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# Metal sulfide ion exchangers: superior sorbents for the capture of toxic and nuclear waste-related metal ions

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Metal sulfide ion-exchangers (MSIEs) represent a new addition to the field of ion exchange materials. This is a growing class of materials that display exceptional selectivity and rapid sorption kinetics for soft or relatively soft metal ions as a result of their soft basic frameworks. Without requiring functionalization, they outperform the most efficient sulfur-functionalized materials. This is the first review focusing on this class of materials; it covers the most important MSIEs, focusing on their synthesis, structural features and ion-exchange chemistry. Furthermore, recent developments in the engineered and composite forms of MSIEs are described. Future research opportunities are also discussed in the hope of inspiring additional scientists to engage in this new area of research on sulfidic ion-exchange materials.

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## 1. Introduction

The treatment of various types of aqueous wastes, such as industrial and nuclear waste effluents, is of major concern for countries all over the world. Radionuclides (<sup>137</sup>Cs, <sup>89</sup>Sr, <sup>235</sup>U, <sup>59</sup>Fe, <sup>57</sup>Co, <sup>65</sup>Zn, etc.) and toxic heavy metal ions (Hg<sup>2+</sup>, Pb<sup>2+</sup>, Cd<sup>2+</sup>, and Tl<sup>+</sup>) are major pollutants in these types of waste and

pose a serious threat to humans and other species.<sup>1</sup> Commonly used and inexpensive methods such as precipitation of the ions from solutions are often not sufficiently effective to lower the concentration of these ions below the acceptable legal limits. For example, precipitation of Hg<sup>2+</sup> ions with Na<sub>2</sub>S cannot reduce the concentration of mercuric ions below 10 to 50 ppb.<sup>2</sup> Such levels are 20 to 100-times higher than the legally accepted limits defined by the European Union (1 ppb) and USA-EPA (2 ppb).<sup>3</sup> The issue of the treatment of nuclear effluents is even more complex because of the harsh conditions of nuclear waste deriving from nuclear waste manufacture, such as

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inhomogeneous samples, extreme pH and very high salt concentrations.<sup>4</sup> Efficient removal of radioactive elements and minimization of long-term storage space is crucial to enable safer and low cost implementation of nuclear energy.<sup>4</sup>

Ion exchange is well recognized as a relatively inexpensive and highly effective method for the elimination of various types of ions from aqueous waste solutions.<sup>5</sup> Clays<sup>6</sup> and zeolites<sup>7</sup> are common and abundant cation exchangers; however, they suffer from low selectivity and capacity for toxic heavy metal ions in the presence of high salt concentrations or under acidic conditions. In addition, these materials are unstable in extreme alkaline or acidic conditions (due to immediate dissolution of aluminum/silicon ions) of nuclear wastes.<sup>8</sup> Other oxidic sorbents, such as titanates, silicates and manganese oxides, can survive under the conditions of nuclear waste; however, they show decreased selectivity for radioactive ions in the presence of high salt concentrations (e.g. Cs<sup>+</sup> absorption by manganese oxides),<sup>9</sup> or they are selective for radioactive ions only within a narrow pH range (e.g. Sr<sup>2+</sup> absorption by sodium titanate).<sup>10</sup>

Organic resins, with functional groups suitable for absorption of specific ions, are extensively used for water purification.<sup>5</sup> These purely organic materials, however, are of limited chemical, radiolytic and thermal stability.<sup>8</sup> In addition, resins display an amorphous porous structure; therefore, they cannot exhibit the molecular sieve separation properties of ordered porous inorganic materials such as zeolites.<sup>5</sup>

Functionalized silica-based materials show remarkable selectivity and binding affinity for a variety of heavy ions. For example, thiol-functionalized mesoporous materials are famous for their exceptional capability to rapidly absorb Hg<sup>2+</sup> from water solutions.<sup>11</sup> Silica-based materials, however, cannot be used for remediation of extreme alkaline or acidic waste water (e.g. nuclear waste) due to their instability under such conditions.<sup>8</sup>

Metal organic frameworks (MOFs) incorporating functional groups with high affinity for toxic or radioactive ions appear to be promising sorbents for various remediation processes.<sup>12</sup> The development of these sorbents is still in its infancy.

From the above, it is clear that “perfect” sorbents that can withstand the harsh conditions of various types of wastes, are highly selective for toxic or radioactive ions, and are affordable are still elusive. The search for new sorbent materials is therefore important.

Recently, metal sulfide ion exchangers (**MSIEs**) with labile extra-framework cations have emerged as a new class of promising sorbents.<sup>13</sup> These materials exhibit a variety of structures, ranging from layered and three-dimensional crystalline frameworks<sup>13</sup> to porous amorphous materials<sup>14</sup> and aerogels.<sup>15</sup> They are proving to be particularly effective for the decontamination of water solutions from various heavy metal ions (e.g. Hg<sup>2+</sup>, Pb<sup>2+</sup>, Cd<sup>2+</sup>, Ni<sup>2+</sup>, and Co<sup>2+</sup>) as well as ions relevant to nuclear waste (e.g. UO<sub>2</sub><sup>2+</sup>, Cs<sup>+</sup>, and Sr<sup>2+</sup>).<sup>13</sup> The unique properties of **MSIEs** arise from their soft S<sup>2-</sup> ligands, which endow these materials with innate selectivity for soft or relatively soft metal ions. **MSIEs** with a soft basic framework thus do not require the introduction of any functional groups. They exhibit exceptional absorption properties for soft metal ions, superior to those of

the best sulfur-functionalized materials.<sup>11</sup> Furthermore, hard ions such as H<sup>+</sup>, Na<sup>+</sup>, and Ca<sup>2+</sup> only weakly interact with the soft S<sup>2-</sup> ligands of **MSIEs**, thus affecting their ion exchange properties to a much lesser degree than those of traditional oxidic materials.<sup>6,7,9,10</sup> Therefore, **MSIEs** may be effective for metal ion absorption over a broad pH range and in the presence of high salt concentration. In this review, we describe the most important **MSIEs** in terms of their synthesis, structural characteristics and metal ion absorption properties. Furthermore, we discuss the recent development of composite and engineered forms of **MSIEs**, which promise to open up paths for the practical applications of these materials. To our knowledge, this is the first review of these systems. Finally, we provide some directions and perspectives for future research on this new family of ion-exchangers.

## 2. Layered crystalline MSIEs

Metal sulfides with layered anionic structures and labile interlayer cations constitute the most well studied class of **MSIEs**. These materials show excellent and selective ion exchange properties due to (a) the facile diffusion of the inserted ions and their easy access to the internal surface of metal sulfide layers and (b) the formation of strong bonds between the incorporated metal ions and S<sup>2-</sup> ligands. In the following, we present the main layered **MSIEs**, highlighting their synthesis, structural features and ion exchange chemistry.

### 2.1. Alkali-ion intercalated metal disulfides

A common route to the preparation of layered **MSIEs** involves partial reduction of the metal ions of a metal disulfide, such as SnS<sub>2</sub> or MoS<sub>2</sub>, by treating it with an alkali ion (A<sup>+</sup>)-containing reducing agent (e.g. *n*-butyl lithium, alkali ion dithionite).<sup>16</sup> An anionic layer is thus formed, and its negative charge is compensated by alkali cations provided by the reducing agent. The cations inserted in the interlayer space of the materials can be rapidly and topotactically exchanged by a variety of inorganic and organic cationic species.<sup>16</sup> The synthesis of such layered materials is represented by the following equation:

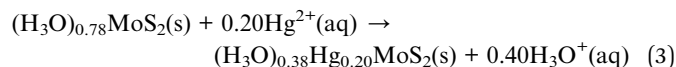
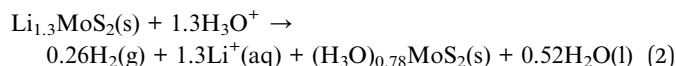


Actually, the earliest known **MSIEs**, which were reported on 1979 by R. Schöllhorn *et al.*, were alkali-ion intercalated metal disulfides, specifically the hydrated layered Sn sulfide phases A<sub>x</sub>(H<sub>2</sub>O)<sub>y</sub>[SnS<sub>2</sub>]<sup>x-</sup> (A<sup>+</sup> = K<sup>+</sup>, Rb<sup>+</sup>, Cs<sup>+</sup>).<sup>17</sup> These materials show facile ion-exchange properties for a series of inorganic cations, such as Li<sup>+</sup>, Na<sup>+</sup>, Mg<sup>2+</sup>, Ca<sup>2+</sup>, and Ni<sup>2+</sup>. The insertion of the various ions in the interlayer space of the materials was probed by powder X-ray diffraction (PXRD) studies. It was observed that the higher the hydration energy of the inserted cation, the larger the interlayer spacings, indicating the incorporation of the ions as hydrated complexes in the space between the layers. These materials, however, are susceptible to oxidation, which results in SnS<sub>2</sub>.

About twenty years after Schöllhorn, the ion-exchange properties of Li<sub>x</sub>MoS<sub>2</sub> (0.25 ≤ x ≤ 1.9) were investigated by A. E.

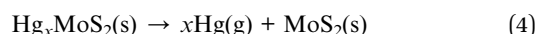


Gash *et al.*<sup>18</sup> This material is particularly effective in binding to  $\text{Hg}^{2+}$  in acidic conditions. The authors suggested a mechanism for the  $\text{Hg}^{2+}$  absorption, which is shown in Fig. 1 and represented by the following equations:



Thus, the first step of the ion-exchange reaction involved the transformation of the  $\text{Li}^+$ -intercalated material to a hydronium-containing material, which in turn reacts with  $\text{Hg}^{2+}$  to yield the final product. The driving force for the second reaction was the higher affinity of the soft basic  $\text{MoS}_2^{x-}$  layers for the soft acid  $\text{Hg}^{2+}$  compared to that for the hard hydronium ions. Inductively coupled plasma-atomic emission (ICP-AES) analytical data indicated that  $\sim 200$  ppm of  $\text{Hg}^{2+}$  (pH  $\sim 1$ ) can be reduced to 6.5 ppb after treatment of the  $\text{Hg}^{2+}$  solution with  $\text{Li}_x\text{MoS}_2$  (the molar ratio of  $\text{Li}_x\text{MoS}_2$  to  $\text{Hg}$  was 5). The Hg content of various exchanged products was found to be 0.24 to 0.32 mole per formula unit of the exchanged material, depending on the initial  $\text{Li}_x\text{MoS}_2/\text{Hg}$  molar ratio.

Interestingly, Hg can be recovered by heating the Hg-exchanged product at 425 °C, which leads to the vaporization of Hg and the formation of  $\text{MoS}_2$  (Fig. 1) according to the following equation:



The Hg vapor is then collected in a cold trap at 77 K. The  $\text{MoS}_2$  can be retransformed to  $\text{Li}_x\text{MoS}_2$  *via* reduction-Li intercalation with *n*-BuLi. As observed for the alkali-intercalated tin disulfide materials,  $\text{Li}_x\text{MoS}_2$  sorbents are also air and moisture-sensitive and thus, they should be stored under anaerobic conditions to retain their  $\text{Hg}^{2+}$  sorption capacity.

$\text{Li}_x\text{MoS}_2$  was also tested for  $\text{Zn}^{2+}$ ,  $\text{Pb}^{2+}$  and  $\text{Cd}^{2+}$  sorption.<sup>18</sup> The results revealed only moderate  $\text{Pb}^{2+}$  removal capacity (40–75% removal of the initial Pb content), relatively low  $\text{Cd}^{2+}$  (4–40% removal capacity) and negligible  $\text{Zn}^{2+}$  sorption (1–4% removal capacity). In contrast, the removal capacities for  $\text{Hg}^{2+}$

were 74–100%. The selectivity of the  $\text{Li}_x\text{MoS}_2$  follows the order  $\text{Hg}^{2+} > \text{Pb}^{2+} > \text{Cd}^{2+} > \text{Zn}^{2+}$ , which indicates the preference of the material for softer metal ions due to their stronger interactions with the soft  $\text{MoS}_2^{x-}$  layer.

## 2.2. KMS materials

These materials have the general formula  $\text{K}_{2x}\text{M}_x\text{Sn}_{3-x}\text{S}_6$  ( $\text{M} = \text{Mn}^{2+}$ , KMS-1;  $\text{M} = \text{Mg}^{2+}$ , KMS-2;  $x = 0.5$  to 1).<sup>13c-h</sup> They can be prepared on a multigram scale with high purity using solid state and hydrothermal synthetic methods. They are exceptionally stable in air and in highly acidic and basic aqueous solutions. Single crystal X-ray measurements, performed on hexagonal-shaped crystals of KMS-1 and 2 (Fig. 2A), revealed that their structure is based on edge sharing “Sn/M” $\text{S}_6$  octahedra ( $\text{CdI}_2$  structure type) with  $\text{Sn}^{4+}$  and  $\text{M}^{2+}$  occupying the same crystallographic position and three-coordinated  $\text{S}^{2-}$  ligands (Fig. 2B). The interlayer space is filled by  $\text{K}^+$  ions (Fig. 3), which compensate for the negative charge of the metal sulfide layers. There is much more room in the interlayer space than that required for all  $\text{K}^+$  cations. As a result, these ions are highly disordered and mobile and are thus easily exchanged by a variety of other cationic species (see below). KMS compounds are actually derivatives of  $\text{SnS}_2$  with partial substitution of  $\text{Sn}^{4+}$  by  $\text{M}^{2+}$  ( $\text{Mn}^{2+}$  or  $\text{Mg}^{2+}$ ) ions. KMS-1 and 2 feature essentially the same structural characteristics; their only differences are related to the stacking of the layers.

KMS-1 and 2 materials were investigated in detail for their ion-exchange properties with cations related to nuclear waste, such as  $\text{Cs}^+$ ,  $\text{Sr}^{2+}$ ,  $\text{Ni}^{2+}$  and  $\text{UO}_2^{2+}$ , and heavy metal ions (such as  $\text{Hg}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Cd}^{2+}$ ) which are common contaminants in industrial wastewater. In the following, we describe the most important ion-exchange results for KMS materials.

**2.2.1.  $\text{Cs}^+$  and  $\text{Rb}^+$  ion exchange properties.** The  $\text{Cs}^+$  ion-exchange process is highly relevant to nuclear waste remediation, since the  $^{137}\text{Cs}^+$  radionuclide represents one of the major contaminants in the fission products of nuclear waste.<sup>4</sup> It is thus of particular importance to discover selective  $\text{Cs}^+$  sorbents and expand the gamut of materials that can be used to capture this ion. For this reason, the  $\text{Cs}^+$  ion-exchange properties of KMS-1 and 2 were investigated in detail. For comparison,  $\text{Rb}^+$  absorption was also studied.

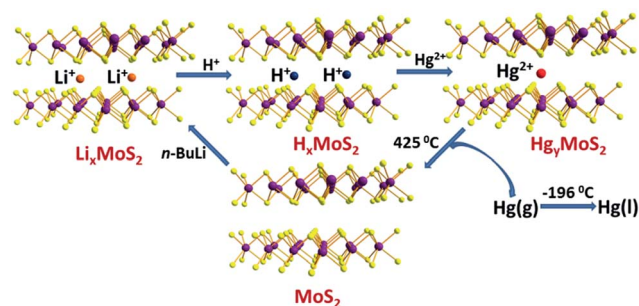


Fig. 1 Suggested mechanism of  $\text{Hg}^{2+}$  absorption/desorption for the  $\text{Li}_x\text{MoS}_2$  material. Mo, purple; S, yellow.

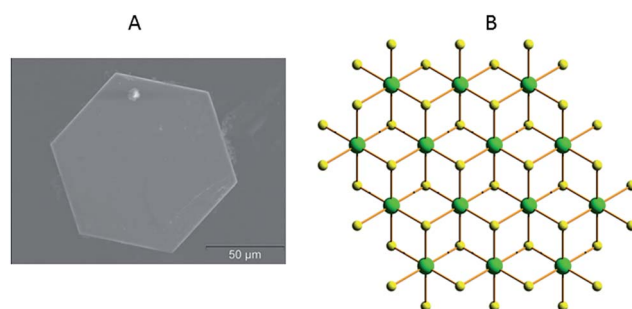


Fig. 2 (A) Scanning electron microscopy (SEM) image of a typical crystal of KMS-1. (B) Representation of part of the layered structure of KMS-1 (S, yellow; Sn/Mn, green).





