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Review

Titanosilicates in cation adsorption and cation exchange – A review

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HIGHLIGHTS

- Titanosilicates are highly stable and efficient sorption materials.
- Sorption ability of Titanosilicates rises with decreasing the structural perfection.
- Crystalline Titanosilicates are the most selective and effective for Cs^{+} and Sr^{2+}.
- Fundamental investigations and pilot-scale approbations still need to be done.

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ABSTRACT

The present work summarizes the relevant literature about Titanosilicates and appraises their current place among other inorganic sorption materials. A brief history of the sorbents of the TiSi family with their structural features is canvassed, typical synthesis approaches are addressed and TiSi cation adsorption and exchange applications are discussed. Suggestions for the directions and perspectives of further investigations are discussed in the reviews' conclusions.

Contents

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1. Introduction

A large variety of inorganic sorption materials (ISM) have been synthesized, developed and described until today. Initially, there were clays and zeolites, thereafter phosphates, silicates, titanates, Titanosilicates (TiSi), heteropolyacid salts, oxides and hydroxides [1–12]. These inorganic adsorbents and ion-exchangers are widely utilized for water softening, water remediation, catalysis, molecular sieving and selective adsorption purposes [13–19]. Utilization of ISMs provides many benefits over the use of organic ion exchangers due to a much higher resistance of inorganics to chemical, thermal and radiation degradation. The crucial characteristic of ISMs is their very high selectivity for target ions and, as a result, higher separation factors of inorganics than those exhibited by organic exchangers. Consequently, ISMs are used in these instances, where organic materials are not selective enough or are unstable in the medium used, such as cation removal from hot organic solutions [20,21].

Adsorption, ion-exchange and membrane filtration are highly promising techniques for metal ions retention from aqueous solutions and thus one of the most frequently studied [6,22,33]. All current physical separation techniques entail strict requirements concerning the materials applied: thermal, chemical and mechanical stability, ionization radiation resistance, high kinetic rates and high sorption capacities [11]. Titanosilicates represent an exceptional good example of sorption materials that meet all of the above mentioned requirements and were tested as adsorbents, ion-exchangers or membranes [6,11,20,34–36]. TiSis have additional benefits of high kinetics, a high sorption capacity and selectivity at a broad pH range in addition to remaining "uncontaminated" by other cations [11,39,129]. These benefits strikingly distinguish TiSis from other ISMs and justify the rising attention to this group of materials.

This review is devoted to a relatively new class of ISMs: Titanosilicates. It is intend to examine the literature in order to appraise the current place of TiSi among the other inorganic sorption materials. A brief history of the TiSi family including their structural features is opening this discussion. Thereafter, typical synthesis approaches and TiSi properties including the latest results of our own research will be addressed. Suggestions and expectations as well as perspectives of further investigations into the use and properties of TiSi will conclude this review.

2. A brief history of Titanosilicates and their structural investigations

2.1. General remarks

Titanosilicates belong to the relatively new class of silicate materials that combine natural minerals and synthesized materials. The history of this class begins with the molecular sieves TS-1 and TS-2 obtained at the end of the 20th century for catalytic purposes [37,38]. Later, other TiSis were synthesized and have found extensive application in catalysis, adsorption, separation and ion exchange [39–45].

In general, TiSi sorption materials are constructed from interconnected polyhedra: octahedra or pentahedra with Ti as the central atom and tetrahedra of SiO_4. The negative charge on the Ti-O groups is compensated by cations that can be exchanged. Variations in the incorporation of these structural components lead to the formation of framework, layered or dense structures. Overall, TiSi materials with framework and layered structures have the highest ion-exchange and adsorption potential and will be discussed below.

2.2. Engelhard Titanosilicates

The first members of the TiSi sorption family were Engelhard Titanosilicates (Engelhard Corporation) reported by S.M. Kuznicki (US Patent 4 853 202, US Patent 4 938 989 and US Patent 5 011 591) [46–48] and were named ETS.

In 1989, this new family of crystalline titanosilicate molecular sieve zeolite materials with a pore size of about 3–8 Å were disclosed (Table 1). Eleven examples for preparing the Engelhard Titanosilicates (ETS) including their characterisation and suggested usage were described. Within this group, the first three examples illustrated the criticality of pH, putting these materials outside of the scope of the invention. Therefore, small attention was paid to structural investigations and the features of the ETS-1–3 samples. Kuznicki suggested that ETS-1 and ETS-2 have a layered structure

Table 1
A brief history, and structural aspects of TiSi sorption materials.

Name	Ideal formula	Mineral analogue	Ti/Si	Ti $_{coordination}$	Structure	r_{pore}, Å	Reported in	References
ETS-1	n.r. $(Na,K)_2O{:}2TiO_2{:}2SiO_2{\cdot}4H_2O$**		1.3	6	L	8	1989	[46,48–50]
ETS-2	n.r. $Na_2O{:}2TiO_2{:}2SiO_2{\cdot}4H_2O$**		1.6	6	L	8	1989	[46,48–50]
ETS-4	$Na_9Si_{12}Ti_5O_{38}(OH){\cdot}12H_2O$	Zorite	0.42	6, 5	M	1.85	1989	[46,48,66]
ETS-10	$Na_{1.5}K_{0.5}TiSi_5O_{13}{\cdot}nH_2O$		0.2	6	M	4	1989	[46,48,75,76].
CTS (TAM-5, STS, CST)	$Na_2Ti_2O_3SiO_4{\cdot}2H_2O$	Sitinakite	2	6	M	1.75	1993	[84,87,91,92]
GTS-1	$HNa_3Ti_4O_4(SiO_4)_3{\cdot}4H_2O$	Pharmacosiderite	1.33	6	M	5	1996	[85,93,94]
AM-2 (STS)	$K_2TiSi_3O_9{\cdot}H_2O$	Ti substituted umbite	0.33	6	M	6.8	1997	[100,103,104]
AM-3 (penkvilksite-2*O*)	$Na_2TiSi_4O_{11}{\cdot}2H_2O$	Penkvilksite	0.25	6	M	3–5	1997	[83,106,109]
AM-4	$Na_3(Na,H)Ti_2O_2[Si_2O_6]_2{\cdot}2H_2O$		0.5	6	L		1997	[97,108,110]
ETS-14	n,r, $Na_2O{\cdot}TiO_2{\cdot}(SiO_2)_{3\text{-}7}{\cdot}nH_2O$**	Penkvilksite	0.21	6	M	3–5	1999	[81]

L: layered structure.
M: microporous framework.
** Approximated chemical formula, suggested based on the reported chemical analysis.

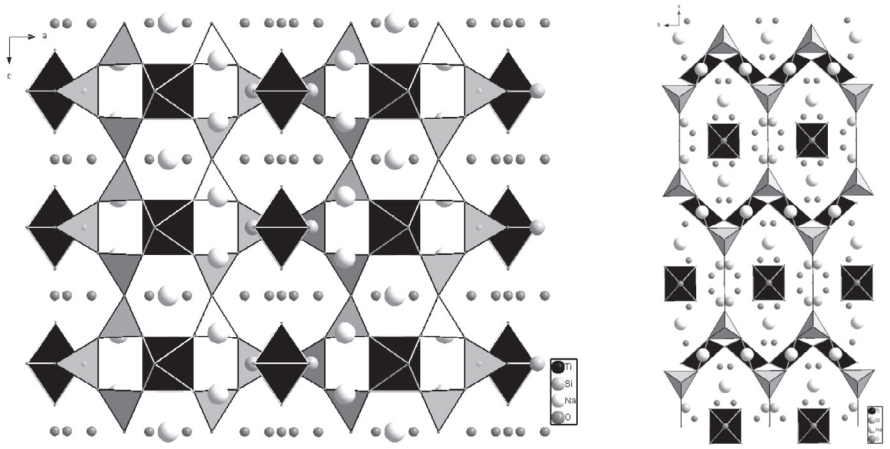

Fig. 1. Schematic representation of the titanosilicate structures of ETS-4 material. The black octahedra and pentahedra have Ti as a central atom and grey tetrahedra are SiO_4, respectively. Figures were produced using Diamond 3.2 software according to the data reported in [66,69].

and mentioned their low thermal stability, exchange activity and lack of molecular sieving properties [47,48]. Nevertheless, Liu et al. [49,50] repeated the synthesis of ETS-1 and ETS-2, supposing they deserve a closer researchers' attention. They confirmed the ETS-1 and ETS-2 layered structure, estimated the parameters of the pore structure and provided the elemental analysis. Unfortunately, no single crystal studies were done, thus no unit cell parameters were provided and therefore no figure presented. The approximate formulas may be estimated based on elemental analysis: the molar ratio for ETS-1 is $n(TiO_2):n(SiO_2):n(Na_2O):n(K_2O):n(H_2O)$ with 1.3:1:0.65:0.23:2.2 and for ETS-2 $n(TiO_2):n(SiO_2):n(Na_2O):n(H_2O)$ with 1.6:1:1.3:2.3 The ideal formulas of ETS-1 and ETS-2 were not reported yet.

Thereafter, the small pored (3–5 Å) Engelhard Titanosilicate Number 4 (ETS-4) with the chemical formula $Na_9Si_{12}Ti_5O_{38}(OH)\cdot 12H_2O$ was described (Fig. 1) (Table 1) [47,48]. Kuznicki suggested for ETS-4, which has a microporous framework structure, usage in adsorption, catalysis (for the small molecule conversion) and water treatment (for mercury or lead uptake). Subsequently, such a potential attracted enormous interest to this material [44,51–68]. It was commonly considered that ETS-4 is a synthetic analogue of zorite until 2001, when the single-crystal study was published by Nair [66].

There are two types of Ti^{4+} coordination in ETS-4: one is coordinated into octahedra and linked into chains and the other is coordinated in pentahedra (semioctahedra with titanyl Ti=O bond) that are isolated by SiO_4 tetrahedra from the chains of TiO_6. In contrast, zorite has a rotating square pyramid form of five coordinated Ti^{4+} and charge balancing protons. The pore structure of ETS-4 can be presented as an intergrowth of 12MR and 8MR channels connected through the short 6MR pores. The important role of water bonds in the channel network structure of ETS-4 must be pointed out, as this makes it a non-thermostable material. At a temperature of about 200 °C water is removed and the framework structure of ETS-4 collapses. Yet, the ion-exchange capacity of ETS-4 is one of the highest among all reported TiSis (6.3 meq/g in dehydrated form) which makes it an appropriate ion exchanger within a limited temperature range [66]. Moreover, the calculations of standard enthalpies of ETS-4 and ETS-l0 formation provided by Xu et al. [67] using high-temperature drop solution calorimetry with lead borate as a solvent (at 974 K) demonstrated that at 298 K and 1013 hPa, ETS-4 is thermodynamically more stable than ETS-l0. In 2001, a unique property of the ETS-4 to temperature-induced contraction of certain cation-exchanged forms was discovered by Kuznicki et al. [70] Usually, zeolites have a rigid pore structure, while the neutron diffraction and in-situ X-ray diffraction data of ETS-4 demonstrated the reproducible and systematical diminishing of the lattice parameters as a function of rising the calcination temperature. Such a phenomenon, identified as the Molecular Gate® effect, allows adjusting the ETS-4 pore structure according to the required size-based process [45,70–73]. The possibility to direct the pore size by the amount and type of anions exserted into the channels was described by Lin et al. [74].

In the same patent, the stable microporous crystalline wide-pore (8 Å) TiSi material named Engelhard Titanosilicate Number 10 (ETS-10) was disclosed (Table 1) [46,48]. The ETS-10 structure was determined only a few years later by Anderson et al. [75] and the chemical formula proposed was $Na_{1.5}K_{0.5}TiSi_5O_{13}\cdot nH_2O$ (Fig. 2). A detailed description of the ETS-10 structure was given by the same group a year later [76]. ETS-10 is a crystalline and,

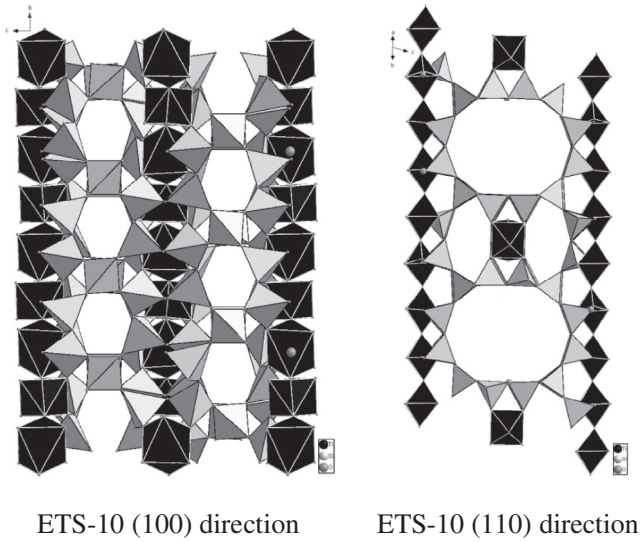

Fig. 2. Schematic representation of the titanosilicate structures of ETS-10 material. The black octahedra and pentahedra have Ti as a central atom and grey tetrahedra are SiO_4, respectively. Extra-framework cations and water molecules were omitted for clarity. Figures were produced using Diamond 3.2 software according to the data reported in [75,76].

at the same time, highly disordered wide-pored microporous framework material. Using scanning electron microscopy, high resolution electron micrograph and electron diffraction, it was identified that ETS-10 has: (i) structural faulting; (ii) stacking disorder of ellipsoidal wide pores (12 Si atom rings); (iii) wide 12 member rings stacked in diagonal or zig-zag arrangement; (iv) straight rows of smaller 3–7 member channels and (v) two identical orthogonal axes in both A and B polymorphs. The layers are connected in such a way that each layer is laterally shifted by one quarter of the unit cell with respect to the previous and the next one. This resulted in disorder and faulting of the material's structure. It must be highlighted that the presence of these defects in the ETS-10 structure is not blocking the channel system, but provides better access for larger molecules and increases the kinetics of the sorption process [76,77].

The other interesting aspect of the ETS-10 structure is the alteration of long and short bonds along O-Ti-O-Ti-O chains. These chains are surrounded by SiO_4 tetrahedra linked to the octahedrally coordinated Ti^{4+} through corner-shared oxygen atoms. The pore system consists of an interconnected 12 Si atom channel network (12-MR) with curvaceous pores in the (001) direction and straight pores in the other directions. The presence of Ti^{4+} in an octahedral coordination generates two negative charges $[TiO_6]^{2-}$ which are balanced by the exchangeable cations Na^+ and K^+. The location of balance Na^+ and K^+ and exchanged cations (*e.g.* Eu^{3+}, Gd^{3+}, Tb^{3+}) in the 7-MR space was recently presented using aberration corrected scanning transmission electron microscopy [78]. Taking into account the Ti:Si ratio of 0.2 in the ETS-10 structure, the ion exchange capacity was calculated to be 4.5 meq/g (in dehydrated form). The combination of structural aspects such as a wide pore diameter and developed three-dimensional pore structure with a high ion-exchange capacity makes ETS-10 a promising sorption material for high-volume metal cation sorption from aqueous solution [76,78–80].

