajima, T.; Petrus, H.T.B.M.; Oosako, Y.; Nonaka, M.; Sasaki, K.; Ando, T. Recovery of cenospheres from coal fly ash using a dry separation process: Separation estimation and potential application. *Int. J. Miner. Process.* **2010**, *95*, 18–24. [CrossRef]
- 26. Ranjbar, N.; Kuenzel, C. Cenospheres: A review. Fuel 2017, 27, 1–12. [CrossRef]
- 27. Danish, A.; Mosaberpanah, M.A. Formation mechanism and applications of cenospheres: A review. *J. Mater. Sci.* 2020, 55, 4539–4557. [CrossRef]
- 28. Anshits, N.N.; Mikhailova, O.A.; Salanov, A.N.; Anshits, A.G. Chemical composition and structure of the shell of fly ash non-perforated cenospheres produced from the combustion of the Kuznetsk coal (Russia). *Fuel* **2010**, *89*, 1849–1862. [CrossRef]
- 29. Fomenko, E.V.; Anshits, N.N.; Solovyov, L.A.; Mikhaylova, O.A.; Anshits, A.G. Composition and morphology of fly ash cenospheres produced from the combustion of Kuznetsk coal. *Energy Fuels* **2013**, *27*, 5440–5448. [CrossRef]
- Fomenko, E.V.; Anshits, N.N.; Vasilieva, N.G.; Mikhaylova, O.A.; Rogovenko, E.S.; Zhizhaev, A.M.; Anshits, A.G. Characterization of fly ash cenospheres produced from the combustion of Ekibastuz coal. *Energy Fuels* 2015, 29, 5390–5403. [CrossRef]

- 31. Fomenko, E.V.; Rogovenko, E.S.; Solovyov, L.A.; Anshits, A.G. Gas permeation properties of hollow glass-crystalline microspheres. *RSC Adv.* 2014, 20, 9997–10000. [CrossRef]
- Vereshchagina, T.A.; Vereshchagin, S.N.; Shishkina, N.N.; Mikhaylova, O.A.; Solovyov, L.A.; Anshits, A.G. One-step fabrication of hollow aluminosilicate microspheres with a composite zeolite/glass crystalline shell. *Microporous Mesoporous Mater.* 2013, 169, 207–211. [CrossRef]
- 33. Fomenko, E.V.; Anshits, A.G.; Bobko, A.A.; Khramtsov, V.V.; Salanov, A.N.; Kirilyuk, I.A.; Grigor'ev, I.A. Perforated cenospheresupported pH-sensitive spin probes. *Rus. Chem. Bull.* **2008**, *57*, 493–498. [CrossRef]
- 34. Vereshchagina, T.A.; Kutikhina, E.A.; Fomenko, E.V.; Solovyov, L.A.; Vereshchagin, S.N.; Anshits, A.G. ZrMo₂O₇(OH)₂(H₂O)₂ coated microsphere glass supports derived from coal fly ash cenospheres as a novel sorbent for radionuclide trapping. *J. Environ. Chem. Eng.* **2019**, *7*, 102887. [CrossRef]
- Vereshchagina, T.A.; Anshits, N.N.; Sharonova, O.M.; Vasil'eva, N.G.; Vereshchagin, S.N.; Shishkina, N.N.; Fomenko, E.V.; Anshits, A.G. Polyfunctional microspherical materials for long-term burial of liquid radioactive wastes. *Glass Phys. Chem.* 2008, 34, 547–558. [CrossRef]
- Vasilieva, N.G.; Vereshchagina, T.A. Solidification of Cs-137-bearing radioactive waste in cenosphere-based mineral-like hosts for long-term disposal in granithoids. SFU J. Chem. 2015, 3, 346–358. [CrossRef]
- Vereshchagina, T.A.; Vereshchagin, S.N.; Shishkina, N.N.; Vasilieva, N.G.; Solovyov, L.A.; Anshits, A.G. Microsphere zeolite materials derived from coal fly ash cenospheres as precursors to mineral-like aluminosilicate hosts for ^{135,137}Cs and ⁹⁰Sr. *J. Nucl. Mater.* 2013, 437, 11–18. [CrossRef]
- Vereshchagina, T.A.; Kutikhina, E.A.; Chernykh, Y.Y.; Solovyov, L.A.; Zhizhaev, A.M.; Vereshchagin, S.N.; Anshits, A.G. One-step immobilization of cesium and strontium from alkaline solutions via a facile hydrothermal route. *J. Nucl. Mater.* 2018, *510*, 243–255. [CrossRef]
- Vereshchagina, T.A.; Kutikhina, E.A.; Chernykh, Y.Y.; Solovyov, L.A.; Zhizhaev, A.M.; Vereshchagin, S.N.; Fomenko, E.V. Cenosphere-sourced hydrothermal synthesis of pollucite-analcime solid solutions as a low-temperature method to immobilize ¹³⁷Cs in a mineral-like form. *J. Nucl. Mater.* 2020, *532*, 152073. [CrossRef]
- 40. Cements and Materials for Cement Production. Chemical Analysis Methods; State Standard (GOST) No. 5382-91; IPK Izdatel'stvo standartov: Moscow, Russia, 1991.
- 41. Rietveld, H. A profile refinement method for nuclear and magnetic structures. J. Appl. Crystallogr. 1969, 2, 65–71. [CrossRef]
- 42. Solovyov, L.A. Full-profile refinement by derivative difference minimization. J. Appl. Crystallogr. 2004, 37, 743–749. [CrossRef]
- Vereshchagina, T.A.; Kutikhina, E.A.; Solovyov, L.A.; Vereshchagin, S.N.; Mazurova, E.V.; Chernykh, Y.Y.; Anshits, A.G. Synthesis and structure of analcime and analcime-zirconia composite derived from coal fly ash cenospheres. *Microporous Mesoporous Mater.* 2018, 258, 228–235. [CrossRef]
- 44. Wise, W.S. *Handbook of Natural Zeolites*; Colella, C., Ed.; International Zeolite Association, Natural Zeolites Commission; A. de Frede Edotore: Napoli, Italy, 2013; 334p.
- Parsons, I. Feldspars. In *Encyclopedia of Geology*, 2nd ed.; Alderton, D., Elias, S.A., Eds.; Academic Press: London, UK, 2021; pp. 271–286.
- 46. McConnell, J.D.C. The hydrated calcium silicates riversideite, tobermorite, and plombierite. *Miner. Mag.* **1954**, *30*, 293–305. [CrossRef]
- 47. Komarneni, S.; White, W.B. Hydrothermal reactions of strontium and transuranic simulator elements with clay minerals, zeolites, and shales. *Clays Clay Miner.* **1983**, *31*, 113–121. [CrossRef]
- 48. Ames, L.L. Cation exchange properties of wairakite and analcime. Am. Miner. 1966, 51, 903–909.
- 49. Redkin, A.F.; Hemley, J.J. Experimental Cs and Sr sorption on analcime in rock-buffered systems at 250–300 °C and P_{sat} and the thermodynamic evaluation of mineral solubilities and phase relations. *Eur. J. Miner.* **2000**, *12*, 999–1014. [CrossRef]