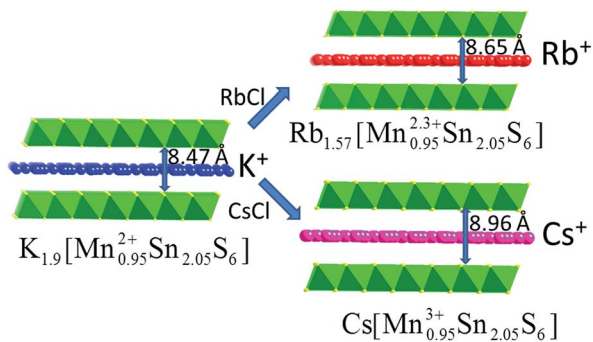


Fig. 3 Representations of the crystal structures of KMS-1 and its  $Rb^+$  and  $Cs^+$ -exchanged analogues and the interlayer spacing.

$K^+$  ions can be completely and topotactically replaced by  $Cs^+$  or  $Rb^+$  by treating KMS-1 with an aqueous solution of the corresponding alkali-ion chloride salt. Interestingly,  $Cs^+$  and  $Rb^+$  sorption can be achieved not only with polycrystalline samples of KMS-1, but also in a single crystal-to-single crystal (SCSC) fashion using large specimens.<sup>13d</sup> When single crystals of  $K_{2x}Mn_xSn_{3-x}S_6$  ( $x = 0.95$ , KMS-1) are immersed in a solution of  $CsCl$  or  $RbCl$ , single crystals of  $Cs^+$  or  $Rb^+$ -exchanged material can be isolated and, thus, their structures can be accurately determined by X-ray crystallography (Fig. 3). X-ray refinement indicated the formulas  $Rb_{1.57}Mn_{0.95}Sn_{2.05}S_6$  and  $CsMn_{0.95}Sn_{2.05}S_6$  for the  $Rb^+$  and  $Cs^+$ -exchanged materials, respectively. Based on these formulas and the charge balance requirements, Mn should be in the 2.3+ and 3+ oxidation states in the  $Rb^+$  and  $Cs^+$ -containing compounds, respectively. The Mn oxidation states in these exchanged materials were also confirmed using X-ray photoelectron spectroscopic (XPS) data. The stability of the  $Mn^{3+}$  oxidation state in the  $Cs^+$ -exchanged analogue was explained on the basis of the increased ionic character of the  $Cs^+ \cdots S^{2-}$  interactions. Thus, in the presence of  $Cs^+$ , the  $[Mn_xSn_{3-x}S_6]^{2x-}$  layer becomes more electron-rich and, as a consequence, becomes more prone to lose an electron.<sup>13d</sup>

Detailed batch  $Cs^+$  ion exchange studies were performed for KMS-1, and the data can be described well with the Langmuir model:

$$q = q_m \frac{bC_e}{1 + bC_e} \quad (5)$$

where  $q$  ( $mg\ g^{-1}$ ) is the amount of the cation absorbed at the equilibrium concentration  $C_e$  (ppm),  $q_m$  is the maximum sorption (exchange) capacity of the sorbent, and  $b$  ( $L\ mg^{-1}$ ) is the Langmuir constant related to the free energy of the sorption.<sup>13d</sup>

The fitting of the data indicated a maximum sorption capacity of  $\sim 1.7\ mmol\ g^{-1}$  ( $226 \pm 2\ mg\ g^{-1}$ ), close to the maximum theoretical capacity ( $1.6\ mmol\ g^{-1}$ ) calculated for the exchange of two  $K^+$  ions by one  $Cs^+$  (Fig. 4A). The material can be regenerated by treating the  $Cs^+$ -loaded compound with a large excess of  $KCl$  aqueous solution. The regenerated compound showed almost identical  $Cs^+$  exchange capacity to that of the pristine KMS-1 material.

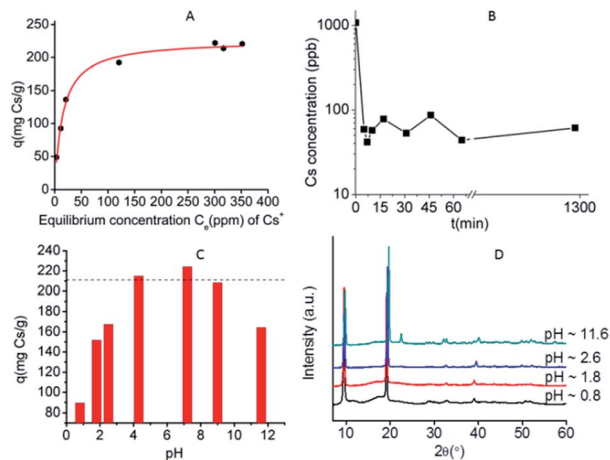


Fig. 4 (A)  $Cs^+$  isotherm sorption data for KMS-1 (at pH  $\sim 7$ ). The solid line represents the fitting of the data with the Langmuir model. (B) Kinetic data for the sorption of  $Cs^+$  (initial concentration  $\sim 1$  ppm) by KMS-1. (C) Maximum  $Cs^+$  sorption capacity of KMS-1 found for different pH values. The dashed line represents the maximum theoretical exchange capacity for KMS-1. (D) PXRD patterns for  $Cs^+$ -exchanged products isolated from highly acidic and alkaline solutions.

Kinetic studies with trace  $Cs^+$  concentrations ( $\sim 1$  ppm) revealed a very fast sorption process at room temperature. Specifically, within less than 5 min of contact with the KMS-1/solution, the  $Cs^+$  ion exchange reached its equilibrium with  $\sim 90\%$  removal of the initial  $Cs^+$  content (Fig. 4B). The material was also capable of efficient  $Cs^+$  ion-exchange in highly acidic (pH  $\sim 1$ ) and alkaline conditions (pH  $\sim 12$ ), as shown in Fig. 4C. PXRD studies indicate that the  $Cs^+$ -exchanged products isolated from either acidic or alkaline solutions were crystalline and retained the layered structure of the parent KMS-1 compound (Fig. 4D).

Finally, ion-exchange studies have been performed with solutions simulating alkaline groundwater contaminated by radioactive elements. These solutions with pH  $\sim 11$  contained low  $Cs^+$  levels ( $\sim 1$  ppm) and relatively high concentrations (7 to 125 ppm) of  $Na^+$ ,  $Mg^{2+}$  and  $Ca^{2+}$ . Despite the presence of various competitive ions, KMS-1 showed high removal capacities (74–99%) for  $Cs^+$  from these complex solutions.

KMS-2 also exhibits  $Cs^+$  ion-exchange properties.<sup>13h</sup> The maximum sorption capacity of KMS-2 is  $531 \pm 28\ mg\ g^{-1}$ . This is  $2.35 \pm 0.12$  times the capacity of KMS-1 and one of the highest capacities ever reported for  $Cs^+$  ion-exchangers.<sup>10</sup> KMS-2 is expected to exhibit twice the  $Cs^+$  exchange capacity of KMS-1 because in the latter, the sorption capacity is reduced by the oxidation of  $Mn^{2+}$  to  $Mn^{3+}$  (see above). This oxidation cannot occur in KMS-2 containing  $Mg^{2+}$ ; thus, two equivalents of  $Cs^+$  can be absorbed by one mole of KMS-2. Furthermore, KMS-2 shows high  $Cs^+$  sorption capacity not only under neutral pH conditions, but also in acidic (pH = 3) and alkaline (pH = 10) environments.

**2.2.2.  $Sr^{2+}$  ion exchange properties.**  $Sr^{2+}$  ion-exchange and capture is also an important process, since radioactive  $^{90}Sr^{2+}$  represents one of the major heat producers and biohazards in



nuclear waste.<sup>4</sup> Thus, detailed Sr<sup>2+</sup> ion-exchange property studies were performed with KMS-1 and 2.<sup>13c,h</sup> The isotherm sorption data for these materials can be fitted with the Langmuir model and revealed maximum Sr<sup>2+</sup> sorption capacities of 77 ± 2 and 87 ± 2 mg g<sup>-1</sup> for KMS-1 and 2, respectively. Both KMS-1 and KMS-2 perform very efficiently in a very broad pH range. The affinity of the sorbents for Sr<sup>2+</sup> was expressed in terms of the distribution coefficient  $K_d$ , which is calculated by the equation:

$$K_d = \frac{V[(C_0 - C_e)/C_e]}{m} \quad (6)$$

where  $C_0$  and  $C_e$  are the initial and equilibrium concentrations of Sr<sup>2+</sup> (ppm), respectively,  $V$  is the volume (mL) of the testing solution and  $m$  is the amount of the ion exchanger (g) used in the experiment.<sup>13</sup> Values of  $K_d$  equal to or above 10<sup>4</sup> mL g<sup>-1</sup> are considered excellent. KMS-1 showed very high  $K_d$  values in the range of 10<sup>4</sup> to 10<sup>5</sup> mL g<sup>-1</sup> from pH 3 to 14.

KMS-1 performs very efficiently for Sr<sup>2+</sup> sorption. Its removal capacity is ~92% ( $K_d \sim 1.2 \times 10^4$  mL g<sup>-1</sup>) at very high salt concentrations (~5 M Na<sup>+</sup>) and pH ~ 14, which are the conditions typically found in alkaline nuclear waste. KMS-1 outperforms oxidic sorbents for Sr<sup>2+</sup> ion exchange under acidic conditions. The KMS-1 material contains soft basic S<sup>2-</sup> ligands with very small affinity for protons. This is not the case for the conventional oxidic exchangers, where the hard H<sup>+</sup> ions show great affinity for O<sup>2-</sup> ligands, which interferes with the process.<sup>19-21</sup>

The comparison of KMS-1 with various Sr<sup>2+</sup> sorbents, in terms of their  $K_d$  values vs. the pH of the solution, is provided in Fig. 5.

KMS-2 is also efficient in removing Sr<sup>2+</sup> under both alkaline and acidic conditions. Thus,  $K_d$  values of 6.3 × 10<sup>4</sup> and 1.5 × 10<sup>5</sup> mL g<sup>-1</sup> were observed for the Sr<sup>2+</sup> exchange of KMS-2 at pH ~ 3 and 10, respectively.

**2.2.3. Ni<sup>2+</sup> ion-exchange properties.** During the nuclear fission process, radioactive byproducts are generated due to the corrosion of the containers by the heat and acidity produced. Among these byproducts, <sup>63</sup>Ni is regulated as a low energy beta contaminant.<sup>4</sup> Thus, the removal of Ni<sup>2+</sup> from aqueous solutions is relevant to the decontamination of nuclear waste from

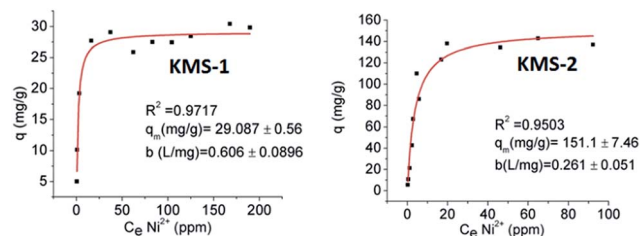


Fig. 6 Ni<sup>2+</sup> isotherm sorption data for KMS-1 and 2. The solid lines represent the fitting of the data with the Langmuir model.

the corrosion products of the fission process. For this reason, the Ni<sup>2+</sup> ion-exchange properties of KMS-1 and 2 were investigated (Fig. 6).<sup>13h</sup>

The isotherm Ni<sup>2+</sup> sorption data for KMS-1 and 2 follow the Langmuir model and indicate maximum sorption capacities of ~29 and 151 mg g<sup>-1</sup>, respectively. The relatively low Ni<sup>2+</sup> sorption capacity of KMS-1 is likely due to the oxidation of Mn<sup>2+</sup> to Mn<sup>3+</sup>. In the case of KMS-2, the observed Ni<sup>2+</sup> sorption capacity is ~1.4 larger than the theoretically expected value. This is attributed to the exchange not only of the interlayer K<sup>+</sup> ions but also the intralayer Mg<sup>2+</sup> ions. KMS materials are highly selective for Ni<sup>2+</sup> in the presence of a tremendous excess of Na<sup>+</sup> ions. Thus, a reasonably high  $K_d$  value of 1.8 × 10<sup>5</sup> mL g<sup>-1</sup> was obtained for Ni<sup>2+</sup> exchange of KMS-2 (initial Ni<sup>2+</sup> concentration of ~6 ppm) in the presence of 5 M Na<sup>+</sup>. The hard Na<sup>+</sup> ions exhibit very weak interactions with the soft metal sulfide layer, in contrast to the relatively soft Ni<sup>2+</sup>, which may interact strongly with the soft S<sup>2-</sup> ligands. As a result, high Na<sup>+</sup> concentrations have a negligible effect on the Ni<sup>2+</sup> exchange of KMS materials. This impressive binding to Ni<sup>2+</sup> ions also indicates that KMS materials may be effective agents in Ni recovery from industrial effluents arising from massive nickel plating operations worldwide.<sup>22</sup>

**2.2.4. Hg<sup>2+</sup>, Pb<sup>2+</sup> and Cd<sup>2+</sup> ion-exchange and capture.** Because Hg<sup>2+</sup>, Pb<sup>2+</sup> and Cd<sup>2+</sup> ions present a major health hazard for drinking and industrial wastewater,<sup>1</sup> it is important to develop highly selective sorbents for these ions with very high loading capacities.<sup>11</sup> The layered structure of KMS-1 sorbent and the presence of soft basic sites (S<sup>2-</sup> ligands) allow for very rapid kinetics for the exchange of interlayer K<sup>+</sup> ions by soft Lewis acids, such as Hg<sup>2+</sup>, Pb<sup>2+</sup> and Cd<sup>2+</sup> ions (Fig. 7).<sup>13e</sup>

PXRD studies indicated that significant contraction of the interlayer space occurs upon exchange of K<sup>+</sup> ions by Hg<sup>2+</sup> (Fig. 7), which is due to the smaller size of the Hg<sup>2+</sup> ion compared to K<sup>+</sup> and the formation of strong Hg<sup>2+</sup>-S<sup>2-</sup> covalent interactions.

The PXRD pattern for the Pb<sup>2+</sup> exchanged product showed the presence of two interlayer spacings because of the different hydrations of the Pb<sup>2+</sup> ions ([Pb(H<sub>2</sub>O)<sub>x</sub>]<sup>2+</sup>). The Cd<sup>2+</sup> ion-exchange process is particularly interesting. The analytical data for the Cd<sup>2+</sup>-exchanged product showed the absence not only of K<sup>+</sup> ions but also of Mn<sup>2+</sup>. Specifically, the average formula of the Cd<sup>2+</sup>-loaded compound was determined as Cd<sub>1.8</sub>Sn<sub>2.1</sub>S<sub>6</sub>, and the ion-exchange process is described by the following equation:

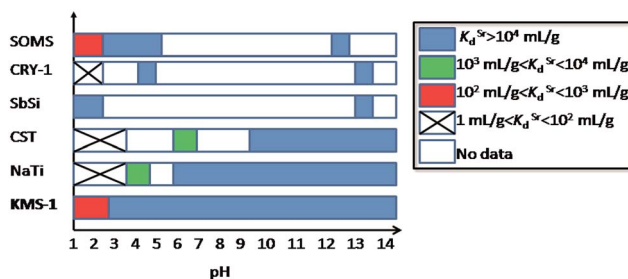


Fig. 5 Comparison diagram indicating the dependence of  $K_d$  on pH for the Sr<sup>2+</sup> ion-exchange of various materials. NaTi: sodium titanate,<sup>19</sup> CST: sodium silicotitanate,<sup>19b,d</sup> CRY-1: cryptomelane-type manganese oxide,<sup>20</sup> SOMS: Sandia octahedral molecular sieves<sup>21</sup> and SbSi: Sb silicate.<sup>19b</sup>



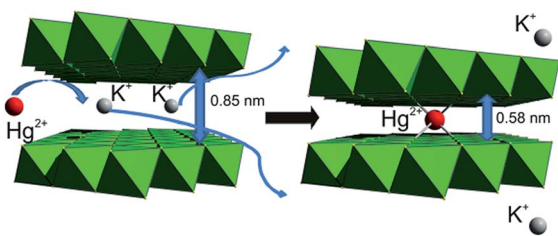
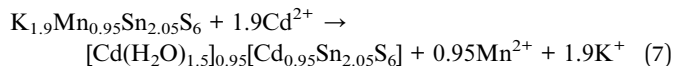


Fig. 7 Capture of  $\text{Hg}^{2+}$  by KMS-1 through exchange of its interlayer potassium cations.