Later, in 1999, Engelhard Titanosilicate Number 14 (ETS-14) was added to the ETS family and the novel crystalline molecular sieve zeolite and its methods of production were described (Table 1) [81]. Based on the similarities in XRD patterns of ETS-14 and the mineral penkvilksite ($Na_4Ti^{4+}_{1.5}Zr_{0.5}[Si_8O_{22}]\cdot 4H_2O$), it was suggested that ETS-14 has a microporous framework structure with regular porosity and capability to ion-exchange and small gas molecules adsorption. ETS-14 was characterized by X-ray powder diffraction and the lines and relative intensities of the XRD pattern were compared with that of penkvilksite. Based on the results, ETS-14 appears to be closer related to the 2*O* polytype than to the 1*M* polytype of penkvilksite, though their X-ray patterns do not exactly match [82]. Morphologically, penkvilksite and ETS-14 can be distinguished on SEM pictures, because ETS-14 has larger platy crystals appearing as well-defined clusters with a "rose" shape, while penkvilksite appears as poorly defined crystal aggregates [81]. Interestingly, unlike the classical (Al-Si) zeolites, ETS materials and other penkvilksite-like phases show basically invariant atomic ratios and composition. Detailed descriptions of the new penkvilksite mineral structures were given by Merlino et al. [82], who reported that the penkvilksite-like structure shows up in spirals of six vertex-sharing SiO_4 tetrahedra in an alternating clockwise and counter clockwise fashion along the (010) direction. They identified two types of connections between the TiO_6 octahedra and the SiO_4 tetrahedra spirals: (i) one of the tetrahedrons shares two vertices with TiO_6 octahedra and two other vertices with other tetrahedra and (ii) a tetrahedron shares one vertex with a TiO_6 octahedron and three other vertices with tetrahedra. Another interesting aspect of the penkvilksite-type structure is the small Ti-O distance in the TiO_6 octahedra. In addition, the O atoms of the TiO_6 octahedron exhibit very similar environments within the same penkvilksite polytype and in comparison to the other penkvilksite polytypes [82,83]. Moreover, there are no Ti-O-Ti bonds in penkvilksite-like phases, which makes ETS-14 closer related to the AM titanosilicate family (Fig. 4). Unfortunately, no single crystal studies and unit cell parameters were provided, therefore no figure is presented.

2.3. TiSis with the "cubane-like" structure

The next group of TiSi materials was synthesized by Clearfield and his team [84–87]. The main structural characteristic of this group is the formation of "cubane-like" structures of Ti_4O_4 formed from TiO_6 octahedra in such a way that every octahedron shares three oxygens with neighbouring TiO_6 octahedra inside the cluster (Fig. 3).

A 1993 report on the synthesis of crystalline titanosilicate material (CTS) with the chemical structure $Na_2Ti_2O_3SiO_4\cdot 2H_2O$ initially called this material TAM-5 (Fig. 3) (Table 1) [84,87]. It has an analogue structure to the mineral sitinakite ($Na_2KTi_3NbO_{4.75}(SiO_4)_2(OH)_{0.25}\cdot 4H_2O$) and therefore, the literature reported synthesis of sitinakite [88]. In CTS, the characteristic "cubane-type" structures are linked to each other by SiO_4 tetrahedrons in the directions of the *a* and *b* axes, while in the direction of the *c* axis, the Ti_4O_{24} clusters are bridged through the top oxygens of octahedrons [87,89]. Half of the Na^+ are "sandwiched" between the SiO_4 tetrahedra and called framework cations. This Na^+ can be exchanged only by protons due to space restrictions. The remaining compensation cations are located near the channel centre,

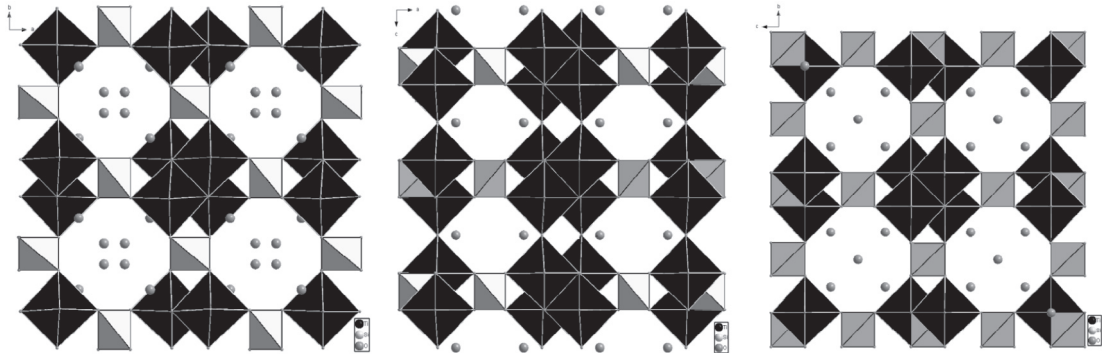

Fig. 3. Schematic representation of the titanosilicate structures of microporous TiSi materials reported by Clearfield's group. The black octahedra represent TiO_6 groups and the grey tetrahedra illustrate the SiO_4 groups. The group of four tetrahedra in the very centre of every structure represent the "cubane-cluster" and dark grey small circles are oxygens. Figures were produced using Diamond 3.2 software according to the data reported in [92,93].

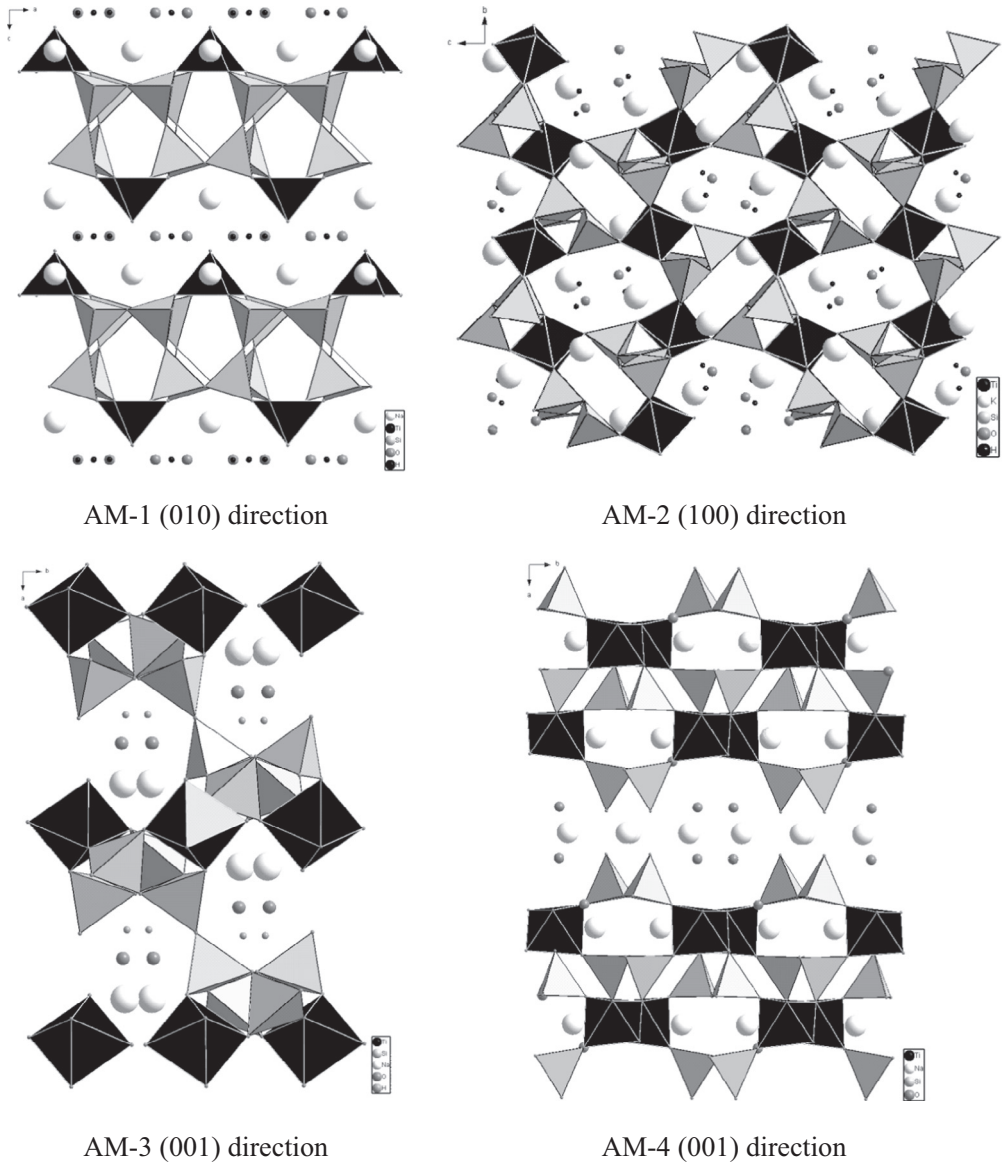

Fig. 4. Schematic representation of the titanosilicate structures of AM TiSi materials. The black polyhedra show the TiO_n groups and the centres of the grey tetrahedra are occupied by Si atoms. The big white circles are the extra framework cations (K for the AM-2 and Na for the rest of the family), the medium grey circles are the oxygen atoms and the smallest dark circles are protons. Figures were produced using Diamond 3.2 software according to the data reported in [103,106–108].

and only one of the four of these is exchangeable for Cs^+ due to the same space restrictions. It must be noted that the H form can exchange 2–4 times more Cs^+ and that the size of the CTS tunnels is ideal for selective adsorption of Cs^+. The affinity of CTS can be increased by decreasing the crystallinity. Nevertheless, the presence of competitive ions in solutions decreases the affinity of CTS to Cs^+ [11,87,90,91].

The titanosilicate analogue of the mineral pharmacosiderite ($KFe_4(AsO_4)(OH)_4{\cdot}7H_2O$) was synthesized in 1990 by Chapman and Roe [94] and was named Grace Titanium Silicate-1 (GTS-1) (Table 1). The alkali cation analogue of pharmacosiderite with the chemical formula $HM_3Ti_4O_4(SiO_4)_3{\cdot}4H_2O$ (M is an alkali metal cation) was reported by Behrens et al. [85]. Thorough studies of the alkali GTS-1 structural and sorption properties have been conducted (Fig. 3) [11,85–87,95]. The main difference to the CTS material is a connection of the cubic Ti_4O_{24} cluster by SiO_4 tetrahedrons in a three-dimensional framework that gives an extra exchangeable space and the tree of four channel cations can be exchanged by Cs^+. X-ray single-crystal studies illustrate the stability of the non-centred position of the exchanged Cs^+ ions in the tunnels of GTS-1 [87,96].

2.4. AM titanosilicate family

The newest and fundamentally different group of TiSi sorption materials was called the AM-n family, because the first member was discovered by researchers from Aveiro and Manchester universities in 1995 (Table 1). In contrast to other TiSis (except, ETS-14), AM materials contain no Ti-O-Ti bonds (Fig. 4) [97].

The first member of the AM group was AM-1, which was described as JDF-L1 in 1996 [98] and as NTS TiSi [99] (Table 1) (Fig. 4). The chemical formula of AM-1 was found to be $Na_4Ti_2Si_8O_{22}{\cdot}4H_2O$. It contains five-coordinated Ti^{4+} ions in the form of TiO_5 square pyramids connected to SiO_4 tetrahedrons through the oxygen at the pyramid base. Clusters of $TiO{\cdot}O_4(SiO_3)_4$ form a continuous layer, which is counterbalanced by Na^+ in the interlamellar space and can be exchanged – but this material is mainly used for catalysis.

The titanium substituted synthetic analogue of the mineral umbite has the identical chemical formula $K_2TiSi_3O_9{\cdot}H_2O$ and was named AM-2 (STS) (Table 1) [100–102]. Zou & Dadachov [103] conducted single-crystal X-ray investigations and determined the AM-2 crystal structure (Fig. 4). Si^{4+} atoms, gathered in the $Si_3O_9^{6-}$ trisilicate groups, develop the linear chains along the *c* axis. Octahedrally coordinated Ti^{4+} atoms tie these silicate chains together into the three-dimensional framework with 6.8 Å pore widths along the *c* axis. Each of these large tunnels consist of 16-member openings which are formed by four Ti, four Si, and eight O atoms and the tunnels are surrounded by four smaller ones. Smaller openings consist of 12 atoms and are enclosed by four larger ones.

These two types of cavities run along the *c* axis. In addition, there are 14-atom openings that link the larger and smaller tunnels with each other and lie scarcely parallel to the *ab* diagonal. To balance the charge of the TiO_6 octahedrons, two exchangeable K^+ cations are in the tunnel space. During mild acid treatment, 80% of the cations in the larger tunnel are exchanged by protons. Based on the ^{29}Si NMR of partially converted H-form samples, it was suggested that the OH^- functional groups in the exchanger belong rather to Si than to the Ti atoms [92,104].

AM-3 is a microporous synthetic analogue of the orthorhombic mineral penkvilksite (penkvilksite 2*O*) with the chemical formula $Na_2TiSi_4O_{11}{\cdot}2H_2O$ (Fig. 4), of which the phase features were discussed above. A substantial difference of AM-3 and the penkvilksite-1*M* is that AM-3 is disordered in a rigid O–H direction. Only one of the two protons could be observed in the Raman spectrum. One of the main structural differences between AM-2 and AM-3 is that AM-3 has SiO_4 tetrahedra linked with isolated TiO_6 octahedra in three-dimensional directions forming a developed open pore structure with a pore diameter of 3–5 Å [36,41,82,83,97,105,106].

Lin et al. [97] reported the synthesis of a layered TiSi material called AM-4 of which the crystal structure was resolved by Dadachov et al. (1997) [108] with the chemical formula found to be $Na_3(Na,H)Ti_2O_2[Si_2O_6]_2{\cdot}2H_2O$ (Table 1). All the Ti atoms in AM-4 are octahedrally coordinated and TiO_6 is connected to the SiO_4 through the oxygens at the edges, forming layers perpendicular to (001). A characteristic aspect of the AM-4 material is a five-level structure of SiO_4-TiO_6-SiO_4-TiO_6-SiO_4 (Fig. 4). Another characteristic of the AM-4 structure is the "zigzag" fashion of edge-sharing TiO_6 octahedra developing the chains along (100) which are connected with each other via corner-sharing with pyroxene type SiO_4 tetrahedra. The Ti. . .Ti cations repulsion within the titanate chains resulted in a shifting of the Ti from the centre of the octahedron and, therefore, distortions of the Ti–O distances, shared edges lengths and angle sizes. Na^+ and K^+ cations which are located in the interlamellar space (exchangeable) and in the space within the layer (structural cations) balance the two charges of Ti^{4+} [108].

3. Synthesis of titanosilicate sorbents

Generally, the process of TiSi synthesis can be divided into the following four stages: mixing the precursors, hydrothermal treatment (HTT), rinsing the obtained materials and, finally, drying. Practically, TiSi synthesis is carried out under hydrothermal conditions in Teflon-lined autoclaves at 120–230 °C from a few hours up to 30 days in the pH range of 9–13. Exceptionally extreme synthesis conditions were reported by Harrison et al. [96] for growing large crystals in order to conduct single-crystal structure studies of the Cs-phase of GTS-1: 40 h at 750 °C under 200 MPa in a sealed gold tube. Optional stages can include adding the seeds of desirable phases to the mixture of precursors or template substances [111]. Recently, the possibility of replacing the HTT stage by microwave treatment was proposed [63,112–114]. Microwave synthesis makes it possible to reduce the TiSi synthesis duration by 2–48 times, but this occasionally requires increasing the temperature and produces materials with a smaller crystal size. Selected examples of typical TiSi synthesis are summarised in Table 2.

Depending on the nature of the precursor, TiSi synthesis can be classified into alkoxide, inorganic or mixed precursor methods. Briefly, the controlled hydrolysis/alcolysis of precursors forces the simultaneous precipitation (coprecipitation) of Ti–O and Si–O

Table 2
Typical synthesis of titanosilicate sorption materials.