The  $\text{Cd}^{2+}$ -exchanged KMS-1 has a layered structure, as indicated by the PXRD data, and the  $\text{Cd}^{2+}$  is inserted as a hydrated ion in the interlayer space and also replaces all intra-layer  $\text{Mn}^{2+}$  ions. Due to the complete exchange of  $\text{Mn}^{2+}$  by  $\text{Cd}^{2+}$ , a dramatic color change of the material from dark brown to orange-brown was observed upon  $\text{Cd}^{2+}$  exchange (Fig. 8).

Isotherm batch sorption data revealed maximum sorption capacities of 320 to 377  $\text{mg g}^{-1}$  for the  $\text{Hg}^{2+}$ ,  $\text{Pb}^{2+}$  and  $\text{Cd}^{2+}$  exchange processes. The capture of these ions by KMS-1 is not affected by the acidity or basicity of aqueous solutions. Thus, very high  $K_d$  values ( $>10^4 \text{ mL g}^{-1}$ ) for these ions in a broad pH range (2.5 to 10) can be achieved. In addition, the presence of a very large excess of  $\text{Na}^+$  and  $\text{Ca}^{2+}$  ions, which are commonly found in high concentrations in drinking water and industrial wastewater, has no effect on the exchange of  $\text{Hg}^{2+}$  and  $\text{Pb}^{2+}$  and only slightly interferes with the  $\text{Cd}^{2+}$  exchange process.

When  $\text{Hg}^{2+}$ ,  $\text{Pb}^{2+}$  and  $\text{Cd}^{2+}$  are present simultaneously in solution, KMS-1 can capture all three ions with no apparent selectivity. The concentrations of all three ions are reduced well below the safety limits within only 2 min of KMS-1/solution contact (Fig. 9). KMS-2 also exhibits exceptional  $\text{Hg}^{2+}$ ,  $\text{Pb}^{2+}$  and  $\text{Cd}^{2+}$  exchange properties.<sup>13e</sup> This result is in marked contrast to thiol-functionalized materials that show selectivity for  $\text{Hg}^{2+}$  and exhibit low to moderate sorption capacity for  $\text{Pb}^{2+}$  and  $\text{Cd}^{2+}$ .<sup>11</sup>

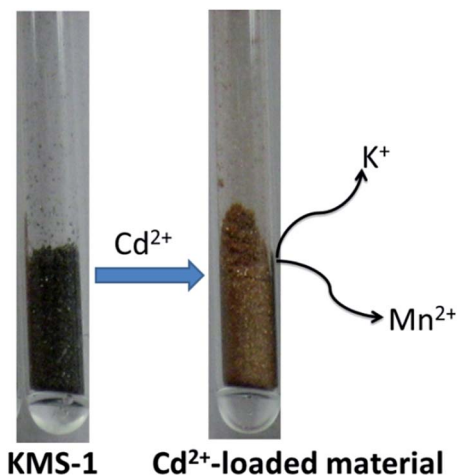


Fig. 8 Color change of KMS-1 upon the  $\text{Cd}^{2+}$  exchange process.

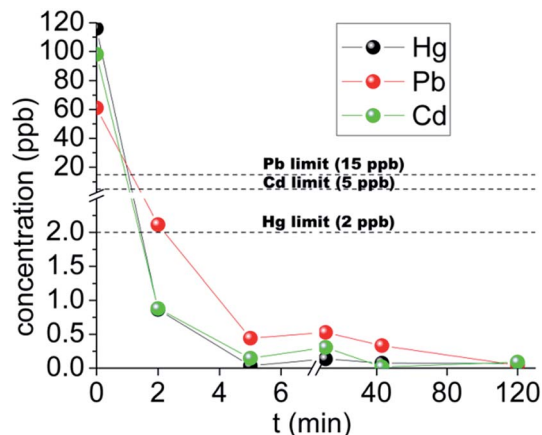


Fig. 9 The kinetics for the decontamination of potable water sample intentionally contaminated by mercury (116 ppb), lead (61 ppb) and cadmium (98 ppb) with KMS-1.

Regeneration of KMS-1/2 from the  $\text{Hg}^{2+}$ ,  $\text{Pb}^{2+}$  or  $\text{Cd}^{2+}$ -loaded materials was not feasible because of the very strong binding of these ions. Because of the extremely high metal ion sorption capacity (up to 50% by weight) and relatively low cost of KMS materials, it may not be necessary to regenerate them; thus, the ion-loaded materials could be considered as a permanent waste form, suitable for safe disposal. Initial investigations indicate negligible leaching of  $\text{Hg}^{2+}$ ,  $\text{Pb}^{2+}$  or  $\text{Cd}^{2+}$  from the corresponding exchange products after their hydrothermal treatment at 70 °C for 24 h.

Finally, a methylammonium analogue of KMS-1, with the formula  $[\text{CH}_3\text{NH}_3]_{2x}\text{Mn}_x\text{Sn}_{3-x}\text{S}_6 \cdot 0.5\text{H}_2\text{O}$  ( $x = 1.0$  to 1.1) (CMS),<sup>23</sup> was recently described, and its  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$  ion-exchange properties were studied. The results of these investigations revealed rapid sorption kinetics, high sorption capacity and exceptional selectivity of CMS for  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$  (see also the section below for a comparison between MS exchangers, and Table 1).

**2.2.5. Extraction of  $\text{Ag}^+$  and  $\text{Hg}^{2+}$  ions from their cyanide complexes.** Cyanide ions are widely used for the dissolution of precious metals, such as gold and silver, from their minerals. In addition to the precious metal ions, the minerals also contain several heavy metal ions that must be removed and separated from the precious metals.<sup>24</sup> One example is the mineral  $\text{Ag}_2\text{Hg}_2\text{S}_2$ . The cyanidation of this mineral results in the formation of  $[\text{Hg}(\text{CN})_4]^{2-}$  and  $[\text{Ag}(\text{CN})_2]^-$  complexes.<sup>25</sup> Remarkably, KMS materials can extract  $\text{Hg}^{2+}$  and  $\text{Ag}^+$  from their cyanide complexes. KMS-2 was studied for these ion-exchange processes.<sup>26</sup> A complete exchange of the  $\text{K}^+$  ions of KMS-2 by  $\text{Hg}^{2+}$  or  $\text{Ag}^+$  was observed after treatment of KMS-2 with aqueous solutions of  $[\text{Hg}(\text{CN})_4]^{2-}$  or  $[\text{Ag}(\text{CN})_2]^-$ . KMS-2 was also capable of simultaneously and quantitatively capturing  $\text{Hg}^{2+}$  and  $\text{Ag}^+$  from water solutions containing both  $[\text{Hg}(\text{CN})_4]^{2-}$  and  $[\text{Ag}(\text{CN})_2]^-$  complexes (removal capacities  $>97\%$ ).

The kinetics of the sorption of  $\text{Hg}^{2+}$  and  $\text{Ag}^+$  from mixed  $[\text{Hg}(\text{CN})_4]^{2-}$ - $[\text{Ag}(\text{CN})_2]^-$  solution (pH  $\sim 10$ ) show that within 3 h, the  $\text{Hg}^{2+}$  and  $\text{Ag}^+$  exchange reached equilibrium, with

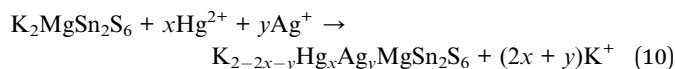
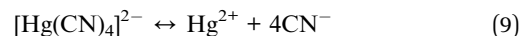
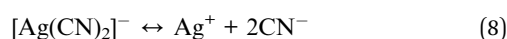


Table 1 Important ion-exchange characteristics of representative MSIEs

Material	$q_m^a$ (mg g <sup>-1</sup> )	$K_d$ (mL g <sup>-1</sup> ) individual (pH ~ 7)	$K_d$ (mL g <sup>-1</sup> ) competitive (Na <sup>+</sup> )	$K_d$ (mL g <sup>-1</sup> ) competitive (Ca <sup>2+</sup> )	Active pH range	Kinetic studies-equilibrium time (min) at RT	Reference
<b>Cs<sup>+</sup></b>							
KMS-1	226 ± 2	≥10 <sup>4</sup>	≥10 <sup>3 e</sup>	≥10 <sup>2 f</sup>	0.8–12	5	13d
KMS-2	531 ± 28	≥10 <sup>3</sup>	≥10 <sup>g</sup>	NA <sup>b</sup>	3–10	NA	13h
KTS-1	205 ± 6	≥10 <sup>5</sup>	NA	NA	NA	NA	33
KTS-3	280 ± 11	≥10 <sup>4</sup>	≥10 <sup>3 h</sup>	NA	2–12	5	13i
FJSM-SnS	409 ± 29 (65 °C)	≥10 <sup>3</sup>	NA	NA	0.7–11	5 (65 °C), 30 (RT)	34
GeSbS-2	231 ± 15 (65 °C)	≥10 <sup>3</sup>	NA	NA	2.8–11	2 (65 °C)	39
K <sub>6</sub> MS	66 ± 4	≥10 <sup>4</sup>	≥10 <sup>4 i</sup>	≥10 <sup>3 j</sup>	2.5–12	NA	42
<b>Sr<sup>2+</sup></b>							
KMS-1	77 ± 2	≥10 <sup>5</sup>	≥10 <sup>5 k</sup>	NA	1–14	NA	13c
KMS-2	87 ± 2	≥10 <sup>4</sup>	≥10 <sup>l</sup>	NA	3–10	NA	13h
KTS-3	102 ± 5	≥10 <sup>5</sup>	≥10 <sup>2 m</sup>	NA	2–12	5	13i
FJSM-SnS	65 ± 5	≥10 <sup>4</sup>	NA	NA	0.7–11	5 (65 °C), 60 (RT)	34
<b>Hg<sup>2+</sup></b>							
KMS-1	377 ± 15 <sup>c</sup>	≥10 <sup>5</sup>	≥10 <sup>5 n</sup>	≥9 × 10 <sup>4 n</sup>	2.5–9.5	5	13e
LHMS-1	87 ± 6 <sup>c</sup>	≥10 <sup>6</sup>	≥10 <sup>5 n</sup>	≥10 <sup>5 n</sup>	0–9	10	13f
K <sub>6</sub> MS	NA	≥10 <sup>6</sup>	≥10 <sup>6 n</sup>	≥10 <sup>6 n</sup>	3–8	60	43
<b>Pb<sup>2+</sup></b>							
KMS-1	319 ± 4 <sup>c</sup>	≥10 <sup>6</sup>	≥8 × 10 <sup>4 n</sup>	≥10 <sup>4 n</sup>	2.5–9.5	5	13e
CMS	1053 <sup>d</sup>	≥10 <sup>6</sup>	≥10 <sup>6 n</sup>	≥10 <sup>6 n</sup>	1–7	30	23
<b>Cd<sup>2+</sup></b>							
KMS-1	329 <sup>d</sup>	≥10 <sup>7</sup>	≥6 × 10 <sup>3 n</sup>	≥7 × 10 <sup>3 n</sup>	0–9	5	13e
CMS	515 <sup>d</sup>	≥10 <sup>5</sup>	≥10 <sup>5 n</sup>	≥10 <sup>5 n</sup>	1–7	90	23
<b>UO<sub>2</sub><sup>2+</sup></b>							
KMS-1	380 ± 20	≥10 <sup>5</sup>	≥10 <sup>5 o</sup>	≥10 <sup>4 p</sup>	2.5–10	120 <sup>q</sup>	13g
KTS-3	287 ± 15	≥10 <sup>4</sup>	≥5 × 10 <sup>3 o</sup>	NA	2–12	50 <sup>r</sup>	13i
<b>Ni<sup>2+</sup></b>							
KMS-1	29 ± 1	≥10 <sup>5</sup>	≥10 <sup>5 s</sup>	NA	3–10	NA	13h
KMS-2	151 ± 8	≥10 <sup>5</sup>	≥10 <sup>5 s</sup>	NA	3–10	NA	13h
<b>Cu<sup>2+</sup></b>							
KMS-1	155	≥10 <sup>5</sup>	≥10 <sup>4 t</sup>	≥10 <sup>4 t</sup>	2–6	20	29
<b>Tl<sup>+</sup></b>							
K <sub>6</sub> MS	508 ± 31 <sup>c</sup>	≥10 <sup>5</sup>	NA	NA	NA	NA	43

<sup>a</sup> Estimated from the fitting of the data with the Langmuir model. <sup>b</sup> Not available. <sup>c</sup> Estimated from the fitting of the data with the Langmuir-Freundlich model. <sup>d</sup> Estimated by averaging the metal uptake values corresponding to the saturation of the exchange sites of the material. <sup>e</sup> Na : Cs molar ratio ~655, pH ~ 7. <sup>f</sup> Ca : Cs molar ratio ~21. <sup>g</sup> Na : Cs molar ratio ~1.1 × 10<sup>5</sup>, pH ~ 7. <sup>h</sup> Na : Cs molar ratio ~1.8 × 10<sup>3</sup>. <sup>i</sup> Na : Cs molar ratio ~1.3 to 6.5 × 10<sup>5</sup>. <sup>j</sup> Ca : Cs molar ratio ~10<sup>5</sup>. <sup>k</sup> Na : Sr molar ratio ~1887. <sup>l</sup> Na : Sr molar ratio ~1.9 × 10<sup>5</sup>. <sup>m</sup> Na : Sr molar ratio ~329. <sup>n</sup> Competitive ion: Hg<sup>2+</sup> (or Pb<sup>2+</sup> or Cd<sup>2+</sup>) molar ratio ≥ 1000. <sup>o</sup> Na : U molar ratio ≥ 10<sup>4</sup>. <sup>p</sup> Ca : U molar ratio ≥ 10<sup>4</sup>. <sup>q</sup> 97% of U removal is achieved within 2 min. <sup>r</sup> 80% removal is achieved within 5 min. <sup>s</sup> Na : Ni molar ratio ~4.8 × 10<sup>4</sup>. <sup>t</sup> Na or Ca/Cu molar ratio ~8.

≥99.9% removal capacities observed (Fig. 10). The fast extraction of Hg<sup>2+</sup> and Ag<sup>+</sup> from their cyanide complexes is attributed to the high mobility of the K<sup>+</sup> ions of KMS-2 and the high affinity of the soft Lewis acids Hg<sup>2+</sup> and Ag<sup>+</sup> for the soft basic sulfide framework of KMS-2. It is suggested that KMS-2 absorbs Hg<sup>2+</sup> and Ag<sup>+</sup> once the ions are released to the solution and reach equilibrium, according to Le Chatelier's principle (reactions 7–9):



The elemental Hg and Ag can be recovered from the Hg<sup>2+</sup>/Ag<sup>+</sup>-loaded KMS-2 *via* a two step process. First, the exchanged product is heated at 425 °C; HgS sublimes and is collected at the end of a tube which is placed outside the furnace. Then, the Hg-





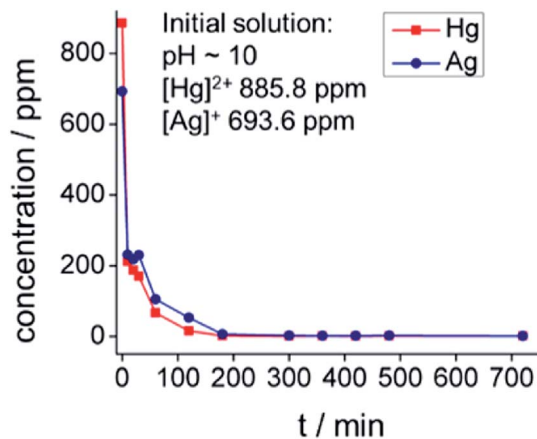


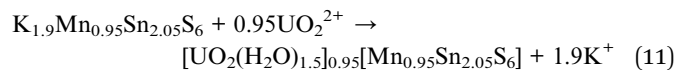
Fig. 10 Kinetic data for the sorption of Hg<sup>2+</sup> and Ag<sup>+</sup> from a mixture of Hg(CN)<sub>4</sub>]<sup>2-</sup>–[Ag(CN)<sub>2</sub>]<sup>-</sup> complexes in solution (pH ~ 10). Reproduced with permission from ref. 26. © 2015, American Chemical Society.

free compound is dissolved in nitric acid, and elemental Ag is isolated by reducing the dissolved Ag<sup>+</sup> with hydrazine.

Overall, the results from these studies suggest that MSIEs are very effective for the recovery of precious metal ions and decontamination of mine wastewater.

**2.2.6. UO<sub>2</sub><sup>2+</sup> exchange properties.** Uranium, which exists primarily as the UO<sub>2</sub><sup>2+</sup> cation, represents the major source of nuclear energy and its waste; it can be released into the environment through various industrial and mining processes.<sup>4</sup> Furthermore, a legacy of uranium-contaminated sites resulted from the closure of various nuclear facilities worldwide.<sup>4</sup> Selective UO<sub>2</sub><sup>2+</sup> ion exchangers to effectively capture this species are thus particularly attractive. In addition to their environmental remediation applications, UO<sub>2</sub><sup>2+</sup> sorbents can find use in the extraction of U from seawater, which contains 1000 times more U than terrestrial ores.