TiSi	Precursors		Additives	Synthesis condition		References
	Ti	Si		*T*, °C	τ, h	
AM-2	$TiCl_3$	SiO_2/Na_2SiO_3	KCl	230	4 h	[125]
		colloidal SiO_2	KF	200	10 h	[126]
	$TiCl_4$	SiO_2	H_2O_2	180	7 h	[104]
	TiO_2 anatase	Na_2SiO_3	–	230	48 h	[127]
AM-3	$TiCl_3$	Na_2SiO_3	KCl, AM-3 seeds	230	4 h	[125]
AM-4	$TiCl_3$	Na_2SiO_3	–	230	4 h	[125]
	TiO_2	Na_2SiO_3	AM-4 seeds	230	96 h	[128]
CTS	$TiCl_4$	$[SiO_x(OH)_{4-2x}]_n$	H_2O_2	200	10 h	[119]
	$Ti(OC_3H_7)_4$	$Si(OC_2H_5)_4$	–	170	3.5 h	[118]
	$TiCl_4$	$Na_2O{\cdot}SiO_2$	Ligand	150	6 h	[129]
	$TiOSO_4$					
ETS-1	$T1_2O_3$	Na_2SiO_3	KF	125	7 d	[48]
ETS-2	$TiCl_3$	Na_2SiO_3	NaF	125	1 d	[48]
ETS-4	$TiCl_3$	Na_2SiO_3	KF	150	7 d	[48]
	$Ti\{OCH(CH_3)_2\}_4$	$(C_2H_5O)_4Si$	$(CH_3)_4N^+Cl^-$	175	15 d	[130]
ETS-10	$TiCl_3$	Na_2SiO_3	ETS-4 seeds	175	6–9 d	[48]
				150	7 d	
	$TiCl_4$	Na_2SiO_3	$(CH_3)_4N^+Cl^-$	160–200	1–20 d	[111]
	$TiCl_4$	Na_2SiO_3	KF	200	14–16 h	[115]
	$Ti(SO_4)_2$				4–10 d	[117]
ETS-14	ETS-10, $TiOCl_2$	Na_2SiO_3	–	200	3–7 d	[81]
GTS-1	$Ti(OC_2H_5)_4$	Colloidal SiO_2	–	200	48 h	[94]
	$TiCl_4$	Silicasol	H_2O_2	160	100 h	[93]
	$Ti(i\text{-}C_3H_7O)_4$					
	$TiCl_4$	SiO_2	–	90	18 h	[131]

groups to form the crystal phase together. Most of the abovementioned TiSi structures can be synthesized as coprecipitated powders (Table 2).

It is also possible to prepare the same structure using other types of precursors. For example, Kuznicki used $TiCl_3$ as a Ti-containing precursor for the synthesis of ETS-10 [48]. Any reactive source of silicon was allowed in the proposed synthesis approach. The temperature range of 100–175 °C and the time range of 12–15 days were patented as preferred conditions for HTT. The main disadvantage of this method is the use of $TiCl_3$, because it is expensive and has a low stability in air. Das et al. [115] used $TiCl_4$ as a Ti source, sodium silicate as a Si precursor and KF for a faster HTT synthesis (14–16 h) of ETS-10 at 200 °C and a 300 rpm stirrer speed. The drawbacks of using the $TiCl_4$ precursor are its aggressiveness and release of HCl into the atmosphere. The advantage is that $TiCl_4$ is cheaper, more stable and easier to handle than $TiCl_3$. Titanium sulphate $Ti(SO_4)_2$ was found to be a better Ti source than $TiCl_4$ and $TiCl_3$, yielding the largest ETS-10 crystals when the HTT was at 200 °C under static conditions [116,117]. Adjusting the Na:K ratio and the reaction water content, without using organic precursors, templates or seeds or F^-, made it possible to control the crystal size of ETS-10. Similar conclusions were reported for the synthesis of all the microporous TiSi by Kostov-Kytin et al. [88,102], varying only the $Na_2O(K_2O)$:TiO_2 ratio using different Ti precursors. Thomas [68] demonstrated how the anatase and rutile phases may be used as a source for TiSi synthesis. The synthesis of ETS-10 reported by Valtchev and Mintova [111] is an example of using the $TiCl_4$ precursor with organic template compounds (tetramethylammonium chloride). It is worth noting that even after HTT for 4–10 days, the products contain the other phases. The approach reported by Chapman and Roe [94] is an example of an organic precursors being used for microporous TiSi synthesis. Titanium (IV) ethoxide $Ti(OC_2H_5)_4$ was the chosen precursor for the synthesis of zorite and GTS-1 at 200 °C during 48 h and other organic compounds were tested as templates. The titanium isopropoxide $Ti(OC_3H_7)_4$ with tetraethyl orthosilicate $Si(OC_2H_5)_4$ was used to synthesize CTS by Medvedev et al. [118] and $TiCl_4$ with H_2O_2 was used for CTS synthesis by Clearfield et al. [119].

An advantage of using alkoxide precursors is the high purity of the obtained materials. There are, however, severe drawbacks: these precursors are unstable, toxic, expensive, sensitive to moisture and difficult to handle, requiring special synthesis equipment, ecotoxic solvents, and the results are not readily reproducible. Therefore, inorganic precursors are more commonly used for synthesis due to their ease of handling, stability and lower cost [41]. Usually, H_2O_2 is used as a ligand for slowing down the hydrolysis rate of inorganic Ti-containing salts to the Si-containing sources, which increases the amount of Ti-O-Si bonds in the resulting TiSi materials. There are some benefits of using H_2O_2 as a ligand, such as its non-toxicity and the eco-friendliness of the products H_2O and O_2. Nonetheless, the main disadvantage is the need for special high-pressure equipment because the autogenous pressure in an autoclave raises up to 7 MPa during HTT due to H_2O_2 thermal decomposition and oxygen release [119]. That disadvantage was overcome by our group: the pre-treatment stage was introduced and CTS precipitates were prepared under HTT with autogenous pressure of water vapours [120,121].

Synthesis of TiSi using organic precursors can be described as in Eq. (1), and an example of an inorganic synthesis is presented in Eq. (2):

$$Ti(OR)_4 + Si(OR)_4 + MeOH \xrightarrow{HTT} Me_xTi_ySi_zO_m \cdot nH_2O \quad (1)$$

$$TiCi_4 + Na_2O \cdot SiO_2 + MeOH \xrightarrow{HTT} Me_xTi_ySi_zO_m \cdot nH_2O \quad (2)$$

where R is the organic group (the organic part of the elementorganic molecule).

Kuznicki [46,48] proposed the method of TiSis preparation yielding the materials in the form of a powder, a granule or a molded product with a possibility of a particle sizes variation (extrudate 4–400 mesh (Tyler) screen). Nonetheless, the most of the reported methods yielded powdered materials, which can cause many difficulties in practical applications, since agglomeration decreases their working surface and active centres' accessibility. Other difficulties with powdered materials include stoppages, a high hydrostatic resistance, bulk compression and poor wettability [122,123]. Granulated or particulate materials do not have the same complications. These types of TiSi can be achieved by the sol-gel method, which can be done without binder substances that would decrease the efficiency of the sorbents.

The main advantages of the sol-gel method are [124]:

- excellent homogenization of the precursors during the sol preparation stage,
- the possibility of obtaining high purity materials with an anticipated structure and properties under comparably mild synthesis conditions and
- the ability to choose the form of the materials (powders, fibres, films or particles).

Traditional inorganic synthesis and the sol-gel method of TiSi preparation using H_2O_2 as a ligand were combined in an experiment [121]. This investigation was based on earlier reported approaches [84,120]. Unfortunately, H_2O_2 thermal decomposition releases oxygen and damages the gel structure and, consequently, TiSi could only be obtained as a powder.

A new sol-gel synthesis of TiSi from inorganic precursors based on gel preparation at room temperature and very promising results for large-scale application was reported recently [120,129,132]. This method results in stable materials with reproducible properties. The crucial feature of this approach is the use of chemicals at essential concentrations (2–5 M), which greatly increases the material yield. This synthesis can be accomplished using a range of eco-friendly ligands, such as polyalcohols, organic hydroxy-, ceto-, di- and tricarboxylic acids and mixtures of these. Using these ligands solved a few problem: firstly, the proposed ligands do not ruin the gel structure as traditional H_2O_2 does, and TiSi xerogels with a particle size of $\leq$4 mm are obtained [129]; secondly, the autogenous pressure in the autoclaves decreases by at least an order of magnitude; and, thirdly, the substitution of the H_2O_2 ligand makes it possible to increase the amount and quantity of the precursor, which can reduce the costs of the target material. The $TiCl_4$ precursor may also be replaced by a pure and technical $TiOSO_4$ solution. In addition, the pure silica sources Na_2SiO_3 and K_2SiO_3 were replaced with inexpensive bulk liquid glass, and stable porous gels with high sorption characteristics were obtained after such precursor substitutions. Using inexpensive precursors (technical $TiOSO_4$, containing iron) would not be possible with H_2O_2, due to the catalytic effect of the Fe^{3+} on the hydrogen peroxide decomposition reaction [120,129,132].

4. Sorption properties of titanosilicate materials

As for other inorganic materials, the chemical, thermal and radiation resistance are typical for TiSis, while their high sorption efficiency, great selectivity in a broad pH range (2–12), fast kinetic and vast sorption capacity strikingly distinguish TiSis from the other ISMs [20,21,39]. Titanosilicate sorbents are proved to be one of the most perspective ISM for decontamination of liquid radioactive

Table 3
Sorption studies using TiSi materials. Alternative names found in the literature are given in brackets.

Name	IEC, meq/g	q_{eq}, mmol/g	K_d, mL/g	Target cation	References
AM-2 (STS, umbite)	5.6			Na^+, Cs^+, Rb^+,NH_4^+, Mn^{2+},Mg^{2+}, Ca^{2+}, Sr^{2+},	[97,100,126,156,157]
		$3.5{\cdot}10^{-7}$		Co^{2+}, UO_2^{2+}, Hg^{2+}	
AM-3 (penkvilksite-2*O*)	n.r.	0.72		K^+, $^{60}Co^{2+}$,Li^+	[106,109,158]
AM-4	7.63		$0.6–4.8{\cdot}10^3$	$^{134,137}Cs^+$,	[88,102,136,138]
			$0.2–1.5{\cdot}10^3$	$^{57,60}Co^{2+}$, Cs^+, Sr^{2+}, Mn^{2+}	
			2693	$^{110}Ag^+$,	
			10–25	$^{125}Sb^{3+}$,	
				$^{238}UO_2^{2+}$,	
			$6.7{\cdot}10^4$	Hg^{2+},	
			$1.2{\cdot}10^5$	$^{236}Pu^{3+}$	
			$9{\cdot}10^6$	$^{241}Am^{3+}$	
ETS-1	6.70	3.45		Ag^+,	[49,50]
		1.41–1.52		Cu^{2+},	
		0.78–0.84		Y^{3+}, La^{3+}, Cr^{3+}, Fe^{3+}, Zr^{4+},	
		1.65–1.83		Cs^+,	
		0.38–0.61		Sr^{2+},	
ETS-2	8.12	3.64		Ag^+,	[49,50]
		1.82		Cu^{2+},	
		1.16–1.20		Y^{3+}, La^{3+}, Cr^{3+}, Fe^{3+}, Zr^{4+},	
		0.36–0.60		Cs^+,	
		1.18–1.29		Sr^{2+},	
ETS-4 (Zorite-type)	6.40	1.22		Hg^{2+}, Cs^+, Sr^{2+},	[52–56,58,60–66,88,102,136,138,139,153,155,159–163]
			2000	UO_2^{2+},	
			732	$^{110}Ag^+$,	
			0	$^{125}Sb^{3+}$,	
			644	$^{204}Hg^{2+}$,	
			$0.1–3.2{\cdot}10^4$	$^{60}Co^{2+}$,	
			583	$^{115m}Cd^{2+}$,	
			$>10^6$	$^{241}Am^{3+}$,	
			$<10^4$	$^{236}Pu^{3+}$,	
			$2.8–4.5{\cdot}10^4$	$^{134}Cs^+$,	
			$3.3–2.1{\cdot}10^4$	$^{137}Cs^+$	
				Y^{3+}	
ETS–10	4.5		$>10^6$	UO_2^{2+},	[57,75,78–80,112,135,136,138,139,143,145–147,149,150,153,155,161,164–168]
			5000	Th^{4+},	
		4.43	800	$^{115}Cd^{2+}$,	
		3.85	627	$^{204}Hg^{2+}$,	
		4.23	$0.35–4.5{\cdot}10^4$	$^{60}Co^{2+}$,	
			$3.02{\cdot}10^3$	$^{204}Tl^+$,	
		4.5	1636	$^{137}Cs^+$,	
			284	$^{110}Ag^+$,	
		5.5		Cs^+,	
		4.8		Sr^{2+},	
		0.7–2.1		Zn^{2+}, Pb^{2+},	
		0.7–1.1	3–13	Cd^{2+},	
		2.1		$^{125}Sb^{3+}$,	
			$2.1{\cdot}10^5$	Hg^{2+},	
		0.04	700	$^{241}Am^{3+}$,	
				$^{236}Pu^{3+}$, Eu^{3+}	
		2.6		Cu^{2+}	
ETS-14 (penkvilksite)	n.r.			Li^+, Mg^{2+}, Sr^{2+}, Ca^{2+}, H^+, NH_4^+	[81]
CTS (TAM–5, sitinakite, CST)	7.5	4.4	$0.2–7.2{\cdot}10^5$	$^{137}Cs^+$,	[86,88,89,102,119,120,129,132,133,136,138–140,142,169–190]
			$0.8–7.8{\cdot}10^5$	$^{134}Cs^+$,	
		7.3		$^{82,90}Sr^{2+}$, $^{90}Y^{3+}$, $^{60}Co^{2+}$,	
			$3.2{\cdot}10^6$	$^{241}Am^{3+}$,	
				$^{152,154}Eu^{3+}$,	
			$1.5{\cdot}10^4$	$^{236,239,240}Pu^{3+}$,	
				Li^+,	
			11300	Na^+,	
			22977	K^+,	
				Cs^+.	
		1.9		Rb^+, Ca^{2+}, Sr^{2+}, Eu^{3+}	

(*continued on next page*)

Table 3 (*continued*)

Name	IEC, meq/g	q_{eq}, mmol/g	K_d, mL/g	Target cation	References
GTS-1 (pharmacosiderite)	3.87			$^{137}Cs^+$, $^{90}Sr^{2+}$,	[11,86,88,102,140,148,191]
			630	Li^+, (Na-form)	
			260	Na^+, (K-form)	
			2580	K^+, (Na-form)	
			6190	Rb^+, (Na-form)	
			15360	Cs^+, (Na-form)	
			4530	Ca^{2+}, (Na-form)	
			6050	Mg^{2+} (Na-form)	
			6487	Sr^{2+}, (Na-form)	
			8800	Ba^{2+} (Na-form)	
		$3.55 \cdot 10^{-7}$		Hg^{2+},	

q_{eq} – sorption capacity at equilibrium.
*n.r. – not reported.

wastes (LRW) from longlived radionuclides such as ^{90}Sr, $^{134,137}Cs$, $^{233–235,238}U$, ^{241}Am, $^{239,240}Pu$, and ^{154}Eu [39,64,90,95,133–142]. Their high sorption ability towards the other cations and small molecules had been reported by [39,44,50,56,58,60,90,138,143,143–147]. Since TiSi is a relatively new material class which is currently being very actively explored, many researchers report properties of the same material using different names and abbreviations, such as [36,106,109] or [85,94,131,148].

As can be seen, most of the sorption studies were conducted with stable nuclides (Table 3). The chemical behaviour of the nuclides of the same element is similar, and therefore this data can be used in a similar way. CTS and ETS-4 have the highest theoretical ion-exchange capacity among the reported framework TiSis, while ETS-10 has the largest pore diameter (8 Å), suggesting that it has larger target cations, such as UO_2^{2+}, $^{234}Th^{4+}$, $^{241}Am^{3+}$ or $^{236,239,240}Pu^{3+}$.

5. Description of selected Titanosilicates

5.1. ETS-10

The sorption of the U cation from water on ETS-10 was studied by Al-Attar's group in 2000, and the process was analysed again by Pavel et al. [112,138,143,149,150]. The first study reported the influence of the Ti precursor, contact time, initial sorbate and sorbent concentration on the ability of ETS-10 to retain U. A high decontamination factor (DF) of about 100% and $K_d > 10^6$ mL/g were found, and ion exchange, surface precipitation and adsorption of dehydrated uranyl UO_2^{2+} ions were suggested as the predominant mechanisms. In contrast, the second group got a lower K_d of ≈1900 mL/g and doubted the mechanisms proposed by the previous study. Based on XRD investigations, the precipitation mechanism was excluded. Sorption of partially dehydrated $[UO_2(H_2O)_5)]^{2+}$, which is connected through sharing oxygen atoms with SiO_4 tetrahedrons, were found during extended X-ray absorption fine structure (EXAFS) studies of molecular level interactions between the ETS-10 and the U cation [112,150].