Traditionally, suitable sorbents for UO<sub>2</sub><sup>2+</sup> are materials with hard basic functional groups,<sup>27a</sup> e.g. carboxylic, phosphonate, or amidoxime groups, taking into account that U, with a 6+ oxidation state, is expected to behave as a typical hard Lewis acid. However, this may be an oversimplified assumption, since there have been reports of uranyl compounds forming reasonably strong covalent bonds with S<sup>2-</sup>.<sup>27b</sup> KMS-1 shows selective UO<sub>2</sub><sup>2+</sup> exchange properties. Complete exchange of the K<sup>+</sup> ions of KMS-1 by UO<sub>2</sub><sup>2+</sup> can be accomplished very fast<sup>13g</sup> according to the following equation:



PXRD studies show that the main UO<sub>2</sub><sup>2+</sup>-exchanged phase contains the linear [O=U=O]<sup>2+</sup> group, ordered parallel to the layer plane (Fig. 11).

Solid-state reflectance NIR/UV-Vis data indicated a significantly lower band gap for the UO<sub>2</sub><sup>2+</sup> exchanged compound (~0.95 eV) compared to that (1.3 eV) of pristine KMS-1. This is indicative of relatively strong UO<sub>2</sub><sup>2+</sup>...S<sup>2-</sup> interactions.

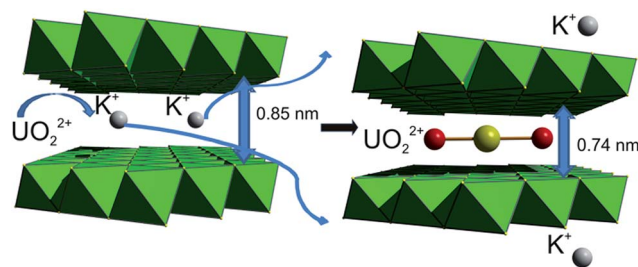


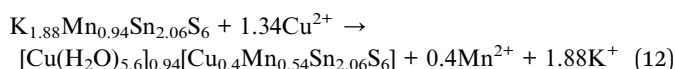
Fig. 11 Schematics for the mechanism of UO<sub>2</sub><sup>2+</sup> capture by KMS-1.

Isotherm batch sorption data fitted to the Langmuir model reveal a maximum capacity of 380 ± 20 mg g<sup>-1</sup>. The material can be regenerated by treating the UO<sub>2</sub><sup>2+</sup>-loaded product with Na<sub>2</sub>CO<sub>3</sub> and can be reused several times for UO<sub>2</sub><sup>2+</sup> ion exchange. KMS-1 performs well for UO<sub>2</sub><sup>2+</sup> sorption in a broad pH range (2 to 10). Interestingly, very high UO<sub>2</sub><sup>2+</sup> removal capacities (94–98%) for KMS-1 were observed even in the presence of tremendous excesses (up to 10<sup>4</sup> times higher concentration) of competitive ions such as Na<sup>+</sup> and Ca<sup>2+</sup>.

Furthermore, KMS-1 was tested for UO<sub>2</sub><sup>2+</sup> exchange under realistic conditions. It was found to be particularly effective for the decontamination of potable and lake water samples intentionally contaminated with traces of U (400 to 1000 ppb). Thus, the treatment of the samples with KMS-1 for only 2 min results in a final U concentration of ~1 ppb, well below the acceptable limit (30 ppb, defined by USA-EPA).

KMS-1 has been tested for recovery of U from seawater samples which contain U in concentrations of 3 to 4 ppb and very high amounts of Na<sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup> and K<sup>+</sup> (200 to 10 000 ppm). KMS-1 efficiently absorbs (removal capacity up to 84%) even this extremely low U content in the presence of reasonably high concentrations of competitive ions. Overall, the results from the UO<sub>2</sub><sup>2+</sup> sorption of KMS-1 revealed that this ion is much softer than previously thought, and MSIEs may provide new strategies for selective UO<sub>2</sub><sup>2+</sup> sorbents. Additional work is required to further evaluate the potential of this material for uranium harvesting from the sea; especially, testing should be performed under more realistic conditions relevant to a scalable practical process.

**2.2.7. Cu<sup>2+</sup> ion-exchange properties.** High concentrations of Cu<sup>2+</sup> in drinking water may result in several health problems, such as liver or kidney damage or gastrointestinal distress.<sup>1,28</sup> KMS-1 was recently tested as a Cu<sup>2+</sup> exchanger.<sup>29</sup> The results indicated that Cu<sup>2+</sup> is inserted as a hydrated cation in the interlayer space, exchanging all K<sup>+</sup>; at the same time, it partially replaces Mn<sup>2+</sup> ions from the layer. The ion-exchange process is described as follows:



A detailed kinetic study has been performed for Cu<sup>2+</sup> exchange by KMS-1. The data revealed that the absorption of Cu<sup>2+</sup> is very fast, with ion-exchange equilibrium reached in 40, 20 and 10 min at 10, 25 and 40 °C, respectively (Fig. 12). In





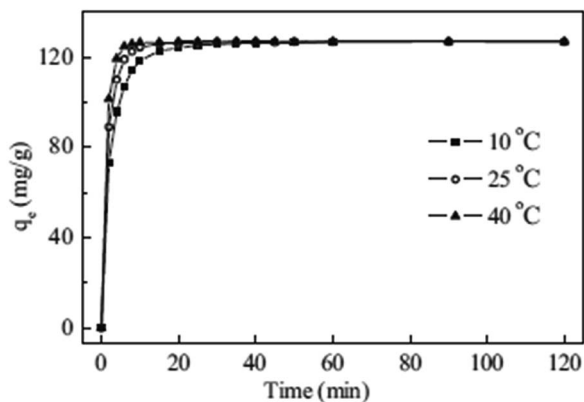


Fig. 12 Kinetic data for the sorption of  $\text{Cu}^{2+}$  by KMS-1, obtained at three different temperatures. Reproduced with permission from ref. 29; © 2014, Elsevier.

addition, fitting of the kinetic data can be readily achieved with the pseudo-second order model, which indicates that the rate limiting step is a chemical adsorption process. Further analysis of the kinetic data revealed that the rate controlling steps were external film and intraparticle diffusion processes.

**2.2.8. Sorption of radionuclides.** KMS-1 was also tested for the sorption of a series of radionuclides, including  $^{233}\text{U}$ ,  $^{239}\text{Pu}$ , and  $^{241}\text{Am}$ .<sup>30</sup> The results revealed that the material was particularly effective for rapid absorption of these radionuclides over a wide pH range (2 to 9), with  $\geq 99\%$  removal capacities observed even in the presence of high  $\text{Na}^+$  concentrations. This study indicated for the first time that **MSIEs** can be highly efficient for the decontamination of radioactive waste.

### 2.3. Protonated KMS:LHMS material

A rare example of a solid acid metal sulfide material is  $\text{H}_{2x}\text{Mn}_x\text{Sn}_{3-x}\text{S}_6$  ( $x = 0.11\text{--}0.25$ ), or LHMS-1 (layered hydrogen metal sulfide-1) compound.<sup>13f</sup> This compound is formed from treatment of KMS-1 with highly acidic solution to exchange  $\text{K}^+$  with  $\text{H}^+$ , a process which also attests to the high stability of the material to strong acids. LHMS-1 can absorb  $\text{Hg}^{2+}$  from a very acidic (pH = 0) to strongly alkaline environment (pH = 9). It is remarkable that LHMS-1 achieves almost 100%  $\text{Hg}^{2+}$  removal under extremely acidic conditions, *e.g.* even in the presence of 6 M  $\text{HNO}_3$ . Thus, this compound could be useful for removing  $\text{Hg}^{2+}$  from acidic wastewater, *e.g.* particular types of nuclear waste.<sup>46,31</sup> The local structure of  $\text{Hg}^{2+}$  in the interlayer space of the  $\text{Hg}^{2+}$ -loaded LHMS material was determined by atomic pair distribution function (PDF) studies, performed for the pristine LHMS-1 material and the  $\text{Hg}^{2+}$ -exchanged product. The results are consistent with an octahedral coordination of  $\text{Hg}^{2+}$  with Hg–S distances of  $\sim 2.57$  Å (Fig. 13).

### 2.4. Layered materials based on the $\text{Sn}_3\text{S}_7^{2-}$ net

Another family of interesting **MSIEs** is based on the  $\text{Sn}_3\text{S}_7^{2-}$  layered framework. The first member of this series,  $(\text{TMA})_2(\text{Sn}_3\text{S}_7)\cdot\text{H}_2\text{O}$  ( $\text{TMA}^+$  = tetramethylammonium ion), was reported by Prof. J. B. Parise and coworkers.<sup>32</sup> The compound was

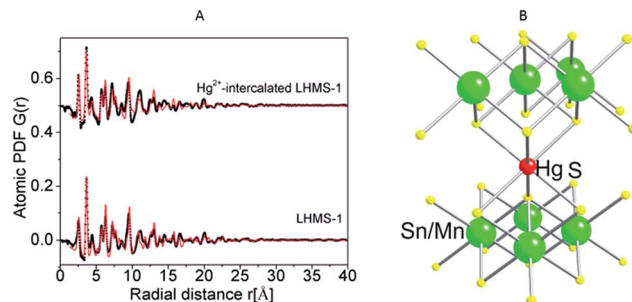


Fig. 13 (A) Experimental atomic PDFs (black) for LHMS-1 and  $\text{Hg}^{2+}$ -exchanged material. The red lines represent the computed atomic PDFs based on the  $\text{SnS}_2$  structure type. (B) The octahedral coordination of  $\text{Hg}^{2+}$  in the exchanged material, which is suggested based on the PDF model.

isolated by the reaction of  $\text{SnS}_2$ , TMAOH and S under hydrothermal conditions. It features a microporous layered framework consisting of edge-sharing  $[\text{Sn}_3\text{S}_4]$  semi-cubes (Fig. 14A). Six  $[\text{Sn}_3\text{S}_4]$  units are connected *via*  $\text{S}^{2-}$  bridges to form a ring surrounded by twelve  $\text{SnS}_5$  trigonal bipyramids. The layers are separated by  $\text{TMA}^+$  cations and guest water molecules (Fig. 14B). Preliminary ion-exchange experiments indicated that the  $\text{TMA}^+$  ions are easily exchanged by alkali and alkaline earth ions and some transition metal ions; however, ion exchange with soft metal ions such as  $\text{Ag}^+$  ions resulted in the breakdown of the layered framework structure.

Additional examples of materials with the  $\text{Sn}_3\text{S}_7^{2-}$  layered structure contain a variety of interlayer organic cations, such as DABCOH<sup>+</sup> (protonated 1,8-diazabicyclooctane), QUIN (quinclidinium), TBA<sup>+</sup> (*tert*-butylammonium) and  $\text{Et}_4\text{N}^+$  (tetraethylammonium).<sup>33</sup>

More recently, a new member of the  $\text{Sn}_3\text{S}_7^{2-}$  family templated by mixed  $\text{MeNH}_2^+$  and  $\text{Me}_3\text{NH}^+$  cations was described. The formula of this material, denoted as FJSM-SnS, was  $(\text{Me}_2\text{NH}_2)_{4/3}(\text{Me}_3\text{NH})_{2/3}\text{Sn}_3\text{S}_7\cdot 1.25\text{H}_2\text{O}$ .<sup>34</sup> The  $\text{Cs}^+$  and  $\text{Sr}^{2+}$  exchange properties of this material at 65 °C indicated that the maximum sorption is achieved within only 5 min, whereas at room temperature, the ion exchange equilibrium is reached within 30 to 60 min. The maximum  $\text{Cs}^+$  and  $\text{Sr}^{2+}$  sorption capacities were  $409 \pm 29$  and  $65 \pm 5$   $\text{mg g}^{-1}$ , respectively. These values are among the highest reported for **MSIEs**. In addition,

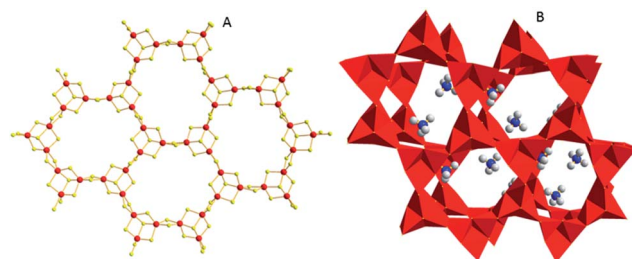


Fig. 14 (A) The layered structure of  $(\text{TMA})_2(\text{Sn}_3\text{S}_7)\cdot\text{H}_2\text{O}$  (Sn, red; S, yellow). (B) The arrangement of two adjacent layers (with a polyhedral representation) and the  $\text{TMA}^+$  cations (C, grey; N, blue) located in the interlayer space (guest water molecules were omitted for clarity).



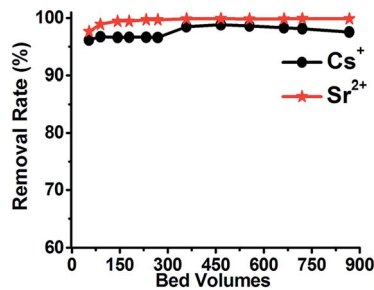


Fig. 15 % removal of  $\text{Sr}^{2+}$  and  $\text{Cs}^+$  vs. the bed volume for a column of the FJSM-SnS material.

pH-dependent experiments revealed good  $\text{Cs}^+$  and  $\text{Sr}^{2+}$  removal capacities in a broad pH range (0.7 to 10). Interestingly, FJSM-SnS can be used as the stationary phase in an ion-exchange column, which was found to be particularly effective in absorbing  $\text{Cs}^+$  and  $\text{Sr}^{2+}$  from aqueous solutions containing both ions (initial concentrations:  $\text{Cs}^+ = 12$  to  $15$  ppm;  $\text{Sr}^{2+} = 6$  ppm). Thus, removal capacities of 96–100%  $\text{Cs}^+$  and  $\text{Sr}^{2+}$  were observed after passing 900 bed volumes (total volume passed = 2.42 L, one bed volume = 2.79 mL) through the ion exchange column (Fig. 15). This represents one of the first reports of the use of **MSIEs** in columns. However, for practical ion-exchange column applications, engineered forms of the sorbents may be required (see below).

## 2.5. KTS materials

An additional example of a tin sulfide layered material with promising ion-exchange properties is  $\text{K}_2\text{Sn}_4\text{S}_9$  (KTS-1). This compound can be isolated *via* solid state synthesis. The crystal structure of KTS-1 is related to the structures of  $\text{Rb}_2\text{Sn}_4\text{S}_9$  and  $\text{Cs}_2\text{Sn}_4\text{S}_9$ .<sup>35</sup> The basic unit of the structure of these materials is the  $\text{Sn}_4\text{S}_9^{2-}$  duster, consisting of two tetrahedrally coordinated  $\text{Sn}^{4+}$  ions and two  $\text{Sn}^{4+}$  ions adopting trigonal bipyramidal geometry. The clusters are connected through  $\text{S}^{2-}$  bridges to form a layered structure perforated with relatively large holes (Fig. 16A). The layers are corrugated, and the interlayer space is filled with highly disordered cations (Fig. 16B).

Preliminary investigations of the  $\text{Cs}^+$  exchange properties of KTS-1 revealed a maximum sorption capacity of  $205 \pm 6 \text{ mg g}^{-1}$  and very high  $K_d$  values in the range of  $10^3$  to  $10^5 \text{ mL g}^{-1}$ . Furthermore, the  $\text{K}^+$  ions of KTS-1 can be fully exchanged by soft metal ions, such as  $\text{Hg}^{2+}$ ,  $\text{Pb}^{2+}$  and  $\text{Cd}^{2+}$ .<sup>36</sup> Thus, KTS-1 appears

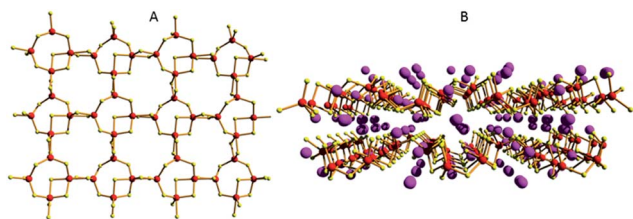


Fig. 16 (A) Part of the  $\text{Sn}_4\text{S}_9^{2-}$  layer (Sn, red; S, yellow). (B) The arrangement of two adjacent layers with the cations ( $\text{Cs}^+$ , pink) filling the interlayer space.