The ability of the ETS-10 to sorb twice as much Th(IV) as U(VI) was explained by the slightly smaller ionic and hydrated Th(IV) *radii* and associated with a similar role of the silanol group in the Th(IV) sorption process [149]. The role of surface acidity and porosity in the sorption of both the U and Th cations was illustrated.

The role of media composition and competitive ions in the sorption of $^{241}Am^{3+}$ and $^{236,239,240}Pu^{3+}$ by ETS-10, ETS-4, AM-4 and CTS TiSi materials was analysed in comparative studies by Al-Attar et al. [136,139]. An ion-exchange mechanism was suggested for the Am uptake, but no mechanism for Pu was found.

The sorption of smaller cations by ETS-10 has also been studied [35,79,136,139,145,146]. The isotope dilution technique was used to study the effects of temperature, surface acidity and porosity modification on the $^{204}Tl^+$ sorption ability of ETS-10 [145]. It was found that chemical surface modifications decrease the kinetic and thermodynamic parameters of the sorption process.

The uptake of $^{115}Cd^{2+}$, $^{204}Hg^{2+}$, $^{60}Co^{2+}$, $^{137}Cs^+$ radiocations by ETS-10 from monosolutions was investigated using the isotope dilution method by Pavel et al. [79]. Sorption was investigated as a function of contact time and temperature under constant batch factors in the absence of competitive ions. The ETS-10 sorption capacity of the studied cations at 20 °C was found to be close to the theoretical exchange capacity of 4.5 meq/g (Table 3) and reported values decreased in the following order $^{137}Cs^+ > {}^{115}Cd^{2+} > {}^{60}Co^{2+} > {}^{204}Hg^{2+}$ [79]. For stable cations, the selectivity of the cation sorption at 20–25 °C was found to be as follows: $Cu^{2+} > Zn^{2+} > Mn^{2+} > Co^{2+}$ and $Pb^{2+} > Cd^{2+} > Cu^{2+}$ from single components and mixed media [35,146] (Table 3). The pH and batch factor dependencies of Cd^{2+} sorption on ETS-10 were described by Chamarinha et al. [151]. They observed that Cd^{2+} sorption increased with a raise in both studied factors. The unusually high sorption capacity of ETS-10 for zeolite type material was emphasized by Zhao et al. [152] using Pb^{2+}. They attributed the extremely high sorption rate and remarkable capacity to the low hydration energy of the sorbate. Sorption of Cs^+, Cd^{2+}, Pb^{2+} and Hg^{2+} by ETS-4 and ETS-10 materials as a function of the dehydration of target cations was reported by De Raffele et al. [153]. The effects of the tetralkylammonium ions as structure directing agents during the TiSi synthesis were studied and the pore structure modification by tetralkylammonium was efficient for the ETS-10 and samples with microporous volume of 0.11–0.13 $cm^3\ g^{-1}$ were obtained. The high dependence of ion exchange on the dehydration extent of the studied cations' was reported for ETS- 10.

In the comparative study of Hg^{2+} sorption by TiSis, ETS-10 demonstrated the best DF of Hg^{2+} from a single solution. Among the investigated materials, AM-2 was found to be the best for removing Hg^{2+} in the presence of competitive cations like Mg^{2+} (97.0%), while GTS-1 was the least efficient (72.4%) material of all [154]. A remarkably high sorption capacity and affinity of ETS-10 to Cs^+ and Sr^{2+} from single and equivalent mixed cation solutions were reported by Pavel et al. [135] (Table 3). They examined the effect of the melting temperature on the retained cation amount in order to test how well ETS-10 solidified for final disposal after retention of Cs^+ and/or Sr^{2+} radionuclides from LRW. Easy solidification was reported in all studied cases. The stable Cs^+ and Sr^{2+} retention mechanisms on ETS-10 and ETS-4 was recently investigated by the same researchers [155]. The sorption capacity and cation selectivity toward the target cations were studied as a func-

tion of temperature and concentration and the results assessed using ion exchange isotherms as well as Kielland and Langmuir plots. Based on the results, ion exchange was suggested for the retention process for both examined materials and target cations. ETS-10 was found to be unselective to Sr^{2+}, while high retention values were obtained for both target cations and little effects of temperature was observed. For both studied TiSi materials, the sorption is highly dependent on the concentration of the target cations [155] (Table 3).

5.2. ETS-4

Despite its smaller pore radius of 3–5 Å, the ability of ETS-4 to sorb large cations like UO_2^{2+}, $^{241}Am^{3+}$ and $^{236,239,240}Pu^{3+}$ was estimated by Al-Attar et al. from 2000–2003 [136,138,139,143]. The selectivity of ETS-4 to UO_2^{2+} was compared with CTS, AM-4 and ETS-10 titanosilicate materials using the batch K_d. The influence of batch factor, contact time, sorbate concentration and structural aspects on the ion-exchange capacity of the studied materials was discussed by Al-Attar and Dyer [138]. A much lower K_d for ETS-4 than for ETS-10 was reported in the first study by Al-Attar [143] (Table 3). For sorption of U on TiSi materials, both surface precipitation and ion exchange mechanisms were suggested. The sorption of trans uranium $^{241}Am^{3+}$ and $^{236}Pu^{3+}$ isotopes on the same type of materials was studied under batch conditions. The K_d value was found to be a function of the sorption media composition, concentration and pH. The effects of structural and surface aspects on the ion-exchange capacity were also discussed. It was also found that ETS-4 $K_d(^{241}Am^{3+}) > 10^6$, but the AM-4 material was more effective than ETS-4 under the experimental conditions [139]. The same group of materials was tested for the sorption of $^{110m}Ag^+$, $^{57,60}Co^{2+}$, $^{134,137}Cs^+$, $^{125}Sb^{3+}$ from real nuclear power plant (NPP) waste waters supplied from the Ginna and Diablo Canyon NPP (USA). The selectivity of the materials was evaluated using K_d as a function of NPP solution composition [136] (Table 3). Based on this study, CTS was the most effective TiSi material tested for radiocesium sorption. The sorption of $^{115m}Cd^{2+}$, $^{60}Co^{2+}$ and $^{203}Hg^{2+}$ radionuclides by ETS-4 from analogues of a radioactive waste water solution was investigated using batch techniques by Popa et al. [64]. Using K_d, the selectivity order was estimated as a function of temperature and contact time and the sorption capacity of ETS-4 was found to decrease in the order $^{203}Hg^{2+} > {}^{115m}Cd^{2+} > {}^{60}Co^{2+}$, which is the reverse of the results obtained in the ETS-10 study [79]. No pH or competitive cation studies were conducted.

The process of Cd^{2+} sorption on ETS-4 under batch experimental conditions was reported by Ferreira et al. [59]. Sorption capacity as a function of contact time, sorbent and sorbate concentration was compared with literature data on zeolite A, clinoptilolite and dolomite sorption ability. The experimental data illustrated that ETS-4 was efficient for Cd^{2+} removal from aqueous solution. The pH effect was described by Barreira et al. [57], who reported a high DF of 99.6% at solution pH 6.

The sorption ability to Hg^{2+} was thoroughly examined by Lopes et al. from 2007–2013 [56,60–62,154,160] and they studied the sorption ability of ETS-4 materials as a function of batch factor, pH, temperature, contact time and pollutant concentration in batch mode. They found that the retention of Hg^{2+} by ETS-4 is an exothermic and thermodynamically favourable process strongly affected by solution pH and the presence of chlorine ions. At the same time, the temperature and presence of competitive ions like Na^+, Ca^{2+} or Mg^{2+} did not substantially affect the ability of ETS-4 to sorb Hg^{2+}. The optimal conditions were determined to be pH 4–6 at 21 °C, while the column study demonstrated that ETS-4 had a sorption capacity of 0.17 mmol/g during the first two cycles. A comparison by Noh and Komarneni [159] found that of the materials studied, ETS-4 has the highest selectivity to Hg^{2+}.

In 2009–2013, Lopes et al. compared the sorption ability of ETS-4 to Hg^{2+} and Cd^{2+} [51,61]. The K_d was evaluated as a function of the sorbent concentration from single solutions and equivalent mixtures and the selectivity coefficient was calculated as a ratio between the obtained K_d. It was found that ETS-4 has higher kinetic parameters and selectivity for Cd^{2+}, but slower kinetics and higher sorption capacity for Hg^{2+}.

Recently, De Raffele et al. compared the ability of ETS-4 and ETS- 10 to sorb Cs^+, Cd^{2+}, Pb^{2+} and Hg^{2+} [153] and studied the kinetics for both materials. They also reported that the dehydration extent of the target cations affects the sorption process of ETS-4 much less than for ETS-10. Figueiredo et al. [162] assessed ETS-4 in relation to Cs^+ removal from aqueous solutions in both batch and fixed-bed operations. They also studied the regeneration ability and after 75 h, 20% regeneration was achieved. Nonetheless, they consider ETS-4 promising for future cyclic industrial use.

Fundamental sorption properties of ETS-4 for Sr^{2+} and Ba^{2+} were compared with CTS sorption abilities by Noh et al. [54], who studied the selectivity of the sorption process under batch conditions as a function of the Sr^{2+}/Na^+ or Ba^{2+}/Na^+ ratio. Their results showed that ETS-4 had a higher selectivity to Ba^{2+} than CTS, but this order was reversed for the Sr^{2+} selectivity. This research highlighted the selective sorption ability of ETS-4 to remove both Sr^{2+} and Ba^{2+} from LRW.

Temperature influences on the retention of stable Cs^+ and Sr^{2+} on ETS-10 and ETS-4 were studied by Pavel et al. [155]. Results of ion exchange isotherms, as well as Kielland and Langmuir plots demonstrated that for both ions, ETS-4 has higher ion exchange capacities than ETS-10, reaching 6 meq of Cs^+ per gram of ETS-4. Contrary to the unselective ETS-10, ETS-4 becomes selective to Sr^{2+} already at ambient temperature and the concentration of the target cations highly influences the ion exchange capacity of both TiSis. Consequently, the study promotes ETS-10 and ETS-4 as very good candidates for the uptake of Cs^+ and Sr^{2+} from nuclear waste solutions [155] (Table 3).

5.3. ETS-1 and ETS-2

Liu et al. [49] compared the sorption ability of ETS-1 and ETS-2 for Cs and Sr removal under batch conditions with ETS-4, Na-Y and Na-ZSM-5 in the study of Liu et al. at ambient temperature and various contact times. ETS-1 demonstrated the highest Cs^+ removal capacity among the studied ISMs, while ETS-2 was better in Sr removal. On the other hand, ETS-1 showed a high sorption capacity, but not selectivity to Cs^+ [49]. They also examined the uptake ability of ETS-1 and ETS-2 to Ag^+, Cu^{2+}, Y^{3+}, La^{3+}, Fe^{3+}, Cr^{3+} and Zr^{4+} cations [50] and reported a high uptake of Ag^+, Cu^{2+}, Y^{3+} and La^{3+} for both ETS-1 and ETS-2, while neither of the TiSis illustrated a priority in Cr^{3+} and Zr^{4+} retention. Sorption abilities of ETS-1 and ETS-2 were compared with mesoporous manganese oxide (MnO_2) which exhibited a higher uptake ability only to Fe^{3+} due to its incorporation into the oxides' matrix structure. None of these ISMs were effective for the sorption of Cr^{3+} and Zr^{4+} and a special affinity of ETS-1 to Ag^+ was highlighted [50].

5.4. ETS-14

ETS-14's ion-exchange behaviour is different from other ETS materials or classical zeolites: H^+, NH_4^+, Ca^{2+}, $Mg^{2+}$and Sr^{2+}, can exchange Na^+ only partially, while Li^+ can displace sodium completely in one exchange step. Unexchanged sodium was detected using NMR in synthesized ETS-14 (Na-form) after exchange with lithium cations. Usually, classical zeolites (including ETS materials) prefer heavier and more polarisable cations, converting into the Li-form reluctantly and only partially. Consequently, the authors suggested to use ETS-14 as an electrode in advanced lithium batteries

as a desiccant for conventional lithium batteries or as a reversible sorbent for lithium [81].

5.5. AM-2

Microporous titanosilicate of the composition $K_2TiSi_3O_9{\cdot}H_2O$ was subjected to ion exchange with H^+, NH_4^+, Li^+, Na^+, Rb^+ and Cs^+ under batch conditions. It was demonstrated that the material can be completely exchanged by NH_4^+ and to different extents with the alkaline cations: $NH_4^+ > Rb^+ = Na^+ > Li^+ > Cs^+$ [100]. Li^+, Na^+, K^+, Cs^+, Ca^{2+}, Sr^{2+}, Ba^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+} and Cr^{3+} ion exchange as a function of pH was studied with AM-2 [104]. Potassium was found to be the most favoured ion in the pH range 3–12 with an ion exchange capacity (IEC) of 5.3 meq/g. An XRD and differential scanning calorimetry study was done on Na^+-, Cs^+-, Mn^{2+}-, Ca^{2+}-, Sr^{2+}- and Rb^+-exchanged forms of AM-2. [126,156] found that the ion-exchange rate followed the sequence $Mn^{2+} > Ca^{2+} > Sr^{2+} > Cs^+$. Adsorption behaviours of AM-2 and AM-4 were compared with ETS-10, ETS-4 and GTS-1 for mercury removal from natural waters. AM-2 was found to be the most efficient in the presence of competitive cations such as Mg^{2+}, with a DF of over 97.0% [154,192]

5.6. AM-3

AM-3 and its ability to sorb the radioactive $^{60}Co^{2+}$ was studied as a function of contact time, target cation and sorbent concentrations using a batch method [154,192]. These authors linked the substantial influence of the batch factor and $^{60}Co^{2+}$ concentration to the equilibrium pH.

The ion-exchange capacity of penkvilksite to K^+ was found to be 0.72 meq/g in 1 M KNO_3 at 80 °C after stirring for 24 h [158]. This low result was attributed to the short reaction time. Li^+, Na^+, K^+, Cs^+, Ca^{2+}, Sr^{2+}, Ba^{2+}, Cd^{2+}, Co^{2+}, Hg^{2+}, Pb^{2+}, Cu^{2+} and Cr^{3+} exchange on AM-3 were recently studied under batch conditions [144]. Dynamic calorimetry was used to investigate K^+, Cs^+, Sr^{2+} and Cu^{2+} exchange by Chukanov et al. [97] and Frost et al. proposed that AM-3 could be used to incorporate actinides and lanthanides from radioactive waste [193].

5.7. AM-4

The sorption properties of TiSi materials with different framework structures and cation exchange capacities were compared by Al-Attar et al. (2001–2003) [138,139]. Uranium uptake from aqueous solutions by AM-4, ETS-4, ETS-10 and CTS was studied as a function of contact time, uranium concentration and the batch factor [138]. This study associated the high sorption capacity for U with surface precipitation ($K_d = 6.7{\cdot}10^4$ mL/g). The K_d of $^{241}Am^{3+}$, $^{236}Pu^{3+}$ and $^{110m}Ag^+$, $^{57,60}Co^{2+}$, $^{134,137}Cs^+$, $^{125}Sb^{3+}$, $^{134}Cs^+/^{137}Cs^+$ isotopes was estimated as a function of the retention media composition, concentration and pH and discussed the effects of structural and surface aspects on ion-exchange capacity. It was established that AM-4 was the most effective material for $^{241}Am^{3+}$ sorption at all sodium concentrations studied. Extraordinary suppression of cesium sorption by competitive ions was also reported for AM-4 [136,139].