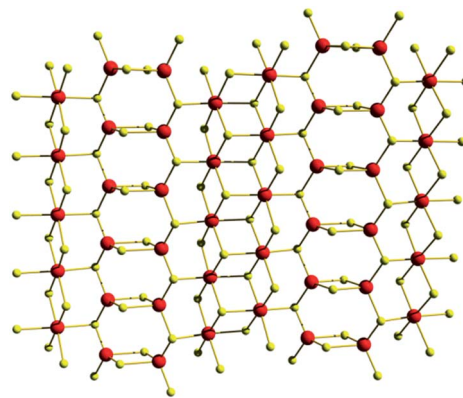


Fig. 17 Structural segment of the KTS-1 layer viewed along the *b*-axis. Sn, red; S, yellow.

to be a promising ion-exchanger, although further studies are required.

KTS-2, another tin sulfide ion-exchanger, is a 3-D material and is discussed below (see Section 2.3).<sup>36</sup>

Very recently, a new compound,  $\text{K}_{2x}\text{Sn}_{4-x}\text{S}_{8-x}$  ( $x = 0.65$  to  $1$ , KTS-3) was reported.<sup>13i</sup> This compound was prepared with a hydrothermal reaction similar to that used for KMS materials, but without adding Mn or Mg to the reaction mixture. The crystal structure of KTS-3 is shown in Fig. 17.  $\text{SnS}_6$  octahedra form ribbons running along the *c*-axis and are interconnected through  $\text{SnS}_4$  units in the form of  $\text{Sn}_2\text{S}_6$  bridges. The interlayer space is filled by disordered  $\text{K}^+$  ions.

KTS-3 is an excellent ion-exchanger for  $\text{Cs}^+$ ,  $\text{Sr}^{2+}$  and  $\text{UO}_2^{2+}$ . The  $\text{Sr}^{2+}$  capacity of this sorbent was found to be  $102 \pm 5 \text{ mg g}^{-1}$  (by fitting of the data with the Langmuir model), the highest reported among **MSIEs**. It also shows high  $\text{Cs}^+$  and  $\text{UO}_2^{2+}$  exchange capacities (Langmuir fitting:  $280 \pm 11 \text{ mg Cs/g}$ ,  $287 \pm 15 \text{ mg U/g}$ ). Interestingly, it exhibits very good selectivity for  $\text{Cs}^+$  ( $K_d$  value of  $4.4 \times 10^3 \text{ mL g}^{-1}$ ) in the presence of  $\text{Na}^+$  in a molar concentration (0.1 M) 2000 times higher than the initial  $\text{Cs}^+$  content (Fig. 18A). Even with a 10 000-fold excess of  $\text{Na}^+$ , the  $K_d$  value for  $\text{Cs}^+$  was  $>10^3 \text{ mL g}^{-1}$ . The effect of  $\text{Na}^+$  seems to be more important in the case of ion-exchange of  $\text{Sr}^{2+}$ ; the  $K_d$  values dropped sharply when the  $\text{Na}^+$  concentration was

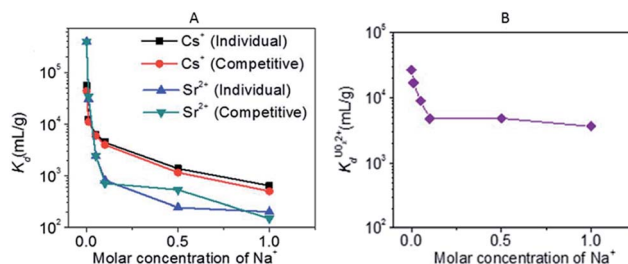


Fig. 18 (A)  $K_d$  of individual and competitive  $\text{Cs}^+$  and  $\text{Sr}^{2+}$  ion exchange vs. molar concentration of  $\text{Na}^+$  (initial concentrations were 7.4 and 6.9 ppm for  $\text{Cs}^+$  and  $\text{Sr}^{2+}$  respectively,  $\text{V m}^{-1}$  ratio was  $1000 \text{ mL g}^{-1}$ , and  $\text{pH} \sim 7$ ). (B)  $K_d$  for  $\text{UO}_2^{2+}$  ion exchange vs. molar concentration of  $\text{Na}^+$  (initial concentration of  $\text{UO}_2^{2+}$  was 1 ppm,  $\text{V m}^{-1}$  ratio was  $1000 \text{ mL g}^{-1}$ , and  $\text{pH} \sim 7$ ).



increased (Fig. 18B). Furthermore, competitive  $\text{Cs}^+/\text{Sr}^{2+}$  ion exchange experiments revealed generally higher  $K_d$  values for  $\text{Cs}^+$  exchange than  $\text{Sr}^{2+}$  exchange (Fig. 18A). Finally,  $\text{Na}^+$  even in huge excess (concentration up to 5 M) has a negligible effect on  $\text{UO}_2^{2+}$  exchange because the  $K_d$  values show only slight variation when the  $\text{Na}^+$  concentration is increased (Fig. 18B). This result further indicates that  $\text{UO}_2^{2+}$  behaves more like a typical soft ion (borderline soft) interacting strongly with the soft basic metal sulfide layer, rather than a hard ion, as  $\text{UO}_2^{2+}$  is generally classified. KTS-3 is also an effective sorbent for heavy metals such as  $\text{Hg}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Ag}^+$ , and  $\text{Tl}^+$ .

## 2.6. Layered sulfides with trivalent metal ions in their framework

The majority of layered MSIEs are based on tetravalent or combined tetravalent/bivalent metal ions. Generally, these metal ions mainly adopt tetrahedral or octahedral coordination; in only a few cases, trigonal bipyramidal coordination has been also observed. An alternative approach to create sulfide materials involves the combination of trivalent ions such as  $\text{In}^{3+}$  or  $\text{Ga}^{3+}$ , which prefer tetrahedral coordination, and  $\text{Sb}^{3+}$ , which tends to adopt a trigonal pyramidal coordination geometry.

**2.6.1.  $[(\text{CH}_3\text{CH}_2\text{CH}_2)_2\text{NH}_2]_5\text{In}_5\text{Sb}_6\text{S}_{19} \cdot 1.45\text{H}_2\text{O}$  (InSbS).** A layered material isolated with this synthetic strategy is  $[(\text{CH}_3\text{CH}_2\text{CH}_2)_2\text{NH}_2]_5\text{In}_5\text{Sb}_6\text{S}_{19} \cdot 1.45\text{H}_2\text{O}$  (InSbS), prepared by a hydrothermal reaction of  $\text{In}_2\text{S}_3$ ,  $\text{Sb}_2\text{S}_3$ , S and dipropylamine.<sup>37</sup> The  $[\text{In}_5\text{Sb}_6\text{S}_{19}]^{5-}$  layer is composed of corner-sharing  $\text{InS}_4$  tetrahedra bridged by  $\text{SbS}_3$  trigonal pyramidal units and  $\text{Sb}_2\text{S}_6$  dimers (Fig. 19A). The layer contains large holes with dimensions  $13.3 \times 3.8 \text{ \AA}^2$ , which are large enough to host some of the organic counter ions, with the remaining organic cations located in the interlayer space (Fig. 19B).

Due to the disordered state of the organic guest ions and the relatively large windows of the layer, this compound displays facile ion-exchange properties with various cationic species. Interestingly,  $\text{Cs}^+$  can completely exchange the organic cations, whereas  $\text{Rb}^+$  exchanges only 37% of the cations. In addition, 12% of ions are replaced by  $\text{Li}^+$ , and a negligible amount of organic guests can be exchanged by  $\text{K}^+$  and  $\text{Na}^+$ .

Competitive experiments with a mixture of equimolar amounts of  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Rb}^+$  and  $\text{Cs}^+$  revealed that the  $\text{Cs}^+$  uptake of InSbS is 10 times higher than that for the other ions. This significant selectivity of the compound for  $\text{Cs}^+$  probably results

from the size-match of this cation with the aperture of the windows in the  $[\text{In}_5\text{Sb}_6\text{S}_{19}]^{5-}$  layer. Thus, the perforated layers of the compound seem to favor its facile ion-exchange properties. This hypothesis is also supported by the lack of any ion-exchange capacity for the lamellar material  $[\text{CH}_2\text{NH}_2]_2\text{In}_2\text{Sb}_2\text{S}_7$ , whose layers are relatively dense and have no holes.

**2.6.2.  $[\text{CH}_2\text{NH}_2]_2\text{Ga}_2\text{Sb}_2\text{S}_7 \cdot \text{H}_2\text{O}$  (GaSbS-1).** Another example of a layered MSIE material containing trivalent metal ions is  $[\text{CH}_2\text{NH}_2]_2\text{Ga}_2\text{Sb}_2\text{S}_7 \cdot \text{H}_2\text{O}$  (GaSbS-1).<sup>38</sup> The building block of the structure is made of two corner-sharing  $\text{GaS}_4$  tetrahedra and two  $\text{SbS}_3$  trigonal pyramidal units further bridging the  $\text{GaS}_4$  moieties (Fig. 20A). There are relatively open windows in the layers that are defined by 16-member rings composed of four building units. Dimethylammonium cations are found in the interlayer space and interact with the layers *via* N–H...S hydrogen bonding.

GaSbS-1 shows facile ion-exchange properties for alkali and alkaline earth metal ions due to its layered structure and the relatively large windows in the layers, which allow the diffusion of species in the ion-exchange reactions. Of particular interest is  $\text{Cs}^+$  sorption by the compound GaSbS-1. This material is particularly selective for  $\text{Cs}^+$  in the presence of a very large (100-fold) excess of  $\text{Na}^+$ . Interestingly, the  $\text{Cs}^+$  exchange can be achieved even *via* a SCSC transformation process. The crystal structure of the  $\text{Cs}^+$ -exchanged product (GaSbS-2) could be thus determined.

The connectivity of the atoms in GaSbS-2 (Fig. 20B) is the same as in GaSbS-1. There is, however, a significant contraction of the layered framework. Thus, the size of the windows changed from  $11.36 \times 4.28 \text{ \AA}^2$  in GaSbS-1 to  $11.85 \times 3.69 \text{ \AA}^2$  (including atomic radii) in GaSbS-2 (Fig. 21). Therefore, it appears that there is a framework response when  $\text{Cs}^+$  ions enter the structure, resulting in shrinkage of the window size in the layers. Two of the three crystallographically independent  $\text{Cs}^+$  ions are located close to the layer, whereas the third one is found between two layers. These ions are tightly bound in the compound, as no  $\text{Cs}^+$  can be leached out by treating the material with large excess of  $\text{Na}^+$  ions. The opening/closing of windows observed for the layered structure of compound GaSbS-1 upon  $\text{Cs}^+$  exchange is reminiscent of the mechanism of insect capture by the Venus flytrap plant.

**2.6.3.  $[\text{CH}_3\text{NH}_3]_{20}\text{Ge}_{10}\text{Sb}_{28}\text{S}_{72} \cdot 7\text{H}_2\text{O}$  (GeSbS-1).** This compound was prepared solvothermally by reacting  $\text{GeO}_2$ , Sb, S

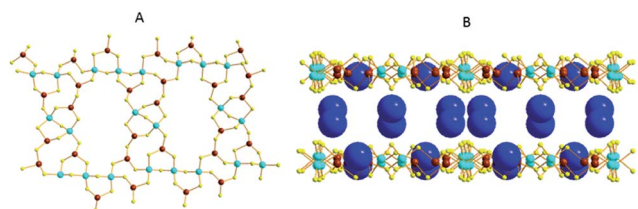


Fig. 19 (A) Part of the  $[\text{In}_5\text{Sb}_6\text{S}_{19}]^{5-}$  layer viewed down the  $b$ -axis. (B) Packing of the layers with the N atoms of dipropylammonium cations showing as large balls (C and H atoms were omitted for clarity). In, cyan; Sb, brown; N, blue; S, yellow.

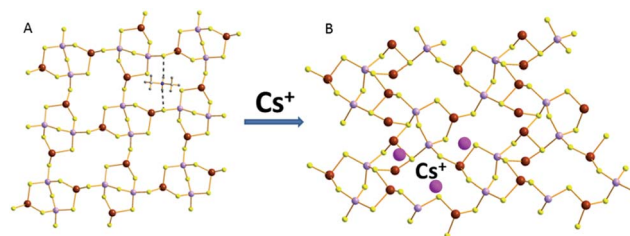


Fig. 20 (A) Part of the layer of GaSbS-1. The dashed lines represent hydrogen bonding interactions between the dimethylammonium ions and the layer. (B) Part of the layer of GaSbS-2 and some of the inter-layer  $\text{Cs}^+$  ions. Ga, purple; Sb, brown; S, yellow; Cs, pink.





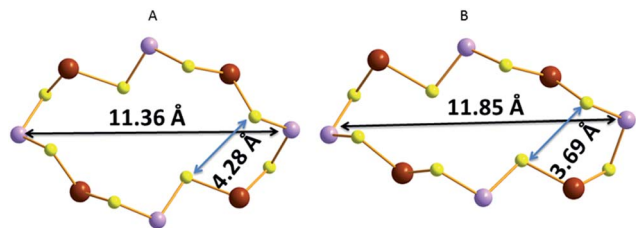


Fig. 21 (A) The 16-member ring in GaSbS-1 with indication of its dimension. (B) The 16-member ring in GaSbS-2 with indication of its dimension. Ga, purple; Sb, brown; S, yellow.

and methylammonium salt.<sup>39</sup> It features an unusual double-layered structure formed by two symmetry-related thick layers joined by Ge<sup>4+</sup> ions (Fig. 22). Each single layer is composed of two parts, L1 and L2. L1 is a 1-D chain of interconnecting [GeSb<sub>3</sub>S<sub>8</sub>]<sup>3-</sup> units, whereas the L2 moiety is a layer based on [GeSb<sub>4</sub>S<sub>11</sub>]<sup>6-</sup> units. Two types of channels are observed in the structure, with dimensions of 10.17 × 9.90 Å<sup>2</sup> and 5.94 × 5.94 Å<sup>2</sup>. The methylammonium cations and guest water molecules are found within these channels as well as in the interlayer space.

GeSbS-1 shows impressive Cs<sup>+</sup> exchange properties. Specifically, it exhibits a Cs<sup>+</sup> exchange capacity of 231 ± 15 mg g<sup>-1</sup>. The kinetics of the Cs<sup>+</sup> sorption is also remarkably fast, with the ion exchange reaching equilibrium within 2 min. In addition, the selectivity of the material for Cs<sup>+</sup> is significant, as revealed by the relatively high *K<sub>d</sub>* values (2 to 4 × 10<sup>3</sup> mL g<sup>-1</sup>) for Cs<sup>+</sup> exchange in the presence of a large excess (20-fold) of Na<sup>+</sup> or Ca<sup>2+</sup>.

### 2.7. Polysulfide and MoS<sub>4</sub><sup>2-</sup>-intercalated layered double hydroxides

Recently, a new type of metal sulfide-like sorbent, with selective sorption properties for heavy metal ions, has been developed.<sup>40</sup>

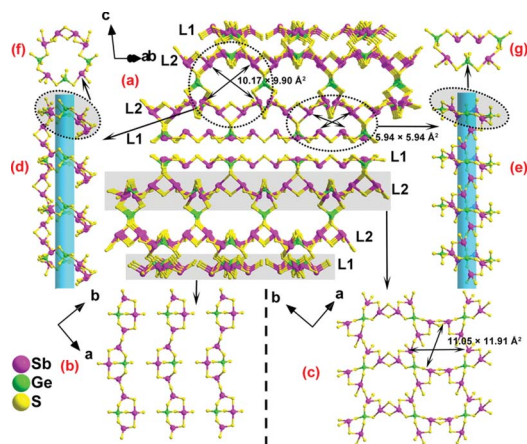


Fig. 22 (a) The double-layered network of GeSbS-1. (b) The L1 unit. (c) The L2 unit. (d and e) The two types of channels in the network. (f and g) The 18- and 14-membered rings that form the channels in the structure. Reproduced with permission from ref. 39 © 2015, American Chemical Society.

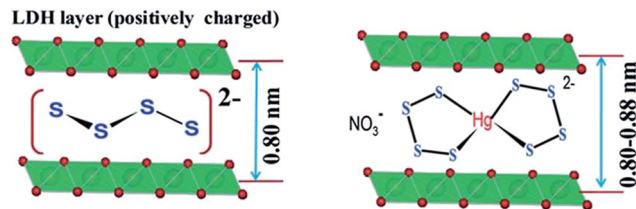


Fig. 23 Left: Arrangement of [S<sub>4</sub>]<sup>2-</sup> groups in the interlayer space of the LDH material. Right: Proposed binding of metal ions with the polysulfide unit. Metal, green; O, red.