In a study of Sr^{2+} uptake as a function of pH and competitive Na^+, K^+, Ca^{2+} and Mg^{2+} concentration from binary solutions, Ca^{2+} was found to be the major competitor. Additionally, AM-4 exhibited a low affinity (K_d < 640 mL/g) for the alkali cations and a high affinity for alkaline earths (K_d Sr^{2+} = 66000 mL/g) in neutral and alkaline media [194].

Lopes et al. [154,192] demonstrated he influence of competitive Na^+, Ca^{2+}, and Mg^{2+} ions on AM-4 uptake of Hg^{2+}. In a comparison with ETS-10, ETS-4, AM-2 and AM-4, the last one was found to be the least effective in retaining Hg^{2+} from natural water.

When AM-4 was exchanged with Ag^+, Zn^{2+} and Cu^{2+} and characterized by XRD and TEM, a certain loss of crystallinity was observed on the exchanged AM-4. The best antimicrobial activity against the bacteria *Staphylococcus aureus* was shown by Ag–AM-4 [195].

5.8. GTS-1

According to literature, the ion-exchange capacity and selectivity of GTS-1 decreases in the order $Cs^+ > K^+ > Na^+ > Li^+$ [87,94,142,191]. Great affinity for Cs^+ was found by Clearfield's group [84,140]. Later, Cs^+ and Sr^{2+} selectivity was investigated in the presence of Na^+, K^+, Mg^{2+} and Ca^{2+} competitive cations [11,85–87,95,140–142,191,196]. Dyer et al. [148] also reported the removal of $^{137}Cs^+$ and $^{89}Sr^{2+}$ by different cationic forms of synthetic pharmacosiderite. In addition, the capacity of GTS-1 to adsorb Hg from natural waters was compared with AM-2, AM-4, ETS-10 and ETS-4, whereas GTS-1 with a DF of only 72.4% was found to be the least efficient material of all [154].

5.9. CTS

Clearfield's group studied the effect of solution pH on the selectivity order and found that in an acidic medium, the CTS selectivity had the following order: $K^+ > Cs^+ \gg Na^+ \gg Li^+$, while in an alkaline medium it was $Cs^+ > Rb^+ \gg K^+ \gg Li^+$. Additionally, the ion-exchange properties of CTS were analysed in terms of framework structure as well as pore space and were compared with GTS-1 [87,119,140].

Sorption capacities of CTS for Cs^+ and Sr^{2+} has interested several researchers. Their studies determined the role of hydroxyl water, framework structure and pore space in the ion-exchange process by X-ray, synchrotron, IR and Raman investigations [11,84,87,118,119,137,140,142,174,176,178,186,188,197–200]. CTS selectivity for radioactive $^{137}Cs^+$ and $^{89}Sr^{2+}$ was studied as a function of contact time, temperature, $NaNO_3$ concentration and Nb^{5+} substitution for Ti^{4+} in the structure. A higher selectivity to Cs^+ than to Sr^{2+} was reported, which increased in Nb-substituted CTS samples. XRD studies identified the position and coordination of the exchanged cations to demonstrate that higher selectivity of the retained cation is correlated with higher coordination in the channel of that cation [197,198]. As mentioned earlier, high sodium concentrations have a negative effect on the Cs^+ uptake of precipitated CTS [11,87,90]. In order to improve the Cs^+ selectivity in highly alkaline solutions, Ti^{4+} was partially substituted by Nb^{5+} in the CST framework. A precipitated CTS with about 15 mol% of Nb^{5+} was noted to be tolerant to sodium concentrations and is manufactured by Union Oil Products as the commercial sorption material IONSIV IE-910 (powder form) and IONSIV IE-911 (beaded form) [119,174,198,201,202]. However, for improving the Sr^{2+} retentivity, no such additions or substitutions to the framework of precipitated CTS were found so far.

Changing the method of synthesis results in the desired effect: the xerogel CTS particles are less sensitive to the Na^+ concentrations and have a higher selectivity to Sr^{2+} before any additions and substitutions. [129,180,181] studied the sorption characteristics of CTS in a special xerogel form for Cs^+ and Sr^{2+} as function of the sol-gel synthesis parameters. A substantial effect of the precursors' chemical nature and the purity on the xerogels' pore structure was observed, while the sorption capacity was affected to a lesser degree. The Fe^{3+} impurities of the precursor promoted the xerogel structure resulting in wider mesopores which increased the kinetic rate for a cheaper (less pure, so-called "technical") material. Both, pure and "technical", TiSi xerogels proved to be highly efficient in a wide pH range (2–12), as the precipitated analogues CTS materials. High sorption affinities for both target cations, $K_d(Cs^+) = 6.9{\cdot}10^4$ mL/g and $K_d(Sr^{2+}) = 6.9{\cdot}10^4$ mL/g, were

evaluated from the media with a complex composition (saline background and sea water/blood plasma imitating solution). However, it must be highlighted that the $K_d(Cs^+)$ values were stronger affected by the presence of competing K^+, Na^+ and Ca^{2+}, while the selectivity and capacity for Sr^{2+} remains in the same order [129,180,181].

The uptake of $^{85}Sr^{2+}$, $^{57}Co^{2+}$ and $^{134}Cs^+$ by CTS was investigated as a function of titanosilicate crystallinity, solution composition and pH [90]. High K_d values were reported for $^{134}Cs^+$ ($2.5{\cdot}10^6$ mL/g) and $^{85}Sr^{2+}$ ($6.8{\cdot}10^4$ mL/g) and the strong interference of K^+ and Na^+ competing cations at very high pH was highlighted. Affinity was also found to increase with decreasing sample crystallinity [186]. Similar observations of the higher sorption capacity for amorphous xerogel CTS samples were also reported by [180].

Four Titanosilicates (CTS, ETS-10, ETS-4 and AM-4) as well as layered manganese oxides and an antimony silicate were tested for their ability to decontaminate the reprocessing spent fuel from the trans uranium isotopes $^{241}Am^{3+}$ and $^{236}Pu^{3+}$ [139]. In batch conditions, the most suitable materials were determined as a function of pH, Na^+ and Ca^{2+} concentrations. A negligible variation of CTS K_d $^{241}Am^{3+}$ ($2.6–3.3{\cdot}10^6$ mL/g) was observed at all studied $NaNO_3$ concentrations. For $^{236}Pu^{3+}$, an increase in K_d of one order of magnitude was established with increasing background salt concentration ($1.6{\cdot}10^4$ mL/g). A comparative sorption investigation with the long-lived radionuclides $^{134}Cs^+$, $^{84,89,90}Sr^{2+}$, $^{238,239,240,241,242}Pu^{3+}$ and $^{243}Am^{3+}$ was conducted by [133]. In this study, the sorption ability of TiSis was compared with the one of iron oxides and natural clay materials with 14% montmorillonite, using natural groundwater, a 0.1 mol/L $NaNO_3$ solution and spent fuel pond water. It was found that TiSis have a higher sorption capacity for all studied radionuclides compared to the other studied ISMs. Thus, 90% of ^{134}Cs was retained in the first 10 min, while for $\sum$Pu, full sorption takes around an hour. This difference in kinetic data is attributed to the steric limitation of big ions like Pu^{3+} and Am^{3+} in the pore structure of TiSi. Laboratory batch investigations further demonstrated the high sorption capacity, kinetic rate, selectivity and radioactive resistance of the xerogel TiSi materials [133].

The CTS, ETS-10, ETS-4 and AM-4 was tested for the sorption of $^{110m}Ag^+$, $^{57,60}Co^{2+}$, $^{134,137}Cs^+$, $^{125}Sb^{3+}$ from real NPP waste waters supplied from the Ginna and Diablo Canyon NPP (USA). The selectivity of the materials was evaluated using K_d as a function of NPP solution composition and pH (Table 3) [136]. Among the studied materials, CTS was found to be the most effective in radiocesium uptake (K_d $^{134}Cs^+/^{137}Cs^+ = 7.1–7.8{\cdot}10^5$).

Sorption of $^{22}Na^+$, $^{134}Cs^+$ and $^{60}Co^{2+}$ radionuclides were studied under batch conditions as a function of contact time, temperature and radionuclide concentration, and a high sorption rate (3–5 min) was reported [169]. The sorption capacity was found to be higher in Na-CTS form and decreased in the order of $Cs^+ > Co^{2+} > Na^+$. It is noteworthy that the sorption capacity was observed to increase with rising temperature for Cs^+, while the opposite was the case for the Co^{2+} and Na^+ uptake [169]. Similar results with rising Cs^+ sorption capacities were reported by [181] and these observations were used in suggesting the sorption mechanism. Currently, our group further studies the sorption abilities of the CTS xerogel samples relative to Co^{2+} and other potentially toxic cations, such as Mn^{2+}, Ni^{2+}, Zn^{2+}, Cd^{2+}, Cu^{2+}, Cr^{3+}, Pb^{2+} in order to estimate the benefit of utilizing the CTS xerogels for decontaminating radioactive polluted bypass and mine water.

In a comparative study of 28 sorption materials including framework and layered TiSis and LRW containing elevated concentrations of Cs^+ and Sr^{2+} Bortun et al. [140] demonstrated that among the studied materials, CTS had the highest sorption capacity, selectivity and retentivity for Cs^+ and Sr^{2+}. Another comparative study of 60 sorption materials carried out at the Los Alamos National Laboratory and Pacific Northwest Laboratory demonstrated that CTS materials are the most promising for Cs^+ retention from an acid-dissolved sludge simulant and slightly neutralized acidic and basic simulants of Hanford tank wastes [170].

6. Conclusions

All adsorption, ion exchange and membrane techniques demand reliable and resistant materials in regards to thermal, chemical, mechanical and ionization radiation effects. This review shows that Titanosilicates fully satisfy the above mentioned demands including high kinetics, sorption capacities and a selectivity over a broad pH range. Over and above, TiSis remain mainly "uncontaminated" by other cations [11,39,129]. These additional benefits strikingly distinguish TiSis from other ISMs and justify the rising attention of researchers to these sorbents. Structural investigations showed an interesting tendency: with decreasing structural order (crystallinity of CTS or structural perfection of ETS-10) the sorption ability of TiSi increases [76,90,129,186]. Successful retention of a wide variety of cations using TiSis was already reported in over 200 papers. Thus, ETS-10 was found to be effective for sorbing large cations and species such as Hg^{2+}, Tl^+, Pb^{2+}, UO_2^{2+}, Am^{3+} and Pu^{3+} [112,143,145,150,167]. Instead, ETS-14 was reported as the most efficient sorbent in Li^+ retention [81]. Using the Molecular Gate® effect, the ETS-4 pore structure can be adjusted and allows the solutions' purification as well as gas separation processes [45,70–73]. Comparative studies of sorbents with real LRW, radioactive polluted ground waters and acid-dissolved sludge simulants demonstrated that among the studied materials, CTS had the highest sorption capacity, selectivity and retentivity for Cs^+ and Sr^{2+} [140,170].

The mechanisms of ion exchange, surface precipitation, chemisorption, activation and specific adsorption mechanisms were considered in order to explain the retention processes on TiSis. Most papers that used batch mode experiments and examined equilibria and kinetics, suggest ion exchange as sorption mechanism. In conclusion, ion exchange can be assumed to be the main, but not obligatory the last stage of the uptake process by TiSi materials. In cases, where the cation uptake exceeded the ion exchange capacity, the effects were attributed to adsorption and precipitation phenomena [39,112,150,180,181].

Numerous authors studied chemical modifications of TiSis and structural substitution in it by elements such as Nb, Ge, Al [18,174,198,203–205]. Nb substituted CTS is an example of increasing sorption capacity and even successful commercialisation as IONSIV® IE-911 [182,206,207]. Though the actual sorption capacity of TiSi materials can be increased, the additional treatments necessary drastically increase the final costs in most cases. Taking into account that these modifications only result in powdered TiSi material, the authors of this review see the sol-gel synthesis for TiSi as a more perspective and cost effective option. Sol-gel synthesis allows production of TiSi with predetermined parameters, and xerogel particles need no binder substances that negatively influence the materials' efficiency. Another benefit of this method is the possibility of bulk grade precursors usage that lower the materials' production costs without decreasing, in some cases even with increasing, the sorption capacity [129,180,181]. Kwon et al., for example, reported an alternative way of separation by using magnetized Fe^{3+}-CTS powders in conjunction with superconducting high-gradient magnetic separation [190]. Magnetization in this case is an additional treatment step, whilst with the sol-gel synthesis the magnetization can simply be achieved by substituting the pure precursor by the iron bearing or iron "polluted" one [129,180,181].

This review of TiSi materials shows that this steadily growing group of sorbents is continuously incorporating into the inorganic sorption materials' family. From the materials suggested for Cs^+ and Hg^{2+} selective exchange, TiSi extensively enlarged their field of application: i) in gas separation for size-selective sorption; ii) in food storing as a component for antimicrobial packing materials; iii) in energy storing as Li battery electrode materials and iv) in water treatment for selective and effective decontamination of Cs^+, Sr^{2+} and other long-lived radionuclides, as well as Hg^{2+} and other potentially toxic cations from different polluted liquids with complex background, including drinking, sea and mine water, LRW and blood plasma. The last position may be separated into two interconnected fields: an exoecological – waste neutralisation and purification the environment and an endoecological – decontamination the human body from the inside (TiSi enterosorption materials) and cleansing the body liquids, such as blood plasma (TiSi sorbents for the haemodialysis or for the portative kidney).

Current methods of TiSi preparation yielded the materials able to compete with ferrocyanides in Cs^+ selective uptake, with antimony silicates in Sr^{2+} selective retention and with zeolites in usability. Temperature dependences, thermodynamic parameters, structural aspects and laboratory tests are investigated in details. At the same time, the most informative investigations such as comparative studies from solutions that contain sorbates and competitive ions simultaneously or tests from real polluted aqueous solutions, as well as column studies are numerous. Fundamental investigations and pilot-scale approbations still need to be done. For example, rheological studies for the sol-gel method, thorough investigations of sorption mechamisms or toxicological studies over medical applications of TiSi are still missing. Studies concerning the economic feasibility are essential before a wide practical application of the various TiSis. However, there is no doubt, that in the nearest future, new efficient synthesis methods and remarkable applications are expected for the titanosilicate sorption family.