These materials consist of layered double hydroxides (LDHs) intercalated by polysulfide [S<sub>x</sub>]<sup>2-</sup> groups (Fig. 23, left).

The mechanism of the metal ion capture by LDH(S<sub>x</sub>) sorbents depends on the metal ion : LDH(S<sub>x</sub>) molar ratio.

In the case of low metal ion concentration and a large excess of sorbent, the following reaction takes place:



Thus, the [S<sub>x</sub>]<sup>2-</sup> groups act as a second host for the incoming ions (Fig. 23, right).

When, however, the concentration of the metal ion is relatively large, the sorption reactions are stoichiometric; thus, two products, LDH(NO<sub>3</sub>) and MS<sub>x</sub>, are formed:



Sorption experiments with aqueous solutions containing a series of metal ions, such as Ni<sup>2+</sup>, Co<sup>2+</sup>, Cu<sup>2+</sup>, Cd<sup>2+</sup>, Hg<sup>2+</sup>, Pb<sup>2+</sup>, Zn<sup>2+</sup> and Ag<sup>+</sup>, indicate higher selectivity of LDH(S<sub>x</sub>) for the softer ions. Extremely high *K<sub>d</sub>* values (up to 10<sup>7</sup> mL g<sup>-1</sup>) are found for the sorption of Ag<sup>+</sup> and Hg<sup>2+</sup>, revealing the high potential of LDH(S<sub>x</sub>) sorbents for the capture of heavy metal ions.<sup>40a</sup>

LDH(S<sub>x</sub>) materials were also tested for UO<sub>2</sub><sup>2+</sup> sorption.<sup>40b</sup> A series of UO<sub>2</sub><sup>2+</sup> sorption experiments reveal the exceptional selectivity of the LDH(S<sub>x</sub>) sorbents for UO<sub>2</sub><sup>2+</sup> in the presence of very large excesses of Na<sup>+</sup> and Ca<sup>2+</sup>. In addition, LDH(S<sub>x</sub>) materials can efficiently absorb U from seawater samples. These results further confirm the potential of sulfide sorbents for selective U capture.

More recently, MoS<sub>4</sub><sup>2-</sup> intercalated LDHs have been reported.<sup>40c</sup> They show extremely high sorption capacities for Hg<sup>2+</sup> (~500 mg g<sup>-1</sup>) and Ag<sup>+</sup> (~450 mg g<sup>-1</sup>). They are also efficient to capture additional metal ions such as Cu<sup>2+</sup>, Pb<sup>2+</sup>, and Co<sup>2+</sup>. It is suggested that in low and medium metal (M<sup>2+</sup>) ion concentrations, the sorption proceeds through the formation of [M(MoS<sub>4</sub>)<sub>2</sub>]<sup>2-</sup> species trapped in the interlayer space of the LDH materials. In high initial metal ion concentrations, neutral amorphous [M(MoS<sub>4</sub>)] salts are produced.

## 3. Three-dimensional crystalline MSIEs

Although a large number of three-dimensional crystalline metal sulfide materials have been reported, relatively few examples





have been thoroughly studied for their ion-exchange properties. Below, we describe some characteristic 3-D MSIEs and their sorption properties for various cations.

### 3.1. $\text{K}_6\text{Sn}[\text{Sn}_4\text{Zn}_4\text{S}_{17}]$ ( $\text{K}_6\text{MS}$ )

This compound was isolated *via* solid state flux synthesis.<sup>41</sup> Its structure is based on the so-called penta-supertetrahedral (P1)  $[\text{Zn}_4\text{Sn}_4\text{S}_{17}]^{10-}$  cluster, constructed by a central  $\{\text{Zn}_4\text{S}\}^{6+}$  core (anti-T1 unit) capped by four  $\text{SnS}_4$  tetrahedral (T1) units. The clusters are interconnected *via* four-coordinated  $\text{Sn}^{4+}$  ions to form a diamond-like framework (Fig. 24).<sup>13a</sup> There are 3 cavities in the structure which host  $\text{K}^+$  ions. The  $\text{K}_1$  cavity accommodates a tightly bound  $\text{K}^+$  ion ( $\text{K}_1$ ), whereas  $\text{K}_2$  and  $\text{K}_3$  cavities contain four ( $\text{K}_2$ ) and one ( $\text{K}_3$ )  $\text{K}^+$  ions, respectively, which are relatively labile. The  $\text{K}_3$  cavity has a relatively large diameter ( $\sim 4.1$  Å) and communicates through narrow passages (with sizes of  $\sim 1.0$  to  $1.5$  Å) with the smaller  $\text{K}_1$  and  $\text{K}_2$  pores (with a diameter of  $\sim 3.0$  Å) (Fig. 25).

**3.1.1.  $\text{Cs}^+$  ion-exchange properties.**  $\text{K}_6\text{MS}$  shows interesting  $\text{Cs}^+$  ion-exchange properties, which may be observed with either polycrystalline samples or single crystals of the material (SCSC transformation).<sup>13b</sup> Reaction of  $\text{K}_6\text{MS}$  with  $\text{CsCl}$  for  $\sim 12$  h gives  $\text{K}_5\text{CsSn}_5\text{Zn}_4\text{S}_{17}$ . The SCSC  $\text{Cs}^+$  ion-exchange reaction resulted in the isolation of single crystals of the  $\text{Cs}^+$ -exchanged product. Determination of its crystal structure revealed the presence of one  $\text{Cs}^+$  ion in the place of  $\text{K}_3^+$  of  $\text{K}_6\text{MS}$  (Fig. 26). For comparison, the corresponding SCSC  $\text{Rb}^+$  ion exchange led to the isolation of a product with 5  $\text{Rb}^+$  replacing  $\text{K}_2^+$  and  $\text{K}_3^+$  ions (only  $\text{K}_1^+$  remained intact). Competitive  $\text{Rb}^+/\text{Cs}^+$  ion-exchange reactions using a large excess of  $\text{Rb}^+$  ( $\text{Rb} : \text{Cs}$  molar ratio = 10 : 1) yielded a material with three  $\text{K}^+$ , two  $\text{Rb}^+$  and one  $\text{Cs}^+$  according to analytical data (the crystal structure was not determined). Despite the high concentration of  $\text{Rb}^+$  related to that of  $\text{Cs}^+$ , the material still absorbs one  $\text{Cs}^+$  per formula unit, thus indicating its strong selectivity for this ion.

An SCSC exchange experiment was also performed in the simultaneous presence of  $\text{Cs}^+$ ,  $\text{Rb}^+$  and  $\text{NH}_4^+$  in equimolar concentrations. The results revealed that the exchange product

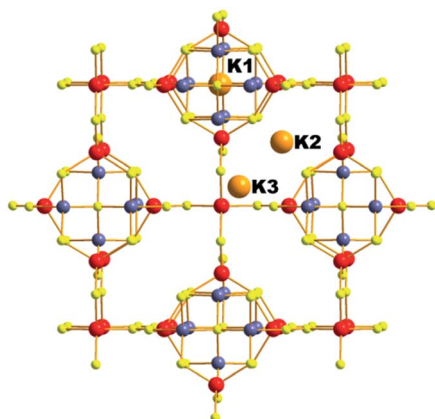


Fig. 24 The three-dimensional framework of  $\text{K}_6\text{MS}$  with labeling of the  $\text{K}^+$  ions. Sn, red; Zn, blue-gray; S, yellow.

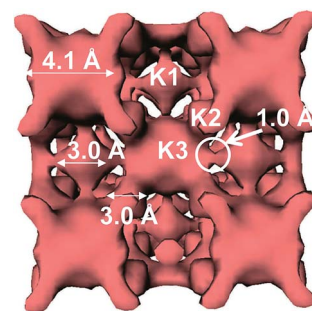


Fig. 25 Plot of the void space of  $\text{K}_6\text{MS}$  with labeling of the three different types of pores and indication of the sizes of the cavities.

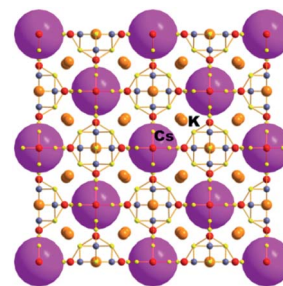


Fig. 26 Representation of the structure of  $\text{K}_5\text{CsSn}[\text{Zn}_4\text{Sn}_4\text{S}_{17}]$ . Sn, red; Zn, blue-gray; S, yellow.

contained only  $\text{K}^+$  in its  $\text{K}_1$  cavity, the  $\text{K}_2$  cavity hosted a mixture of  $\text{Rb}^+/\text{NH}_4^+$  and the  $\text{K}_3$  cavity was filled exclusively with  $\text{Cs}^+$  (Fig. 27). Therefore, the  $\text{K}_3$  cavity seems to be suitably sized for  $\text{Cs}^+$ , which explains the selectivity of  $\text{K}_6\text{MS}$  for this ion. Interestingly,  $\text{K}_6\text{MS}$  shows absolutely no exchange capacity for  $\text{Li}^+$ ,  $\text{Na}^+$  and  $\text{Ca}^{2+}$  because the large hydration sphere of these ions prevents them from entering the framework. The ion-exchange reactions for  $\text{K}_6\text{MS}$  are summarized in Scheme 1.

Encouraged by the above excellent  $\text{Cs}^+$  exchange results, more detailed batch ion-exchange studies have been performed.<sup>42</sup> Ion-exchange isotherm data, which fit the Langmuir model (Fig. 28A), reveal a maximum  $\text{Cs}^+$  ion-exchange capacity of  $66 \pm 4$   $\text{mg g}^{-1}$ , corresponding to  $0.81 \pm 0.06$  mole of  $\text{Cs}^+$  per

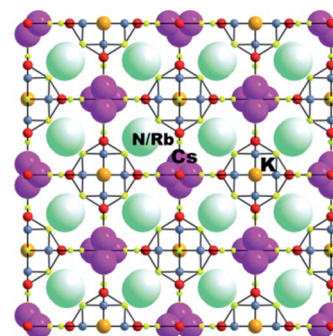


Fig. 27 Representation of the structure of  $\text{KCsRb}_{1.29}(\text{NH}_4)_{2.71}\text{Sn}[\text{Zn}_4\text{Sn}_4\text{S}_{17}]$ . Sn, red; Zn, blue-gray; S, yellow.



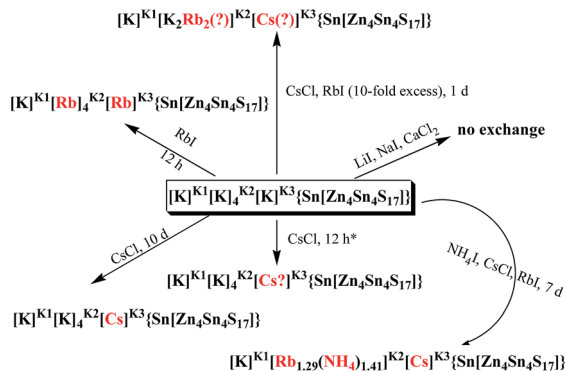
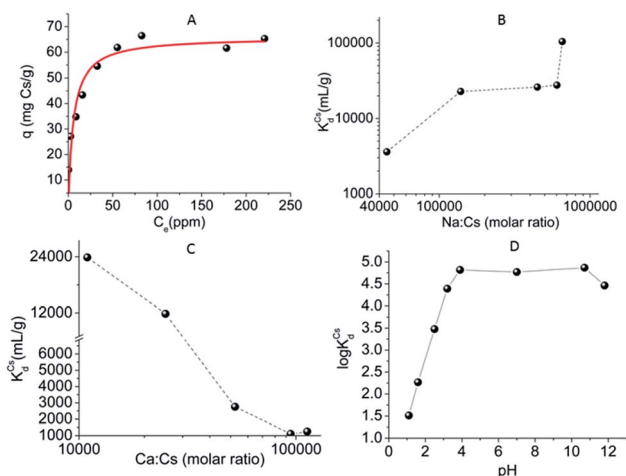
Scheme 1 Representation of the ion-exchange reactions for  $K_6MS$ .

Fig. 28 (A) Isotherm  $Cs^+$  sorption data for  $K_6MS$ . The solid line represents the fitting of the data with the Langmuir model ( $q_m = 66 \pm 4 \text{ mg g}^{-1}$ ;  $b = 0.17 \pm 0.05 \text{ L mg}^{-1}$ ;  $R^2 = 0.89$ ). (B) The distribution coefficient  $K_d$  for  $Cs^+$  ion exchange versus the  $Na^+ : Cs^+$  molar ratio. (C) The distribution coefficient  $K_d$  for  $Cs^+$  ion exchange versus the  $Ca^+ : Cs^+$  molar ratio. (D) The logarithm values of the distribution coefficient  $K_d$  for  $Cs^+$  ion exchange versus the pH.

formula unit, *i.e.* close to the expected maximum  $Cs^+$  capacity (1 mole per formula unit).

The sorption of low concentration ( $\sim 1 \text{ ppm}$ )  $Cs^+$  in the presence of extremely high concentrations of  $Na^+$  (0.4 to 5 M) is exceptional. Specifically,  $>95\%$   $Cs^+$  sorption and large distribution coefficients  $K_d$  in the range of  $10^4$  to  $10^5 \text{ mL g}^{-1}$  were estimated, even with 1.3 to  $6.5 \times 10^5$ -fold excesses of  $Na^+$  (Fig. 28B). Surprisingly, an enhancement of the  $Cs^+$  sorption by  $K_6MS$  was observed upon increasing the  $Na^+$  concentration.

Very high  $Ca^{2+}$  concentrations (0.1 to 1 M) partially reduce the  $Cs^+$  sorption capacity of  $K_6MS$ . High  $Cs^+$  removal capacity ( $\sim 68\%$ ) and distribution coefficients above  $1000 \text{ mL g}^{-1}$  were observed even in the presence of a  $10^5$ -fold excess of  $Ca^{2+}$  (Fig. 28C).

$K_6MS$  also exhibits excellent affinity and selectivity for  $Cs^+$ , showing  $K_d$  values  $\geq 10^4 \text{ mL g}^{-1}$  within a very wide pH range (3 to 12), Fig. 28D. These data indicate that  $K_6MS$  may be effective for  $Cs^+$  decontamination for both alkaline and acidic waste

solutions. The above results confirm the exceptional selectivity of  $K_6MS$  for  $Cs^+$ , which results from the perfect fit of the  $K_3$  cavity for  $Cs^+$  (see above).

**3.1.2.  $NH_4^+$  ion-exchange properties.** This material also exhibited very interesting  $NH_4^+$  exchange properties.<sup>13b</sup> Treating single crystals of compound  $K_6MS$  with  $NH_4I$  for 1 week resulted in the isolation of an exchange product with 5  $NH_4^+$  and only one  $K^+$  per formula unit. Surprisingly,  $NH_4^+$  replaced all  $K^+$  except the highly disordered  $K_3^+$  ion. It is remarkable that  $NH_4^+$  can diffuse even through the very narrow passages connecting the  $K_1$  and  $K_3$  cavities. This highly unusual  $NH_4^+$  exchange capability of  $K_6MS$  is attributed to the flexibility of the framework of this material. The M–S–M' angles in  $K_6MS$  are relatively small ( $\sim 110^\circ$ ), which facilitates breathing phenomena and, thus, the movement of ions through the tunnel network. This behavior of  $K_6MS$  is in marked contrast to that of zeolites, which are characterized by wide Al–O–Si angles ( $160$  to  $180^\circ$ ) and do not favor swelling processes to the same degree.

**3.1.3. Heavy metal ion sorption properties.**  $K_6MS$  selectively absorbs soft metal ions.<sup>43</sup>  $Hg^{2+}$  exchange experiments with various initial  $Hg^{2+}$  concentrations indicated very high removal capacities (95–100%) and  $K_d$  values of up to  $2 \times 10^6 \text{ mL g}^{-1}$  (Fig. 29A). In addition, experiments at various pH values (3 to 8) revealed no effect of the pH on the  $Hg^{2+}$  sorption, which reaches almost 100% removal capacity over the whole pH range tested (Fig. 29B). The investigation of kinetics for the  $Hg^{2+}$  ion exchange (initial  $Hg^{2+}$  concentration  $\sim 441 \text{ ppm}$ , pH  $\sim 5$ ) revealed that equilibrium is reached within only one hour (Fig. 29C). Fitting of the kinetic data was performed with the Lagergren's equation describing first-order kinetics:

$$q_t = q_c[1 - \exp(-K_1 t)], \quad (15)$$

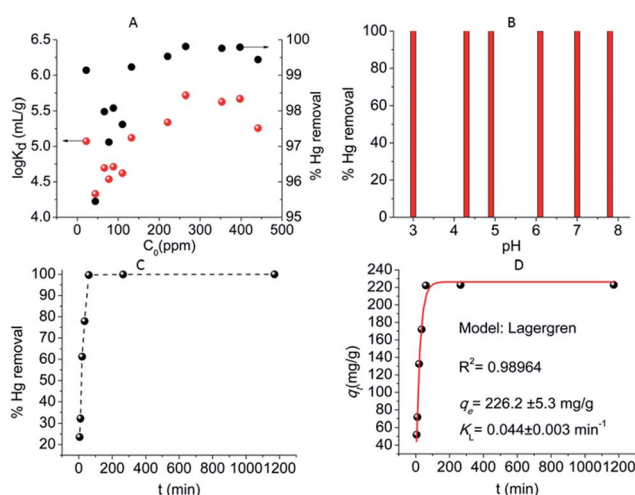


Fig. 29 (A) Representation of the %  $Hg$  removal and  $\log K_d$  values versus the initial  $Hg^{2+}$  concentration for  $K_6MS$ . (B) %  $Hg$  removal vs. pH (initial  $Hg^{2+}$  concentration =  $441 \text{ ppm}$ ,  $V m^{-1} = 500 \text{ mL g}^{-1}$ ). (C) %  $Hg$  removal vs. time (min) (initial  $Hg^{2+}$  concentration =  $441 \text{ ppm}$ ,  $V m^{-1} = 500 \text{ mL g}^{-1}$ ). (D) Fitting of the kinetic data with Lagergren's equation (red solid line).



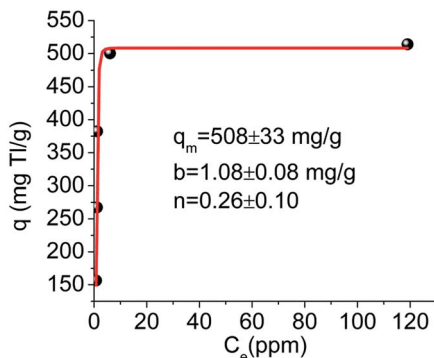


Fig. 30 Isotherm  $\text{Tl}^+$  sorption data for  $\text{K}_6\text{MS}$  ( $\text{pH} \sim 7$ ). The solid line represents the fitting of the data with the Langmuir Freundlich model.

where  $q_e$  = the amount ( $\text{mg g}^{-1}$ ) of metal ion absorbed in equilibrium,  $K_L$  = the Lagergren or first-order rate constant ( $\text{min}^{-1}$ ).<sup>12b</sup> The fitting (Fig. 29D) indicated a maximum  $\text{Hg}^{2+}$  sorption capacity of  $226 \pm 5 \text{ mg g}^{-1}$  (for an initial  $\text{Hg}^{2+}$  concentration of 441 ppm) and a rate constant of  $0.044 \pm 0.003 \text{ min}^{-1}$ .

Extremely high  $\text{Na}^+$  and  $\text{Ca}^{2+}$  concentrations (1 to 5 M) had no influence on the  $\text{Hg}^{2+}$  sorption by  $\text{K}_6\text{MS}$ , and the  $K_d$  values obtained under these conditions were  $\geq 10^6 \text{ mL g}^{-1}$ .

$\text{K}_6\text{MS}$  can efficiently remove a variety of other heavy metal ions, such as  $\text{Pb}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Ag}^+$  and  $\text{Tl}^+$ . Specifically,  $\text{K}_6\text{MS}$  absorbed 98.7–99.7% each of  $\text{Hg}^{2+}$  (166 ppm),  $\text{Pb}^{2+}$  (67 ppm) and  $\text{Cd}^{2+}$  (40 ppm) from a solution containing all three ions. Furthermore,  $\text{K}_6\text{MS}$  exhibited very high  $K_d$  values (up to  $10^7 \text{ mL g}^{-1}$ ) for  $\text{Ag}^+$  exchange.

$\text{K}_6\text{MS}$  was also highly efficient for the removal of  $\text{Tl}^+$ . This ion presents very high toxicity, and its removal from contaminated water resources is of high priority.<sup>44</sup> Isotherm  $\text{Tl}^+$  exchange data (Fig. 30) for  $\text{K}_6\text{MS}$  can be fitted with the Langmuir–Freundlich model:

$$q = q_m \frac{(bC_e)^{\frac{1}{n}}}{1 + (bC_e)^{\frac{1}{n}}} \quad (16)$$

where  $n$  and  $b$  ( $\text{L mg}^{-1}$ ) are constants and  $q_m$  ( $\text{mg g}^{-1}$ ) is the maximum sorption capacity at the equilibrium concentration  $C_e$  (ppm).<sup>13</sup>

The fitting indicated a maximum sorption capacity of  $508 \pm 33 \text{ mg Tl g}^{-1}$ , which is consistent with the absorption of  $\sim 4$  moles of  $\text{Tl}^+$  per formula unit of  $\text{K}_6\text{MS}$ .  $K_d$  values for  $\text{Tl}^+$  exchange were found high (up to  $2.2 \times 10^5 \text{ mL g}^{-1}$ ) revealing the high affinity of  $\text{K}_6\text{MS}$  for  $\text{Tl}^+$ .

### 3.2. $[(\text{Me})_2\text{NH}_2]_2[\text{Sb}_2\text{GeS}_6]$ ( $\text{GeSbS-2}$ )

This compound was isolated *via* a solvothermal reaction of  $\text{GeO}_2$ ,  $\text{Sb}$  and  $\text{S}$  in  $\text{DMF}$ .<sup>45</sup> The structure is chiral and based on the interconnection of helical chains (Fig. 31A). Specifically, there are two types of chains: one chain is left-handed, formed by  $[\text{Sb}_3\text{S}_{10}]$  units and  $\text{GeS}_4$  tetrahedra (Fig. 31B). The second chain is right-handed constructed by  $\text{GeS}_4$  units linked with the middle trigonal bipyramidal  $\text{SbS}_4$  moieties (Fig. 31C). The

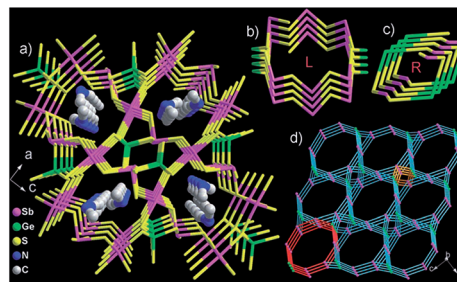


Fig. 31 (a) Structure of  $[(\text{Me})_2\text{NH}_2]_2[\text{Sb}_2\text{GeS}_6]$  along the  $b$ -axis. (b) The left-handed helical chain parallel to the  $b$ -axis. (c) The right-handed helical chain parallel to the  $b$ -axis. (d) The  $(3^2 \times 10^4)$  net topology of the structure. The left-handed and right-handed helical chains are highlighted with red and orange, respectively. Reproduced with permission from ref. 45; © 2008, Wiley-VCH.

$\text{Me}_2\text{NH}_2^+$  ions are located in the pores forming  $\text{N-H}\cdots\text{S}$  hydrogen bonds with the framework (Fig. 31A). From the topological point of view, the structure can be described as a 4-connected net  $[(3^2 \times 10^4)$  net topology], with both  $\text{GeS}_4$  and  $\text{SbS}_4$  units acting as 4-connected nodes (Fig. 31D).

The compound shows ion-exchange properties for alkali metal ions. The  $\text{Cs}^+$  ion-exchange study indicated that  $\sim 93\%$  of the organic cations can be replaced with  $\text{Cs}^+$ . The crystal structure of the  $\text{Cs}^+$ -exchanged compound was also determined indicating topotactic ion-exchange. The material shows high selectivity for  $\text{Cs}^+$ , as revealed by competitive  $\text{Cs}^+$ – $\text{Na}^+$  exchange studies. Thus, the ion-exchange reaction with a  $\text{Na}^+ : \text{Cs}^+$  molar ratio of 10 afforded a product containing only  $\text{Cs}^+$ .

In addition, ion-exchange with a mixture of  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Rb}^+$  and  $\text{Cs}^+$  in a ratio of 10 : 10 : 10 : 1 yielded an exchanged compound with no  $\text{Na}^+$  and  $\text{K}^+$ ,  $\text{Rb}^+$ ,  $\text{Cs}^+$  with a ratio of 1 : 4.6 : 6.3. Thus, despite the large excess of competitive ions, the compound shows high preference for  $\text{Cs}^+$ . The ion-exchange selectivity of this compound is probably due to its microporous framework, which excludes ions with large hydration spheres such as  $\text{Na}^+$  and allows the entrance of ions with limited hydration shells, such as  $\text{Cs}^+$ . **MSIEs** containing relatively rare elements such as  $\text{Ge}$ ,  $\text{In}$ , and  $\text{Ga}$  are not cost-effective; however, their study contributes to our understanding of  $\text{Cs}^+$  and other ion capture processes.

### 3.3. Other crystalline three-dimensional metal sulfides

There are a number of additional **MSIEs** with 3-D structures for which some ion-exchange properties were reported. Characteristic examples are open framework compounds based on T2 (*e.g.*  $\text{Ge}_4\text{S}_{10}^{4-}$ ) or T3 (*e.g.*  $\text{In}_{10}\text{S}_{20}^{10-}$ ) supertetrahedral units, which can exchange their extra-framework organic cations with alkali ions.<sup>46</sup> Another example is  $\text{K}_2\text{Sn}_2\text{S}_5$  ( $\text{KTS-2}$ ), which shows exchange capacity for  $\text{Cs}^+$ ,  $\text{Sr}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Hg}^{2+}$ .<sup>36</sup> However, no detailed ion-exchange studies have been performed for these materials.

In this review we focused on metal sulfides rather than selenides and tellurides, because the relatively high toxicity of selenium and tellurium makes them impractical for





environmental applications. Nevertheless, it should be mentioned that metal selenides also exhibit interesting ion-exchange properties.<sup>47</sup> Characteristic examples are  $(\text{NH}_4)_4\text{-In}_{12}\text{Se}_{20}$ <sup>47a</sup> showing selective heavy metal ion sorption properties and  $(\text{Cs}_6\text{Cl})_2\text{Cs}_5[\text{Ga}_{15}\text{Ge}_9\text{Se}_{48}]$ <sup>47b</sup> displaying both cation and anion exchange capacity.

## 4. Chalcogels with sorption properties for heavy metal ions

Chalcogels are gels based on all chalcogenide frameworks (Fig. 32).<sup>48</sup> They are usually prepared *via* a metathesis reaction involving anionic metal chalcogenide units (Fig. 32) and linking metal ions.

These are highly porous materials combining various interesting properties, such as catalytic activity, photoluminescence, selective gas adsorption, and sorption of organic and inorganic pollutants.<sup>48</sup>

Chalcogels have proven to be excellent sorbents for  $\text{Hg}^{2+}$ .<sup>48a</sup> Specifically, chalcogen-1 which is composed of  $[\text{Ge}_4\text{S}_{10}]^{2-}$  units linked by  $\text{Pt}^{2+}$  shows nearly 100% removal capacity for  $\text{Hg}^{2+}$  solutions.  $K_d$  values for  $\text{Hg}^{2+}$  sorption were found to be enormous (up to  $10^7 \text{ mL g}^{-1}$ ), revealing the potential of chalcogels as heavy metal ion sorbents. The chalcogels show preference for the softer ions, since competitive experiments with the simultaneous presence of  $\text{Hg}^{2+}$  and  $\text{Zn}^{2+}$  indicated only  $\text{Hg}^{2+}$  absorption.<sup>48d</sup> Fig. 33 provides a schematic for the capture of heavy metal ions by chalcogels.

Recently, metal polysulfide chalcogels with anionic frameworks and easily exchangeable cations have been reported. Examples of such materials are  $\text{KC}_6\text{S}_{21}$ ,  $\text{K-Pt-S}_x$  and  $(\text{NH}_4)_{0.2}\text{MoS}_4$ .<sup>15</sup> They show ion-exchange capacity, as demonstrated by the complete replacement of their extra-framework cations by  $\text{Cs}^+$ . These materials, with a combination of significant porosity, soft polysulfide ligands and highly mobile cations, appear to be particularly promising as ion-exchange materials. Thus, further studies of their ion-exchange properties would be interesting.

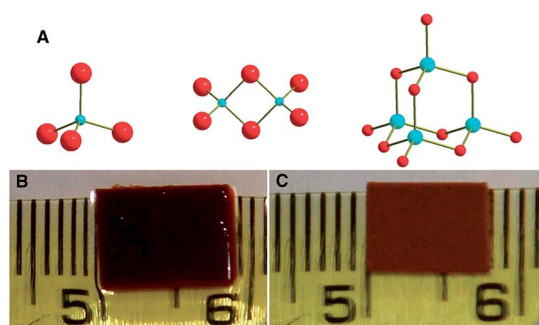


Fig. 32 (A) Different building blocks for the formation of chalcogels. (B) Monolithic gel composed of  $[\text{Ge}_4\text{S}_{10}]^{2-}$  building blocks linked by  $\text{Pt}^{2+}$  ions before supercritical drying. (C) The chalcogel after supercritical drying. Reproduced with permission from ref. 48a © 2007, American Association for the Advancement of Science.

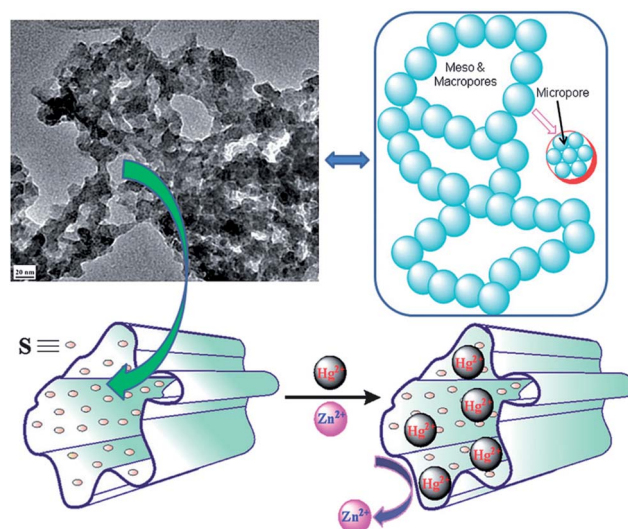


Fig. 33 Schematic for the selective capture of soft heavy metal ions by chalcogels.

## 5. Engineered forms-composites of MSIEs

As described above, almost all **MSIEs** have been tested for their ion exchange properties using the so-called batch (stirring) method. Many industrial and wastewater treatment processes, however, rely on the use of continuous bed flow ion-exchange columns. A material suitable for use as a stationary phase in ion-exchange columns should combine the following characteristics: (i) high sorption capacity and rapid ion-exchange kinetics for the targeted ion, (ii) proper particle size distribution to allow continuous flow through the column and achieve the smallest possible pressure drop of the water coming through the column and (iii) sufficient mechanical strength to tolerate high water pressures. Note that for column applications, the sorbent material should generally display a particle size close to 1 to 2 mm, a size resulting from a practical compromise between limiting the pressure drop and providing adequate surface area of the sorbent for sorption of the ions.<sup>49</sup> **MSIEs** are usually isolated as small size crystals ( $\leq 300 \mu\text{m}$ ).<sup>13</sup> Thus, these materials tend to form fine suspensions in water that may either pass through the column or result in column clogging. To overcome these limitations of **MSIEs**, new approaches are essential to produce engineered forms of these materials to satisfy the requirements of the column testing. Below, we present some results on this new research direction for **MSIEs**.