References

[1] C.B. Amphlett, Inorganic Ion Exchangers, Elsevier, 1964.
[2] J. Albertsson, Inorganic Ion Exchangers. IV. The sorption on Crystaline Zirconium Phosphate and its dependence upon the crystalinity, Acta Chem. Scand. 20 (1966) 1689–1702.
[3] V. Veselý, V. Pekárek, Synthetic inorganic ion-exchangers—I: hydrous oxides and acidic salts of multivalent metals, Talanta 19 (1972) 219–262.
[4] V. Pekarek, V. Veselý, Synthetic inorganic ion exchangers—II: salts of heteropolyacids, insoluble ferrocyanides, synthetic aluminosilicates and miscellaneous exchangers, Talanta 19 (1972) 1245–1283.
[5] A. Clearfield, Inorganic Ion Exchange Materials, CRC Press, United States, 1982.
[6] A. Clearfield, Role of ion exchange in solid-state chemistry, Chem. Rev. 88 (1988) 125–148.
[7] G. Cao, H.G. Hong, T.E. Mallouk, Layered metal phosphates and phosphonates: from crystals to monolayers, Acc. Chem. Res. 25 (1992) 420–427.
[8] R.G. Anthony, C.V. Philip, R.G. Dosch, Selective adsorption and ion exchange of metal cations and anions with silico-titanates and layered titanates, Waste Manage. 13 (1993) 503–512.
[9] A.K. Cheetham, G. Férey, T. Loiseau, Open-framework inorganic materials, Angew. Chem. Int. Ed. 38 (1999) 3268–3292.
[10] E.N. Coker, Inorganic Ion Exchangers, 2000, 1584-1595.
[11] A. Clearfield, Inorganic ion-exchangers, past, present and future, Solvent Extr. Ion Exc. 18 (2000) 655–678.
[12] X. Sun, Y. Li, Synthesis and characterization of ion-exchangeable titanate nanotubes, Chem. Eur. J. 9 (2003) 2229–2238.
[13] K. Vaaramaa, J. Lehto, Removal of metals and anions from drinking water by ion exchange, Desalination 155 (2003) 157–170.
[14] H.P. Stephens, R.G. Dosch, F.V. Stohl, Hydrous metal oxide ion exchangers for preparation of catalysts for direct coal liquefaction, Ind. Eng. Chem. Prod. Res. Dev. 24 (1985) 15–19.
[15] W. Schmidt, Synthetic inorganic ion exchange materials, in: Inamuddin, Luqman Mohammad (Eds.), Ion Exchange Technology I: Theory and Materials, Springer, Dordrecht, 2012, pp. 277–298.
[16] R. Koivula, Inorganic Ion Exchangers for Decontamination of Radioactive Wastes Generated by the Nuclear Power Plants, University of Helsinki, 2003.
[17] D.A. Clifford, Ion exchange and inorganic adsorption, in: F.W. Pontius (Ed.), Water Quality and Treatment: A Handbook of Community Water Supplies, American Water Works Association, McGraw-Hill, New York, 1999, pp. 561–564.
[18] P. De Luca, T.G. Poulsen, A. Salituro, A. Tedeschi, D. Vuono, Z. Kónya, D. Madarász, J.B. Nagy, Evaluation and comparison of the ammonia adsorption capacity of titanosilicates ETS-4 and ETS-10 and aluminotitanosilicates ETAS-4 and ETAS-10, J. Therm. Anal. Calorim. 122 (2015) 1257–1267.
[19] H.S.A. Hosseinzadeh, A. Rajendran, J.A. Sawada, S.M. Kuznicki, Dynamic column breakthrough and process studies of high-purity oxygen production using silver-exchanged titanosilicates, Ind. Eng. Chem. Res. 55 (2016) 5993–6005.
[20] A. Clearfield, Inorganic ion exchangers: a technology ripe for development, Ind. Eng. Chem. Res. 34 (1995) 2865–2872.
[21] J.E. Miller, N.E. Brown, Development and properties of crystalline silicotitanate (CST) ion exchangers for radioactive waste applications, Sandia National Laboratories SAND97-0771 l UC-721, UC-510, 1997.
[22] F. Fu, Q. Wang, Removal of heavy metal ions from wastewaters: a review, J. Environ. Manage. 92 (2011) 407–418.
[23] D. Rana, T. Matsuura, M.A. Kassim, A.F. Ismail, Radioactive decontamination of water by membrane processes — A review, Desalination 321 (2013) 77–92.
[24] R.D. Ambashta, M.E.T. Sillanpää, Membrane purification in radioactive waste management: a short review, J. Environ. Radioactiv. 105 (2012) 76–84.
[25] R.O.A. Rahman, H.A. Ibrahium, Y. Hung, Liquid radioactive wastes treatment: a review, Water 3 (2011) 551.
[26] N. Bolong, A.F. Ismail, M.R. Salim, T. Matsuura, A review of the effects of emerging contaminants in wastewater and options for their removal, Desalination 239 (2009) 229–246.
[27] A. Dąbrowski, Adsorption — from theory to practice, Adv. Colloid Interface Sci. 93 (2001) 135–224.
[28] A.K. Pabby, Membrane techniques for treatment in nuclear waste processing: global experience, Membr. Tech. 2008 (2008) 9–13.
[29] L.I. Rudenko, O.V. Dzhuzha, V.E. Khan, Semipermeable dynamic membranes for ultrafiltration treatment of ground waters to remove radionuclides, Radiochemistry 49 (2007) 201–203.
[30] L.I. Rudenko, V.E. Khan, Membrane Methods for Treating Liquid Radioactive Wastes from the Shelter To Remove Transuranic Elements, Radiochemistry 47 (2005) 89–92.
[31] L. Buckley, S. Bushart, V. Efremenkov, Y. Karlin, R. Kohout, A. Pabby, G. Tapsell, Application of membrane technology for liquid radioactive waste processing, IAEA 431 (2004) 1–145.
[32] G. Zakrzewska-Trznadel, M. Harasimowicz, Application of ceramic membranes for hazardous wastes processing: pilot plant experiments with radioactive solutions, Desalination 162 (2004) 191–199.
[33] G. Zakrzewska-Trznadel, M. Harasimowicz, A.G. Chmielewski, Membrane processes in nuclear technology-application for liquid radioactive waste treatment, Sep. Purif. Technol. 22–23 (2001) 617–625.
[34] M. Abou-Mesalam, Retention behavior of nickel, copper, cadmium and zinc ions from aqueous solutions on silico-titanate and silico-antimonate used as inorganic ion exchange materials, J. Radioanal. Nucl. 252 (2002) 579–583.
[35] A. Nalaparaju, Z.Q. Hu, X.S. Zhao, J.W. Jiang, Exchange of heavy metal ions in titanosilicate Na-ETS-10 membrane from molecular dynamics simulations, J. Membr. Sci. 335 (2009) 89–95.
[36] S.P. Cardoso, P.F. Lito, J. Rocha, Z. Lin, C.M. Silva, Synthesis and permeation properties of small-pore Titanosilicate AM-3 membranes, Procedia Eng. 44 (2012) 926–927.
[37] M. Taramasso, G. Perego, B. Notari, Preparation of porous crystalline synthetic material comprised of silicon and titanium oxides, US Pat. US4410501, 1983.
[38] G. Bellussi, A. Carati, M.G. Clerici, A. Esposito, R. Millini, F. Buonomo, Belg. Pat. 100 (1989) 1038.
[39] K. Popa, C.C. Pavel, Radioactive wastewaters purification using titanosilicates materials: State of the art and perspectives, Desalination 293 (2012) 78–86.
[40] M.W. Anderson, J. Rocha, Synthesis of Titanosilicates and related materials, Handbook of Porous Solids, Wiley-VCH, 2002, pp. 876–903.
[41] J. Rocha, M.W. Anderson, Microporous titanosilicates and other novel mixed octahedral – tetrahedral framework oxides, Eur. J. Inorg. Chem. 801–818 (2000).
[42] J. Jänchen, D. Ackermann, H. Stach, Adsorption properties of aluminophosphate molecular sieves–potential applications for low temperature heat utilization, ISHPC (2002) 24–27.
[43] N.A. Milne, C.S. Griffith, J.V. Hanna, M. Skyllas-Kazacos, V. Luca, Lithium Intercalation into the Titanosilicate Sitinakite, Chem. Mater. 18 (2006) 3192–3202.
[44] A. Anson, C.C.H. Lin, S.M. Kuznicki, J.A. Sawada, Adsorption of carbon dioxide, ethane, and methane on titanosilicate type molecular sieves, Chem. Eng. Sci. 64 (2009) 3683–3687.
[45] C.C.H. Lin, S.M. Kuznicki, Evolving applications of zeolite molecular sieves, Canad. J. Chem. Eng. 90 (2012) 207–216.
[46] S.M. Kuznicki, Large-pored crystalline titanium molecular sieve zeolites, US Pat. US5011591 A, 1991.
[47] S.M. Kuznicki, Preparation of small-pored crystalline titanium molecular sieve zeolites, US Pat. US 07/449,032, 1990.

[48] S.M. Kuznicki, Large-pored crystalline titanium molecular sieve zeolites, US Pat. US 07/094,237, 1989.
[49] H. Liu, A. Yonezawa, K. Kumagai, M. Sano, T. Miyake, Cs and Sr removal over highly effective adsorbents ETS-1 and ETS-2, J. Mater. Chem. A 3 (2015) 1562–1568.
[50] H. Liu, M. Sano, T. Suzuki, Y. Kakutani, Y. Adachi, T. Miyake, Engelhard titanosilicate-1 and Engelhard titanosilicate-2 as promising adsorbents in multivalence heavy metal removal, J. Environ. Chem. Eng. 3 (2015) 1081–1087.
[51] S.P. Cardoso, C.B. Lopes, E. Pereira, A.C. Duarte, C.M. Silva, Competitive removal of Cd^{2+} and Hg^{2+} ions from water using titanosilicate ETS-4: kinetic behaviour and selectivity, Water Air Soil Poll. 224 (2013) 1–6.
[52] R.P. Nikolova, B.L. Shivachev, S. Ferdov, Crystal structures of Mg^{2+}, Ba^{2+} and Cs^{+} exchanged K-Na–ETS-4, Micropor. Mesopor. Mat. 165 (2013) 121–126.
[53] L. Liu, W. Tan, P. Xiao, Y. Zhai, A novel synthesis process of ETS-4 titanosilicate using commercial anatase in the absence of fluoride ions, Int. J. Miner. Metall. Mat. 19 (2012) 675–678.
[54] Y.D. Noh, S. Komarneni, K.J.D. Mackenzie, Titanosilicates: Giant exchange capacity and selectivity for Sr and Ba, Sep. Purif. Technol. 95 (2012) 222–226.
[55] M. Sacerdoti, G. Cruciani, Comparison of structural changes upon heating of Zorite and Na-ETS-4 by in situ synchrotron powder diffraction, in: S.V. Krivovichev (Ed.), Minerals as Advanced Materials II, Springer, Berlin, 2012, pp. 187–197.
[56] C.B. Lopes, M. Otero, Z. Lin, C.M. Silva, E. Pereira, J. Rocha, A.C. Duarte, Effect of pH and temperature on Hg^{2+} water decontamination using ETS-4 titanosilicate, J. Hazard. Mater. 175 (2010) 439–444.
[57] L.D. Barreira, P.F. Lito, B.M. Antunes, M. Otero, Z. Lin, J. Rocha, E. Pereira, A.C. Duarte, C.M. Silva, Effect of pH on cadmium (II) removal from aqueous solution using titanosilicate ETS-4, Chem. Eng. J. 155 (2009) 728–735.
[58] S. Cavenati, C.A. Grande, F.V.S. Lopes, A.E. Rodrigues, Adsorption of small molecules on alkali-earth modified titanosilicates, Micropor. Mesopor. Mat. 121 (2009) 114–120.
[59] T.R. Ferreira, C.B. Lopes, P.F. Lito, M. Otero, Z. Lin, J. Rocha, E. Pereira, C.M. Silva, A. Duarte, Cadmium (II) removal from aqueous solution using microporous titanosilicate ETS-4, Chem. Eng. J. 147 (2009) 173–179.
[60] C.B. Lopes, M. Otero, Z. Lin, C.M. Silva, J. Rocha, E. Pereira, A.C. Duarte, Removal of Hg^{2+} ions from aqueous solution by ETS-4 microporous titanosilicate—Kinetic and equilibrium studies, Chem. Eng. J. 151 (2009) 247–254.
[61] M. Otero, C.B. Lopes, J. Coimbra, T.R. Ferreira, C.M. Silva, Z. Lin, J. Rocha, E. Pereira, A.C. Duarte, A.C. Duarte, Priority pollutants (Hg^{2+} and Cd^{2+}) removal from water by ETS-4 titanosilicate, Desalination 249 (2009) 742–747.
[62] C.B. Lopes, P.F. Lito, M. Otero, Z. Lin, J. Rocha, C.M. Silva, E. Pereira, A.C. Duarte, Mercury removal with titanosilicate ETS-4: Batch experiments and modelling, Micropor. Mesopor. Mat. 115 (2008) 98–105.
[63] D. Coutinho, J.A. Losilla, J. Balkus, J. Kenneth, Microwave synthesis of ETS-4 and ETS-4 thin films, Micropor. Mesopor. Mat. 90 (2006) 229–236.
[64] K. Popa, C.C. Pavel, N. Bilba, A. Cecal, Purification of waste waters containing $^{60}Co^{2+}$, $^{115m}Cd^{2+}$ and $^{203}Hg^{2+}$ radioactive ions by ETS-4 titanosilicate, J. Radioanal. Nucl. 269 (2006) 155–160.
[65] B. Yilmaz, P.Q. Miraglia, J. Warzywoda, A. Sacco Jr., Synthesis of titanosilicate ETS-4 with controlled morphology and investigation of its crystallization kinetics, Micropor. Mesopor. Mat. 71 (2004) 167–175.
[66] S. Nair, H.K. Jeong, A. Chandrasekaran, C.M. Braunbarth, M. Tsapatsis, S.M. Kuznicki, Synthesis and Structure Determination of ETS-4 Single Crystals, Chem. Mater. 13 (2001) 4247–4254.
[67] H. Xu, Y. Zhang, A. Navrotsky, Enthalpies of formation of microporous titanosilicates ETS-4 and ETS-10, Micropor. Mesopor. Mat. 47 (2001) 285–291.
[68] J.K. Thomas, Synthesis of microporous titanosilicates ETS-10 and ETS-4 using solid TiO_2 as the source of titanium, Chem. Commun. 1435–1436 (1996).
[69] G. Cruciani, P. De Luca, A. Nastro, P. Pattison, Rietveld refinement of the zorite structure of ETS-4 molecular sieves, Micropor. Mesopor. Mat. 21 (1998) 143–153.
[70] S.M. Kuznicki, V.A. Bell, S. Nair, H.W. Hillhouse, R.M. Jacubinas, C.M. Braunbarth, B.H. Toby, M. Tsapatsis, A titanosilicate molecular sieve with adjustable pores for size-selective adsorption of molecules, Nature 412 (2001) 720–724.
[71] S.M. Kuznicki, V.A. Bell, I. Petrovic, B.T. Desai, Small-Pored Crystalline Titanium Molecular Sieve Zeolites and their Use in Gas Separation Processes, US Patent 6068682, 2000.
[72] R.P. Marathe, K. Mantri, M.P. Srinivasan, S. Farooq, Effect of ion exchange and dehydration temperature on the adsorption and diffusion of gases in ETS-4, Ind. Eng. Chem. Res. 43 (2004) 5281–5290.
[73] B. Majumdar, S.J. Bhadra, R.P. Marathe, S. Farooq, Adsorption and diffusion of methane and nitrogen in barium exchanged ETS-4, Ind. Eng. Chem. Res. 50 (2011) 3021–3034.
[74] C.C.H. Lin, J.A. Sawada, L. Wu, T. Haastrup, S.M. Kuznicki, Anion-controlled pore size of titanium silicate molecular sieves, J. Am. Chem. Soc. 131 (2008) 609–614.
[75] M.W. Anderson, O. Terasaki, T. Ohsuna, A. Philippou, S.P. MacKay, A. Ferreira, J. Rocha, S. Lidin, Structure of the microporous titanosilicate ETS-10, Nature 367 (1994) 347–351.
[76] M.W. Anderson, O. Terasaki, T. Ohsuna, P.J.O. Malley, A. Philippou, S.P. MacKay, A. Ferreira, J. Rocha, S. Lidin, Microporous titanosilicate ETS-10: a structural survey, Philos. Mag. B 71 (1995) 813–841.
[77] A. Mayoral, J. Coronas, C. Casado, C. Tellez, I. Díaz, Atomic resolution analysis of microporous Titanosilicate ETS-10 through aberration Corrected STEM imaging, ChemCatChem 5 (2013) 2595–2598.
[78] A. Mayoral, R.M. Hall, R. Jackowska, J.E. Readman, Imaging the atomic position of light cations in a porous network and the europium (III) ion exchange capability by aberration-corrected electron microscopy, Angew. Chem. Int. Ed. 128 (2016) 16361–16365.
[79] C.C. Pavel, K. Popa, N. Bilba, A. Cecal, D. Cozma, A. Pui, The sorption of some radiocations on microporous titanosilicate ETS-10, J. Radioanal. Nucl. 258 (2003) 243–248.
[80] M. Koç, S. Galioglu, D. Toffoli, H. Ustunel, B. Akata, Understanding the effects of ion-exchange in Titanosilicate ETS-10: a joint theoretical and experimental study, J. Phys. Chem. C 118 (2014) 27281–27291.
[81] S.M. Kuznicki, J.S. Curran, X. Yang, ETS-14 crystalline titanium silicate molecular sieves, manufacture and use thereof, US Patent US 08/790,944, (1999) 1.
[82] S. Merlino, M. Pasero, G. Artioli, A.P. Khomyakov, Penkvilksite, a new kind of silicate structure: OD character, X-ray single-crystal (IM), and powder Rietveld (2O) refinements of two MDO polytypes, Am. Mineral. 79 (1994) 1185–1193.
[83] I.V. Bussen, Y.P. Menshikov, A.N. Merkova, A.P. Nedoresova, Y.I. Uspenskaya, A.P. Khomyakov, Penkvilksite, a new titanium–sodium hydrosilicate, Dokl. Acad. Sci. USSR 217 (1975) 126–129.
[84] D.M. Poojary, R.A. Cahill, A. Clearfield, Synthesis, crystal structures, and ion-exchange properties of a novel porous Titanosilicate, Chem. Mater. 6 (1994) 2364–2368.
[85] E.A. Behrens, D.M. Poojary, A. Clearfield, Syntheses, crystal structures, and ion-exchange properties of porous Titanosilicates, $HM_3Ti_4O_4(SiO_4)_3{\cdot}4H_2O$ ($M = H^+, K^+, Cs^+$), structural analogues of the mineral pharmacosiderite, Chem. Mater. 8 (1996) 1236–1244.
[86] E.A. Behrens, A. Clearfield, Titanium silicates, $M_3HTi_4O_4(SiO_4)_3 \cdot 4H_2O$ ($M = Na^+, K^+$) with three-dimensional tunnel structures for the selective removal of strontium and cesium from wastewater solutions, Micropor. Mater. 11 (1997) 65–75.
[87] A. Clearfield, Structure and ion exchange properties of tunnel type titanium silicates, Solid State Sci. 3 (2001) 103–112.
[88] V. Kostov-Kytin, B. Mihailova, Y. Kalvachev, M. Tarassov, Atomic arrangements in amorphous sodium titanosilicate precursor powders, Micropor. Mesopor. Mat. 86 (2005) 223–230.
[89] A. Clearfield, A. Tripathi, D. Medvedev, A.J. Celestian, J.B. Parise, In situ type study of hydrothermally prepared titanates and silicotitanates, J. Mater. Sci. 41 (2006) 1325–1333.
[90] T. Möller, R. Harjula, J. Lehto, Ion exchange of ^{85}Sr, ^{134}Cs and ^{57}Co in sodium titanosilicate and the effect of crystallinity on selectivity, Sep. Purif. Technol. 28 (2002) 13–23.
[91] B.R. Cherry, M. Nyman, T.M. Alam, Investigation of cation environment and framework changes in silicotitanate exchange materials using solid-state ^{23}Na, ^{29}Si, and ^{133}Cs MAS NMR, J. Solid State Chem. 177 (2004) 2079–2093.
[92] D.M. Poojary, A.I. Bortun, L.N. Bortun, A. Clearfield, Structural studies on the ion-exchanged phases of a porous Titanosilicate, $Na_2Ti_2O_3SiO_4{\cdot}2H_2O$, Inorg. Chem. 35 (1996) 6131–6139.
[93] M.S. Dadachov, W.T.A. Harrison, Synthesis and crystal structure of $Na_4[(TiO)_4(SiO_4)_3]{\cdot}6H_2O$, a rhombohedrally distorted sodium titanium silicate pharmacosiderite analogue, J. Solid State Chem. 134 (1997) 409–415.
[94] D.M. Chapman, A.L. Roe, Synthesis, characterization and crystal chemistry of microporous titanium-silicate materials, Zeolites 10 (1990) 730–737.
[95] E.A. Behrens, P. Sylvester, A. Clearfield, Assessment of a sodium nonatitanate and pharmacosiderite-type ion exchangers for strontium and cesium removal from DOE waste simulants, Environ. Sci. Technol. 32 (1998) 101–107.
[96] W.T.A. Harrison, T.E. Gier, G.D. Stucky, Single-crystal structure of Cs $HTi_4O_4(SiO_4)_3{\cdot}4H_2O$, a titanosilicate pharmacosiderite analog, Zeolites 15 (1995) 408–412.
[97] Z. Lin, J. Rocha, P. Brandao, A. Ferreira, A.P. Esculcas, J. Pedrosa de, D. Júlio, J. Rocha, M.W. Anderson, Synthesis and structural characterization of microporous umbite, penkvilksite, and other titanosilicates, J. Phys. Chem. B. 101 (1997) 7114–7120.
[98] M.A. Roberts, G. Sankar, J.M. Thomas, R.H. Jones, H. Du, J. Chen, W. Pang, R. Xu, Synthesis and structure of a layered titanosilicate catalyst with five-coordinate titanium, Nature 381 (1996) 401–404.
[99] G. Sankar, J.M. Thomas, C.R.A. Catlow, C.M. Barker, D. Gleeson, N. Kaltsoyannis, The three-dimensional structure of the titanium-centered active site during steady-state catalytic epoxidation of alkenes, J. Phys. Chem. B 105 (2001) 9028–9030.
[100] V. Valtchev, J.L. Paillaud, S. Mintova, H. Kessler, Investigation of the ion-exchanged forms of the microporous titanosilicate $K_2TiSi_3O_9{\cdot}H_2O$, Micropor. Mesopor. Mat. 32 (1999) 287–296.
[101] V. Kostov-Kytin, S. Ferdov, Investigations in the System Na_2O-K_2O-TiO_2-$SiO_2{\times}H_2O$, C. R. Acad. Bulg. Sci. 54 (2001) 51.
[102] V. Kostov-Kytin, S. Ferdov, Y. Kalvachev, B. Mihailova, O. Petrov, Hydrothermal synthesis of microporous titanosilicates, Micropor. Mesopor. Mat. 105 (2007) 232–238.
[103] X.D. Zou, M.S. Dadachov, $K_2TiSi_3O_9{\cdot}H_2O$, Acta Crystallogr. C: Cryst. Struct. Commun. 56 (2000) 738–739.
[104] A.I. Bortun, L.N. Bortun, D.M. Poojary, O. Xiang, A. Clearfield, Synthesis, characterization, and ion exchange behavior of a framework potassium

titanium Trisilicate $K_2TiSi_3O_9{\cdot}H_2O$ and its protonated phases, Chem. Mater. 12 (2000) 294–305.
[105] B.L. Sherriff, B. Zhou, ^{29}Si and ^{23}Na MAS NMR spectroscopic study of the polytypes of the titanosilicate penkvilksite, Can. Mineral. 42 (2004) 1027–1035.
[106] M. Cadoni, G. Ferraris, Penkvilksite-2*O*: $Na_2TiSi_4O_{11}{\cdot}2H_2O$, *Acta Crystallogr*, Sect. C: Cryst. Struct. Commun. 64 (2008) 87–90.
[107] S. Ferdov, U. Kolitsch, C. Lengauer, E. Tillmanns, Z. Lin, R.A. Sá Ferreira, Refinement of the layered titanosilicate AM-1 from single-crystal X-ray diffraction data, Acta Crystallogr. 63 (2007), pp. i186–i186.
[108] M.S. Dadachov, J. Rocha, A. Ferreira, Z. Lin, M.W. Anderson, Ab initio structure determination of layered sodium titanium silicate containing edge-sharing titanate chains (AM-4) $Na_3(Na, H)Ti_2O_2[Si_2O_6]2.2H_2O$, Chem. Comm. (1997) 2371–2372.
[109] Y. Koudsi, A. Dyer, Sorption of ^{60}Co on a synthetic titanosilicate analogue of the mineral penkvilksite-2O and antimonysilicate, J. Radioanal. Nucl. 247 (2001) 209–219.
[110] S. Merlino, M. Pasero, A.P. Khomyakov, The crystal structure of lintisite, $Na_3LiTi_2[Si_2O_6]_2O_2{\cdot}2H_2O$, a new titanosilicate from Lovozero (USSR), Z. Kristallogr. Cryst. Mater. 193 (1990) 137–148.
[111] V. Valtchev, S. Mintova, Synthesis of titanium silicate ETS-10: the effect of tetrametylammonium on the crystallization kinetics, Zeolites 14 (1994) 697–700.
[112] C.C. Pavel, M. Walter, K. Popa, Improvement of retention capacity of ETS-10 for uranyl ions by porosity modification and their immobilization into a titanosilicate matrix, J. Mater. Chem. 18 (2008) 3342–3346.
[113] J.A. Losilla, K.J. Balkus Jr., Microwave assisted synthesis of ETS-10, J. Porous Mater. 16 (2009) 487–496.
[114] H.J. Sung, J. Taihuan, K.H. Young, C. Jong-San, Microwave effect in the fast synthesis of microporous materials: which stage between nucleation and crystal growth is accelerated by microwave irradiation?, Chem Eur. J. 13 (2007) 4410–4417.
[115] T.K. Das, A.J. Chandwadkar, S. Sivasanker, A rapid method of synthesizing the titanium silicate ETS-10, Chem. Commun. 1105–1106 (1996).
[116] Z. Ji, J. Warzywoda, A. Sacco, Synthesis and morphological control of large titanosilicate ETS-10 crystals, Micropor. Mesopor. Mat. 109 (2008) 1–11.
[117] Z. Ji, B. Yilmaz, J. Warzywoda, A. Sacco, Hydrothermal synthesis of titanosilicate ETS-10 using $Ti(SO_4)_2$, Micropor. Mesopor. Mat. 81 (2005) 1–10.
[118] D.G. Medvedev, A. Tripathi, A. Clearfield, A.J. Celestian, J.B. Parise, J. Hanson, Crystallization of sodium titanium silicate with sitinakite topology: evolution from the sodium nonatitanate phase, Chem. Mater. 16 (2004) 3659–3666.
[119] A. Clearfield, L.N. Bortun, A.I. Bortun, Alkali metal ion exchange by the framework titanium silicate $M_2Ti_2O_3SiO_4{\cdot}nH_2O$ (M = H, Na), React. Funct. Polym. 43 (2000) 85–95.
[120] V.G. Kalenchuk, S.V. Meleshevych, V.A. Kanibolotsky, V.V. Strelko, O.V. Oleksiienko, N.M. Patryliak, A method for producing titanosilicate ionexchanger, UA patent 48457, 2010.
[121] O.V. Oleksiienko, S.I. Meleshevych, V.V. Strelko, O.I. V'yunov, O.K. Matkovsky, V.G. Milgrandt, M.M. Tsyba, V.A. Kanibolotsky, Effect of hydrothermal treatment on the formation of the titanosilicates porous structure, Probl. Chem. Chem. Technol. 2 (2013) 101–105.
[122] R. Freeman, Measuring the flow properties of consolidated, conditioned and aerated powders — A comparative study using a powder rheometer and a rotational shear cell, Powder Technol. 174 (2007) 25–33.
[123] J. Bridgwater, Fundamental powder mixing mechanisms, Powder Technol. 15 (1976) 215–236.
[124] C.J. Brinker, G.W. Scherer, Sol-Gel Science: The Physics and Chemistry of Sol-Gel Processing, Academic Press, United States, 1990.
[125] Y. Liu, H. Du, Y. Xu, H. Ding, W. Pang, Y. Yue, Synthesis and characterization of a novel microporous titanosilicate with a structure of penkvilksite-1M, Micropor. Mesopor. Mat. 28 (1999) 511–517.
[126] N. Döbelin, T. Armbruster, Microporous titanosilicate AM-2: Ion-exchange and thermal stability, Micropor. Mesopor. Mat. 99 (2007) 279–287.
[127] V. Sebastián, I. Díaz, C. Tellez, J. Coronas, J. Santamaría, Spheres of microporous titanosilicate umbite with hierarchical pore systems, Adv. Funct. Mater. 18 (2008) 1314–1320.
[128] C. Casado, D. Ambroj, Á. Mayoral, E. Vispe, C. Téllez, J. Coronas, Synthesis, swelling, and exfoliation of microporous lamellar titanosilicate AM-4, Eur. J. Inorg. Chem. 2011 (2011) 2247–2253.
[129] O. Oleksiienko, S. Meleshevych, V. Strelko, C. Wolkersdorfer, M.M. Tsyba, Y.M. Kylivnyk, I. Levchuk, M. Sitarz, M. Sillanpaa, Pore structure and sorption characterization of titanosilicates obtained from concentrated precursors by the sol-gel method, RSC Adv. 5 (2015) 72562–72571.
[130] P.Q. Miraglia, B. Yilmaz, J. Warzywoda, S. Bazzana, A. Sacco, Morphological and surface analysis of titanosilicate ETS-4 synthesized hydrothermally with organic precursors, Microporous Mesoporous Mater. 69 (2004) 71–76.
[131] S. Ferdov, C. Lengauer, O. Petrov, V. Kostov-Kytin, A rapid method for low-temperature synthesis of the Na analogue of the microporous titanosilicate GTS-1, J. Mater. Sci. 39 (2004) 4343–4344.
[132] V.V. Strelko, S.V. Meleshevych, V.A. Kanibolotsky, O.V. Oleksiienko, A method for producing titanosilicate ionexchanger, UA Patent 66489 (2012).
[133] G. Lujaniene, S. Meleshevych, V. Kanibolotskyy, J. Sapolaite, V. Strelko, V. Remeikis, O. Oleksiienko, K. Ribokaite, T. Sciglo, Application of inorganic sorbents for removal of Cs, Sr, Pu and Am from contaminated solutions, J. Radioanal. Nucl. Chem. 282 (2009) 787–791.
[134] T. Möller, Selective crystaline inorganic materials as ion exchangers in the treatment of nuclear waste solutions, Rep. Ser. Radiochem. (2002) 1–66.
[135] C.C. Pavel, M. Walter, P. Pöml, D. Bouëxière, K. Popa, Contrasting immobilization behavior of Cs^+ and Sr^{2+} cations in a titanosilicate matrix, J. Mater. Chem. 21 (2011) 3831–3837.
[136] L. Al-Attar, A. Dyer, A. Paajanen, R. Harjula, Purification of nuclear wastes by novel inorganic ion exchangers, J. Mater. Chem. 13 (2003) 2969–2974.
[137] A. Dyer, J. Newton, L. O'Brien, S. Owens, Studies on a synthetic sitinakite-type silicotitanate cation exchanger. Part 2. Effect of alkaline earth and alkali metals on the uptake of Cs and Sr radioisotopes, Microporous Mesoporous Mater. 120 (2009) 272–277.
[138] L. Al-Attar, A. Dyer, Sorption of uranium onto titanosilicate materials, J. Radioanal. Nucl. 247 (2001) 121–128.
[139] L. Al-Attar, A. Dyer, R. Harjula, Uptake of radionuclides on microporous and layered ion exchange materials, J. Mater. Chem. 13 (2003) 2963–2968.
[140] A.I. Bortun, L.N. Bortun, A. Clearfield, Evaluation of synthetic inorganic ion exchangers for Cesium and Strontium removal from contaminated groundwater and wastewater, Solvent Extr. Ion. Exch. 5 (1997) 909–929.
[141] P. Sylvester, E.A. Behrens, G.M. Granziano, A. Clearfield, An assessment of inorganic ion-exchange materials for the removal of strontium from simulated hanford tank wastes, Sep. Sci. Technol. 34 (1999) 1981–1992.
[142] E.A. Behrens, P. Sylvester, G. Graziano, A. Clearfield, Evaluation of a sodium nonatitanate, sodium titanosilicate, and pharmacosiderite-type ion exchangers for strontium removal from DOE waste and hanford N-springs groundwater simulants, in: W.W. Schulz, N.J. Lombardo (Eds.), Science and Technology for Disposal of Radioactive Tank Wastes, Springer, New York, 1998, pp. 287–299.
[143] L. Al-Attar, A. Dyer, R. Blackburn, Uptake of uranium on ETS-10 microporous titanosilicate, J. Radioanal. Nucl. 246 (2000) 451–455.
[144] B. El-Gammal, Adsorption profiles of some heavy metal ions from aqueous waste solutions using sodium-doped zirconium titanoslicate, Desalin. Water Treat. 52 (2014) 5952–5964.
[145] C. Borcia, K. Popa, C.C. Pavel, A. Dascălu, C. Vitelaru, B.A. Apetrăchioaei, Sorption of thallous ion from acidic aqueous solutions onto ETS-10 titanosilicate, J. Radioanal. Nucl. 288 (2011) 25–30.
[146] J.H. Choi, S.D. Kim, Y.J. Kwon, W.J. Kim, Adsorption behaviors of ETS-10 and its variant, ETAS-10 on the removal of heavy metals, Cu^{2+}, Co^{2+}, Mn^{2+} and Zn^{2+} from a waste water, Microporous Mesoporous Mater. 96 (2006) 157–167.
[147] L. Lv, G. Tsoi, X.S. Zhao, Uptake equilibria and mechanisms of heavy metal ions on microporous titanosilicate ETS-10, Ind. Eng. Chem. Res. 43 (2004) 7900–7906.
[148] A. Dyer, M. Pillinger, S. Amin, Ion exchange of caesium and strontium on a titanosilicate analogue of the mineral pharmacosiderite, J. Mater. Chem. 9 (1999) 2481–2487.
[149] R. Grădinaru, S.O. Vălu, Ş. Postolache, C.C. Pavel, I. Sandu, K. Popa, On the influence of ETS-10 porosity and surface properties in retention of some nanoions and nanomolecules, Environ. Eng. Manage. J. 8 (2009) 901–905.
[150] C.C. Pavel, L.V. Pavel, I. Cretescu, K. Popa, Some aspects concerning the interaction between uranium and ETS-10 titanosilicate, Rev. Chim. (Bucharest) 60 (2009) 19–22.
[151] E.D. Camarinha, P.F. Lito, B.M. Antunes, M. Otero, Z. Lin, J. Rocha, E. Pereira, A. C. Duarte, C.M. Silva, Cadmium(II) removal from aqueous solution using microporous titanosilicate ETS-10, Chem. Eng. J. 155 (2009) 108–114.
[152] G.X.S. Zhao, J.L. Lee, P.A. Chia, Unusual adsorption properties of microporous titanosilicate ETS-10 toward heavy metal lead, Langmuir 19 (2003) 1977–1979.
[153] G. De Raffele, A. Aloise, P. De Luca, D. Vuono, A. Tagarelli, J.B. Nagy, Kinetic and thermodynamic effects during the adsorption of heavy metals on ETS-4 and ETS-10 microporous materials, J. Porous Mater. 23 (2016) 389–400.
[154] C.B. Lopes, J. Coimbra, M. Otero, E. Pereira, A.C. Duarte, Z. Lin, J. Rocha, Uptake of Hg^{2+} from aqueous solutions by microporous titano-and zircono-silicates, Quim. Nova 31 (2008) 321–325.
[155] C.C. Pavel, K. Popa, Investigations on the ion exchange process of Cs^+ and Sr^{2+} cations by ETS materials, Chem. Eng. J. 245 (2014) 288–294.
[156] N. Döbelin, T. Armbruster, Microporous titanosilicate AM-2: Rb-exchange and thermal behaviour, Mater. Res. Bull. 42 (2007) 113–125.
[157] C.S. Fewox, A. Clearfield, A.J. Celestian, In situ X-ray diffraction study of cesium exchange in synthetic umbite, Inorg. Chem. 50 (2011) 3596–3604.
[158] Y. Liu, H. Du, F. Zhou, W. Pang, Synthesis of a new titanosilicate: an analogue of the mineral penkvilksite, Chem. Commun. 1467–1468 (1997).
[159] Y.D. Noh, S. Komarneni, Mercury (II) exchange by highly charged swelling micas, Sodium Engelhard titanosilicate-4, and Sodium titanosilicate, Environ. Sci. Technol. 45 (2011) 6954–6960.
[160] C.B. Lopes, E. Pereira, Z. Lin, P. Pato, M. Otero, C.M. Silva, J. Rocha, A.C. Duarte, Fixed-bed removal of Hg^{2+} from contaminated water by microporous titanosilicate ETS-4: Experimental and theoretical breakthrough curves, Micropor. Mesopor. Mat. 145 (2011) 32–40.
[161] C.C. Pavel, D. Vuono, L. Catanzaro, P. De Luca, N. Bilba, A. Nastro, J.B. Nagy, Synthesis and characterization of the microporous titanosilicates ETS-4 and ETS-10, Micropor. Mesopor. Mat. 56 (2002) 227–239.
[162] B.R. Figueiredo, I. Portugal, J. Rocha, C.M. Silva, Fixed-bed removal of Cs^+ from aqueous solutions by microporous silicate ETS-4: measurement and modeling of loading-regeneration cycles, Chem. Eng. J. 301 (2016) 276–284.