### 5.1. KMS-2-alginate composite

As described above, KMS-2 shows excellent batch ion-exchange properties; however, the small particle sizes ( $\leq 50 \mu\text{m}$ ) preclude its use in ion-exchange columns. The alginate encapsulation method is a common way to produce materials with particles of specific shape and of suitable size for column applications.<sup>12b</sup> This method involves (a) addition of the sorbent to a water solution of sodium alginate (SA) so that the sorbent particles are





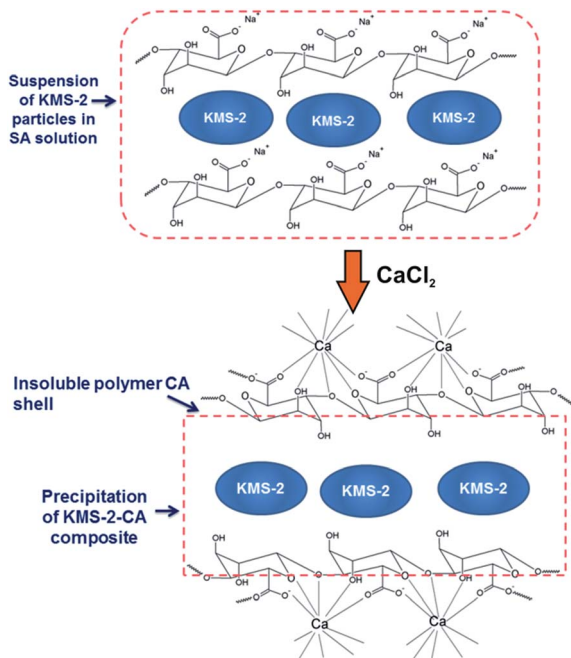


Fig. 34 Schematic process for the isolation of the KMS-2-CA composite material.

enclosed by one or more monolayers of alginate-saturated water and (b) addition of  $\text{CaCl}_2$  to the SA-sorbent suspension, which results in the transformation of the alginate monolayer to a water-insoluble calcium alginate (CA) polymer encapsulating the sorbent particulates (Fig. 34).<sup>12b</sup> Thus, *via* the above method, paper-like KMS-2-CA composite can be prepared (Fig. 35).<sup>50</sup> Note that only a small alginate content ( $\sim 4\%$  wt) is needed to form the composite; thus, KMS-2-CA largely retains the ion-exchange properties of the pristine MSIE material, albeit with somewhat slower kinetics. In addition, the relatively large (mm-size) pieces of the KMS-2-CA composite are suitable for use in columns. To obtain, however, a more stable flow in the column and immobilize the KMS-2-CA particles, the composite was mixed with an inert material such as sand.

KMS-2-CA/sand (mass ratio 1 : 1) columns were tested for  $\text{Ag}^+$  ion-exchange. Nearly 100%  $\text{Ag}^+$  sorption (initial  $\text{Ag}$  concentration was 100 ppm) was observed for at least 80 bed volumes. Interestingly, the column is capable of simultaneous

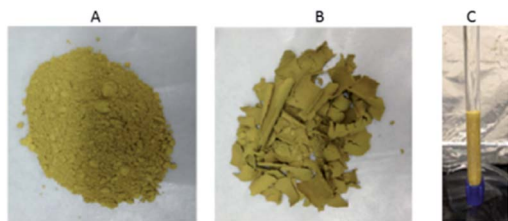


Fig. 35 (A) Pristine layered metal sulfide (KMS-2) with particle size  $\leq 50$   $\mu\text{m}$ . (B) KMS-2-CA composite (particle size  $\geq 1$  mm). (C) Column made with a mixture of KMS-2/CA composite (particle size 1 to 2 mm) and sand (50 to 70 mesh).

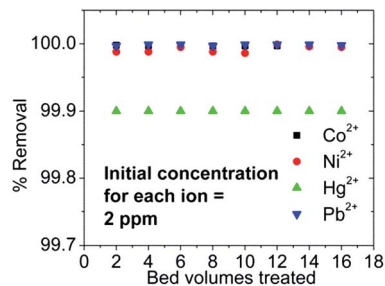


Fig. 36 % removal of  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Hg}^{2+}$  and  $\text{Pb}^{2+}$  vs. bed volume for the column ion exchange with a KMS-2-CA/sand column.

and almost 100% sorption of  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Hg}^{2+}$  and  $\text{Pb}^{2+}$  from a mixture of these ions (initial concentration  $\sim 2$  ppm for each of the ions) (Fig. 36). The final concentrations of all ions in the effluents were found to be well below the EPA acceptable limits.

## 5.2. KMS-1-PAN composite

Polyacrylonitrile (PAN) is a binding polymer suitable for inorganic ion-exchangers. KMS-1-PAN beads (Fig. 37) were prepared by forming a suspension of KMS-1 and PAN in DMSO and adding this suspension to water, resulting in precipitation of the KMS-1-PAN composite.<sup>51</sup> KMS-1-PAN composite samples with different KMS contents were prepared and tested for  $\text{Cs}^+$  ion-exchange with the batch method.

A sample with  $\sim 71\%$  wt KMS-1 showed the optimum  $\text{Cs}^+$  absorption. The results revealed that the composite retains the properties of the pristine KMS-1 material in a significant degree, although the  $\text{Cs}^+$  ion exchange is much slower with the composite. Nevertheless, the separation of the KMS-1-PAN beads from the water solution is easily accomplished.

## 5.3. Porous amorphous MSIEs

A different approach to produce an engineered form of MSIE consists of the synthesis of porous glassy materials that are melt-processable and, thus, can be made in any user defined shape and size. Porous amorphous sulfides were prepared by mixing inorganic salts with a presynthesized compound of the general formula  $\text{A}_2\text{Sn}_2\text{SbS}_6$  ( $\text{A} = \text{K}^+$  or  $\text{Cs}^+$ ), flame-melting the mixture, rapid quenching in water and liquid extraction of the salt (Fig. 38).<sup>52</sup>

The materials with the composition  $\text{Na}_{2-x}\text{K}_x\text{Sn}_2\text{SbS}_6$  and  $\text{Cs}_{2-x}\text{K}_x\text{Sn}_2\text{SbS}_6$  were tested for  $\text{Hg}^{2+}$ ,  $\text{Pb}^{2+}$  and  $\text{Cd}^{2+}$  ion-exchange. Both materials perform excellently as ion-exchangers

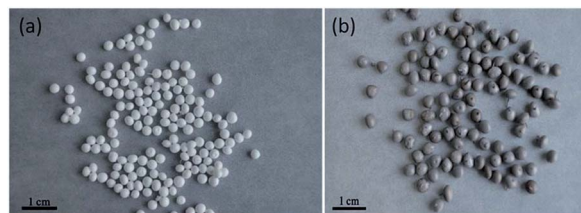


Fig. 37 Images of (a) PAN beads, (b) KMS-1-PAN composite beads.



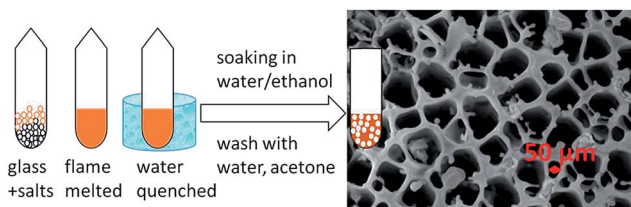


Fig. 38 Procedure for the isolation of porous amorphous MS ion exchangers. Reproduced with permission from ref. 52 © 2015, American Chemical Society.

for these soft metal ions. 99.99%  $\text{Hg}^{2+}$  removal capacities and enormous  $K_d$  values of  $6.2 \times 10^7$  to  $7.2 \times 10^8$   $\text{mL g}^{-1}$  were obtained with these ion exchangers. In addition, significant removal capacities (70–90%) were observed for  $\text{Pb}^{2+}$  and  $\text{Cd}^{2+}$ . Considering that these materials are isolated as melts that can be cut in particles of specific size and shape, they may be appropriate for column testing. Column ion-exchange studies therefore would be interesting.

## 6. Comparison between MSIEs

Some ion-exchange characteristics of representative **MSIEs** are summarized in Table 1. It can be seen that all materials show highly efficient  $\text{Cs}^+$  ion exchange properties, with significant sorption capacities in a relatively wide pH range, rapid sorption kinetics and moderate to excellent selectivity for  $\text{Cs}^+$  vs.  $\text{Na}^+$ .

The highest capacity for  $\text{Cs}^+$  is shown by KMS-2;<sup>13f</sup> however, the most selective  $\text{Cs}^+$  **MSIE** is  $\text{K}_6\text{MS}$ , which exhibits molecular sieve properties excluding ions with large hydration spheres such as  $\text{Na}^+$  and  $\text{Ca}^{2+}$ .<sup>13b</sup> At the same time, one of its cavities is an exact fit for  $\text{Cs}^+$ ; thus, the  $K_d$  values for  $\text{Cs}^+$  exchange are high ( $10^3$  to  $10^4$   $\text{mL g}^{-1}$ ) even with a  $\geq 10^5$ -fold excess of  $\text{Na}^+$  or  $\text{Ca}^{2+}$ .

The **MSIE** with the highest  $\text{Sr}^{2+}$  exchange capacity is KTS-3;<sup>13f</sup> however, the most selective sorbent is KMS-1, showing  $K_d \geq 10^5$   $\text{mL g}^{-1}$  in the presence of a  $\sim 1900$ -fold excess of  $\text{Na}^+$ .<sup>13c</sup> KMS-1 also showed the highest  $\text{Hg}^{2+}$  sorption capacity;<sup>13e</sup> however, LHMS-1 is an exceptional sorbent for  $\text{Hg}^{2+}$ , even under extremely acidic conditions ( $\text{pH} \leq 0$ ).<sup>13f</sup>  $\text{K}_6\text{MS}$  was also studied for its  $\text{Hg}^{2+}$  ion exchange properties, and the results also indicated the exceptional capacity and selectivity of this material to absorb  $\text{Hg}^{2+}$ .<sup>43</sup> KMS-1<sup>13e</sup> and its methylammonium analogue CMS<sup>23</sup> show excellent selectivity for  $\text{Pb}^{2+}$  and  $\text{Cd}^{2+}$  even in the presence of a tremendous excess of  $\text{Na}^+$  or  $\text{Ca}^{2+}$ . CMS exhibits higher  $\text{Pb}^{2+}$  and  $\text{Cd}^{2+}$  sorption capacities but somewhat slower sorption kinetics than KMS-1. KMS-1 also exhibits high affinity for  $\text{Cu}^{2+}$  ion in the presence of  $\text{Na}^+$  and  $\text{Ca}^{2+}$ .

KMS-1<sup>13g</sup> and KTS-3<sup>13f</sup> show similar  $\text{UO}_2^{2+}$  exchange properties. Both materials exhibit very high  $\text{UO}_2^{2+}$  removal capacities which are only slightly affected by hard ions such as  $\text{H}^+$ ,  $\text{Na}^+$  or  $\text{Ca}^{2+}$ .

Furthermore, KMS-2 has significantly higher  $\text{Ni}^{2+}$  sorption capacity<sup>13h</sup> than KMS-1; however, both materials display similar and exceptional selectivity for  $\text{Ni}^{2+}$  ( $K_d \geq 10^5$   $\text{mL g}^{-1}$ ) in the presence of a  $\geq 10^4$ -fold excess of  $\text{Na}^+$ .

Finally,  $\text{K}_6\text{MS}$  is the only **MS** exchanger investigated for its  $\text{Tl}^+$  sorption properties.<sup>43</sup> The first results of these investigations revealed the high  $\text{Tl}^+$  sorption capacity of the material and very high  $K_d$  values for  $\text{Tl}^+$  exchange.

## 7. Comparison of MSIE with other sorbents

At this point, it will be useful to compare the metal ion sorption properties of **MSIEs** with those of other sorbents. The unique characteristic of **MSIE** materials is their soft Lewis basic frameworks, which favor stronger interactions with soft, borderline Lewis acids and the heavier alkali and alkaline earth metal ions, in contrast to the interactions favored by oxidic materials. In addition, typical hard ions, such as  $\text{H}^+$ ,  $\text{Na}^+$ , and  $\text{Ca}^{2+}$ , which strongly interact with oxides, have relatively low or negligible effect on the ion-exchange properties of **MSIEs**. Thus, **MSIE** materials are effective for ion-exchange in the pH range of 1 to 12, whereas typical oxidic sorbents are inactive for  $\text{pH} \leq 3$ –4.<sup>9,10</sup> Furthermore, as discussed above, **MSIEs** achieve very high metal ion removal capacities in the presence of high excesses of  $\text{Na}^+$  or  $\text{Ca}^{2+}$  (and, presumably, other ions such as  $\text{Mg}^{2+}$  and  $\text{Al}^{3+}$ ), which in relatively high concentration cause a drastic decrease of the sorption capacity of oxides.<sup>6,7</sup>

Comparing the **MSIEs** with sulfur-functionalized materials, it can be seen that both types of materials are highly efficient and selective for the sorption of heavy metal ions. However, **MSIEs**, e.g. the **KMS** layered materials, are effective for simultaneous removal of various toxic metal ions, such as  $\text{Hg}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Co}^{2+}$ , and  $\text{UO}_2^{2+}$ , whereas thiol-containing mesoporous silica tends to absorb mainly  $\text{Hg}^{2+}$ .<sup>11</sup> Thus, **MSIEs** may find broader applications in the field of heavy metal ion remediation. The inexpensive hydrothermal synthesis of **MSIEs** is much more attractive than the multistep preparation of sulfur-functionalized materials requiring high cost organic reagents and solvents.<sup>11</sup>

Several studies also indicated that **MSIEs** are extremely stable in air and in both acidic (up to  $\text{pH} \sim 1$ ) and alkaline (up to  $\text{pH} \sim 13$  to 14) water. Their stability in water seems superior to that of silicates and aluminosilicates, which are soluble in both acidic ( $\text{pH} < 3$ ) and alkaline ( $\text{pH} > 9$ ) environments.<sup>8</sup>

A drawback of **MSIEs** is the lack of regeneration capability and reusability after being saturated with heavy metal ions. The very high capacities (up to 50% heavy metal by weight) can compensate for this non-regenerability. An exception to this rule is  $\text{UO}_2^{2+}$ -loaded and  $\text{Cs}^+$  loaded **MSIEs**, which can be easily converted to pristine phases; the regenerated materials can be reused for  $\text{Cs}^+$  and  $\text{UO}_2^{2+}$  sorption.<sup>13d,g</sup> In some cases, **MSIEs** can often be regenerated after the  $\text{Cs}^+$  exchange process and reused with no loss of their exchange capacity.<sup>13d</sup> It is not always necessary, however, to regenerate a sorbent because this causes large amount of secondary liquid waste that needs to be stored. Solid waste occupies much less space, and if it is very stable, it can be properly buried without concern. The heavy metal ion-containing **MSIEs** can be probably considered as ultimate solid waste safe for disposal, since preliminary investigations



indicated minimum leaching of heavy metals from these materials.<sup>13e,f,28</sup>

## 8. Conclusions and prospects

**MSIEs** represent a recently developed and growing class of ion-exchangers, which seems highly promising for environmental remediation applications. They combine various attractive features, such as potential for low cost synthesis, rapid sorption kinetics, high capacity and exceptional selectivity for toxic cations. At the same time, they do not require functionalization, since selectivity for soft ions is innate to these materials. Concerning the sorption of soft heavy metal ions, **MSIEs** outperform any other known material class. The sorption of heavy metal ions by **MSIEs** represents a textbook case of the Pearson's hard-soft-acid-base theory<sup>53</sup> in action: Soft Lewis acids, such as  $\text{Hg}^{2+}$ ,  $\text{Cd}^{2+}$ , and  $\text{Pb}^{2+}$ , are preferentially absorbed by the soft basic ( $\text{S}^{2-}$ -containing) framework of **MSIEs**. Waste minimization is one of the most pressing environmental issues currently facing society, and **MSIEs** by virtue of their high loading capacities could play a significant role in meeting this challenge.

Despite progress in the research on **MSIEs**, this class of ion-exchange materials remains largely unexplored. There are many known phases that may be excellent candidates as ion exchangers; however, their ion-exchange properties were overlooked in the past and were never studied in detail. These include some microporous<sup>46</sup> and layered<sup>54</sup> metal sulfide materials templated by organic cations, as well as various all-inorganic compounds with labile extra-framework alkali ions.<sup>41</sup> Of course, exploratory synthesis may be also a fruitful source of **MSIEs**. The recent development of engineered forms and composites of **MSIEs** is an important milestone, as it forecasts good potential for many real-world applications in the field of wastewater treatment.

Finally, it would be challenging to develop metal sulfide materials that can capture toxic anionic species, such as dichromate, arsenate, and cyanate anions. A possible approach towards this challenge would be the intercalation of species into layered metal sulfide cation exchangers that will have high affinity for specific anions. Of course, the development of **MSIEs** with anion-exchange properties will open an entirely new research direction in the area of ion exchange materials. This task may require the development of cationic metal sulfides. The synthesis of such materials is feasible, as revealed by the recent reports of layered cationic metal chalcogenides.<sup>55</sup> Moving forward, a wealth of research opportunities thus exist for **MSIEs**, and further progress in the understanding of these materials is anticipated in the next few years.

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