[163] A.J. Celestian, C.J. Chappell, M.J. Rucks, P. Norris, Structure determination and time-resolved raman spectroscopy of yttrium ion exchange into microporous Titanosilicate ETS-4, Inorg. Chem. 55 (2016) 11057–11063.
[164] C.C. Pavel, H. Park, A. Dreier, B. Tesche, S. Schmidt, Structural defects induced in ETS-10 by Postsynthesis treatment with H_2O_2 solution, Chem. Mater. 18 (2006) 3813–3820.
[165] R. Tykva, K.S. Din, C. Pavel, A. Cecal, K. Popa, Contribution to the external surface of a titanium-rich sand (Abou-Khashaba, Egypt) in the uranium uptake processes, J. Radioanal. Nucl. 279 (2009) 811–816.
[166] L. Lv, M.P. Hor, F. Su, X.S. Zhao, Competitive adsorption of Pb^{2+}, Cu^{2+}, and Cd^{2+} ions on microporous titanosilicate ETS-10, J. Colloid Interface Sci. 287 (2005) 178–184.
[167] L. Lv, Y. Zhang, K. Wang, A.K. Ray, X.S. Zhao, Modeling of the adsorption breakthrough behaviors of Pb^{2+} in a fixed bed of ETS-10 adsorbent, J. Colloid Interface Sci. 325 (2008) 57–63.
[168] P.F. Lito, J.P.S. Aniceto, C.M. Silva, Maxwell-stefan based modelling of ion exchange systems containing common species (Cd2+, Na+) and distinct sorbents (ETS-4, ETS-10), Int. J. Environ. Sci. Technol. 12 (2015) 183–192.
[169] I.M. Ali, E.S. Zakaria, H.F. Aly, Highly effective removal of ^{22}Na, ^{134}Cs and ^{60}Co from aqueous solutions by titanosilicate: a radiotracer study, J. Radioanal. Nucl. Ch. 285 (2010) 483–489.
[170] R.G. Anthony, R.G. Dosch, D. Gu, C.V. Philip, Use of silicotitanates for removing cesium and strontium from defense waste, Ind. Eng. Chem. Res. 33 (1994) 2702–2705.
[171] Z. Zheng, C.V. Philip, R.G. Anthony, J.L. Krumhansl, D.E. Trudell, J.E. Miller, Ion exchange of group I metals by hydrous crystalline silicotitanates, Ind. Eng. Chem. Res. 35 (1996) 4246–4256.
[172] Z. Zheng, D. Gu, R.G. Anthony, E. Klavetter, Estimation of cesium ion exchange distribution coefficients for concentrated electrolytic solutions when using crystalline silicotitanates, Ind. Eng. Chem. Res. 34 (1995) 2142–2147.
[173] Z. Zheng, R.G. Anthony, J.E. Miller, Modeling multicomponent ion exchange equilibrium utilizing hydrous crystalline silicotitanates by a multiple interactive ion exchange site model, Ind. Eng. Chem. Res. 36 (1997) 2427–2434.
[174] V. Luca, J.V. Hanna, M.E. Smith, M. James, D.R.G. Mitchell, J.R. Bartlett, Nb-substitution and Cs ion-exchange in the titanosilicate sitinakite, Micropor. Mesopor. Mat. 55 (2002) 1–13.
[175] I.M. Latheef, M.E. Huckman, R.G. Anthony, Modeling cesium ion exchange on fixed-bed columns of crystalline silicotitanate granules, Ind. Eng. Chem. Res. 39 (2000) 1356–1363.
[176] A.J. Celestian, A. Clearfield, The origin of ion exchange selectivity in a porous framework titanium silicate, J. Mater. Chem. 17 (2007) 4839–4842.
[177] K.A. Venkatesan, V. Sukumaran, M.P. Antony, T.G. Srinivasan, Studies on the feasibility of using crystalline silicotitanates for the separation of cesium-137 from fast reactor high-level liquid waste, J. Radioanal. Nucl. 280 (2009) 129–136.
[178] A.J. Celestian, J.D. Kubicki, J. Hanson, A. Clearfield, J.B. Parise, The mechanism responsible for extraordinary Cs ion selectivity in crystalline silicotitanate, J. Am. Chem. Soc. 130 (2008) 11689–11694.
[179] T.M. Nenoff, J.E. Miller, S.G. Thoma, D.E. Trudell, Highly selective inorganic crystalline ion exchange material for Sr^{2+} in acidic solutions, Environ. Sci. Technol. 30 (1996) 3630–3633.
[180] O. Oleksiienko, I. Levchuk, M. Sitarz, S. Meleshevych, V. Strelko, M. Sillanpää, Removal of strontium (Sr^{2+}) from aqueous solutions with titanosilicates obtained by the sol–gel method, J. Colloid Interface Sci. 438 (2015) 159–168.
[181] O. Oleksiienko, I. Levchuk, M. Sitarz, S. Meleshevych, V. Strelko, M. Sillanpää, Adsorption of Caesium (Cs^+) from aqueous solution by porous titanosilicate xerogel, Desalin. Water Treat. 1–13 (2015).
[182] N.R. Mann, T.A. Todd, Removal of cesium from acidic radioactive tank waste by using Ionsiv IE-911, Sep. Sci. Technol. 39 (2005) 2351–2371.
[183] I.M. El-Naggar, E.A. Mowafy, E.A. Abdel-Galil, Diffusion mechanism of certain fission products in the particles of silico(IV)titanate, Colloid. Surface A 307 (2007) 77–82.
[184] L. Oji, K. Martin, D. Hobbs, Development of prototype titanate ion-exchange loaded-membranes for strontium, cesium and actinide decontamination from aqueous media, J. Radioanal. Nucl. 279 (2009) 847–854.
[185] L.M. Wang, J. Chen, R.C. Ewing, Radiation and thermal effects on porous and layer structured materials as getters of radionuclides, Curr. Opin. Solid State Mater. Sci. 8 (2004) 405–418.
[186] A. Clearfield, D.G. Medvedev, S. Kerlegon, T. Bosser, J.D. Burns, J. Milton, Rates of exchange of Cs^+ and Sr^{2+} for poorly crystalline sodium titanium silicate (CST) in nuclear waste systems, Solvent Extr. Ion Exc. 30 (2012) 229–243.
[187] T.A. Todd, T.A. Batcheller, J.D. Law, R.S. Herbst, Cesium and Strontium Separation Technologies, DOE USA INEEL/EXT-04-01895, 2004.
[188] A.J. Celestian, J.B. Parise, A. Clearfield, Crystal growth and ion exchange in titanium silicates, Springer Handbook of Crystal Growth, Springer, Berlin, 2010, pp. 1637–1662.
[189] K.M.L. Taylor-Pashow, T.C. Shehee, D.T. Hobbs, Advances in inorganic and hybrid ion exchangers, Solvent Extr. Ion Exc. 31 (2013) 122–170.
[190] H.W. Kwon, J.F. Kim, D.W. Ha, Y.H. Kim, Decontamination of cesium from contaminated water using a selective adsorbent and magnetic separation, IEEE Trans. Appl. Supercond. 26 (2016) 1–4.
[191] N. Lihareva, V. Kostov-Kytin, Sorption of Cs by nano-sized microporous titanium silicates with pharmacosiderite structure, Bulg. Chem. Commun. 46 (2014) 569–575.
[192] C.B. Lopes, M. Otero, J. Coimbra, E. Pereira, J. Rocha, Z. Lin, A. Duarte, Removal of low concentration Hg^{2+} from natural waters by microporous and layered titanosilicates, Micropor. Mesopor. Mat. 103 (2007) 325–332.
[193] R.L. Frost, Y. Xi, Vibrational spectroscopic study of the mineral penkvilksite $Na_2TiSi_4O_{11}{\cdot}2H_2O$ –a mineral used for the uptake of radionuclides, Radiat. Eff. Defects Solids. 168 (2013) 72–79.
[194] J.G. Decaillon, Y. Andres, B.M. Mokili, J.C. Abbe, M. Tournoux, J. Patarin, Study of the ion exchange selectivity of layared titanosilicate Na_3(Na, H) $Ti_2O_2[Si_2O_6]_2x2H_2O$, AM-4, for strontium, Solvent Extr. Ion Exc. 20 (2002) 273–291.
[195] J. Pérez-Carvajal, P. Lalueza, C. Casado, C. Téllez, J. Coronas, Layered titanosilicates JDF-L1 and AM-4 for biocide applications, Appl. Clay. Sci. 56 (2012) 30–35.
[196] A.M. Puziy, Cesium and strontium exchange by the framework potassium titanium silicate $K_3HTi_4O_4(SiO_4)_3{\cdot}4H_2O$, J. Radioanal. Nucl. 237 (1998) 73–80.
[197] A. Tripathi, D.G. Medvedev, A. Clearfield, The crystal structures of strontium exchanged sodium titanosilicates in relation to selectivity for nuclear waste treatment, J. Solid State Chem. 178 (2005) 253–261.
[198] A. Tripathi, D.G. Medvedev, M. Nyman, A. Clearfield, Selectivity for Cs and Sr in Nb-substituted titanosilicate with sitinakite topology, J. Solid State Chem. 175 (2003) 72–83.
[199] A. Dyer, J. Newton, L. O'Brien, S. Owens, Studies on a synthetic sitinakite-type silicotitanate cation exchanger: Part 1: measurement of cation exchange diffusion coefficients, Micropor. Mesopor. Mat. 117 (2009) 304–308.
[200] A.J. Celestian, M. Powers, S. Rader, In situ Raman spectroscopic study of transient polyhedral distortions during cesium ion exchange into sitinakite, Am. Mineral. 98 (2013) 1153–1161.
[201] R.G. Anthony, R.G. Dosch, C.V. Philip, Method of using novel silico-titanates, US Pat. US 08/507,419, 2000.
[202] R.G. Anthony, R.G. Dosch, C.V. Philip, Silico-titanates and their methods of making and using, US Pat. US 09/503,230 (2002).
[203] N. Talaie, H.R. Aghabozorg, S.A. Milani, Synthesis and characterization of Nb–Ge doped titanosilicate nanoparticles and study of their selectivity for absorption of ^{137}Cs and ^{90}Sr, J. Radioanal. Nucl. 292 (2012) 473–479.
[204] E.A. Behrens, D.M. Poojary, A. Clearfield, Syntheses, X-ray Powder Structures, and Preliminary Ion-Exchange Properties of Germanium-Substituted Titanosilicate Pharmacosiderites: $HM_3(AO)_4(BO_4)_3{\cdot}4H_2O$ (M = K, Rb, Cs; A = Ti, Ge; B = Si, Ge), Chem. Mater. 10 (1998) 959–967.
[205] C.C. Pavel, J.B. Nagy, N. Bilba, A. Nastro, C. Perri, D. Vuono, P. De Luca, I.V. Asaftei, P. De Luca, Influence of the TAABr salts on the crystallization of ETS-10, Micropor. Mesopor. Mat. 71 (2004) 77–85.
[206] B.M. Rapko, S.I. Sinkov, T.G. Levitskaia, Removal of 137Cs from Dissolved Hanford Tank Saltcake by Treatment with IONSIV® IE-911, Sep. Sci. Technol. 40 (2005) 91–107.
[207] T.J. Tranter, R.D. Tillotson, T.A. Todd, Evaluation of Ionsiv™ IE-911 as a Cesium Removal Option for Ineel Acidic Tank Waste, Sep. Sci. Technol. 40 (2005) 157–170.