Layered metal sulfides: Exceptionally selective agents for radioactive strontium removal

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In this article, we report the family of robust layered sulfides $K_{2x}Mn_xSn_{3-x}S_6$ ($x = 0.5$–0.95) (KMS-1). These materials feature hexagonal $[Mn_xSn_{3-x}S_6]^{2x-}$ slabs of the CdI$_2$ type and contain highly mobile K^+ ions in their interlayer space that are easily exchangeable with other cations and particularly strontium. KMS-1 display outstanding preference for strontium ions in highly alkaline solutions containing extremely large excess of sodium cations as well as in acidic environment where most alternative adsorbents with oxygen ligands are nearly inactive. The implication of these results is that simple layered sulfides should be considered for the efficient remediation of certain nuclear wastes.

chalcogenide | environmental remediation | ion exchange | layered materials | nuclear waste

Current growing interest in nuclear power as a potential solution for global energy may also raise serious environmental and health concerns due to highly radioactive nuclear waste. ^{90}Sr is one of the major heat producers and biohazards in nuclear wastes. The removal of radioactive strontium is essential to reducing the risk of human exposure to radiation and for the considerable cost savings due to minimization of the storage space requirements for the nuclear waste (1, 2). There is a long-standing and continuous research effort to develop highly selective strontium adsorbents for application in a variety of wastes. Inorganic ion exchangers possess a number of advantages as Sr^{2+} adsorbents over the conventional organic ion-exchange resins, such as superior chemical, thermal, and radiation stability (3). The naturally abundant ion exchangers such as clays (3, 4) and zeolites (3) are not effective as strontium adsorbents in nuclear waste solutions with extreme pH values because of their immediate decomposition (i.e., dissolution of their aluminum). Commercial inorganic adsorbents capable for Sr^{2+} adsorption in highly alkaline solutions with extremely high salt concentrations [i.e., conditions present in many nuclear waste types (1)] are mainly limited to titanates and silicotitanates (3, 5, 6). These materials, however, are not effective for Sr^{2+} capture even at mildly acidic conditions (pH < 4–5) because protons inhibit ion exchange (7). Only doped antimony silicates represent Sr^{2+} ion exchangers efficient in strongly acidic environment (pH ≲ 1) (8). Finally, solvent extraction and extraction chromatography methods have proven promising for strontium decontamination of acidic and alkaline nuclear wastes (9–11).

We show here that layered sulfide compounds with ion-exchangeable interlayer cations are not inhibited by protons and can be very efficient Sr^{2+}-ion-removers over a wide pH range. Layered chalcogenides with ion-exchange properties are relatively few (12–16) and are mainly limited to alkali intercalated early transition metal dichalcogenides A_xMQ_2 (A = alkali ion; M = early transition metal from groups 4,5 and 6; Q = S, Se, Te) (13–16). Such materials, however, are not suitable for practical applications because of their hydrolytic instability (16).

Here, we report that the layered $K_{2x}Mn_xSn_{3-x}S_6$ ($x = 0.5$–0.95) (KMS-1) exhibit huge selectivity for Sr^{2+} ions in both acidic and basic environments. They are especially effective in strongly alkaline environments in the presence of an enormous excess of

Na^+ ions. This property is highly relevant to the problem of nuclear waste remediation and points to the class of metal sulfide compounds as a highly promising source of materials for helping to solve it.

Results and Discussion

The KMS-1 materials can be easily prepared on a multigram scale and high purity with solid-state or hydrothermal synthesis techniques. They are extremely stable in atmosphere and water, while they display high thermal stability [see supporting information (SI) Figs. 5–7 (complete materials, instrumentation, and methods are provided in SI Materials and Methods, SI Figs. 5–12, and SI Table 2)]. Single-crystal data,§ obtained from hexagonal-shaped crystals (Fig. 1A) synthesized hydrothermally, revealed a layered structure of $K_{1.9}Mn_{0.95}Sn_{2.05}S_6$ (CdI$_2$ structure type). The layer is built up by edge-sharing "Mn/Sn"S$_6$ octahedra with Mn and Sn atoms occupying the same crystallographic position and all sulfur ligands being three-coordinated (Fig. 1C). K^+ ions are found between the layers and are positionally disordered, a feature that gives them high mobility and the ability to exchange with other ions particularly with strontium (Fig. 1D).

Indeed, polycrystalline samples (Fig. 1B) of KMS-1 can completely replace the K^+ ions with Sr^{2+} within a few hours. This was confirmed with energy dispersive spectroscopy (EDS). Powder x-ray diffraction (PXRD) measurements showed that the exchanged material is isostructural with the pristine confirming a topotactic ion exchange (Fig. 2). A shift of the (003) and (006) Bragg peaks to lower 2θ values (or higher d-spacing) was observed in the diffraction patterns of Sr^{2+}-exchanged products. Alkaline earth ions have a great tendency to be hydrated, and this results in the large c-axes for the Sr^{2+}-exchanged materials. For example, thermal analysis data for Sr^{2+}-exchanged samples revealed the presence of ≈5 H$_2$O molecules per formula unit (SI Fig. 7). The expected Sr:Mn ratio in the exchanged materials should be 1 to satisfy the charge-balance requirements. Surprisingly, a Sr:Mn ratio of ≈0.5 was found because of an unusual oxidation of Mn^{2+} to Mn^{3+} occurring during the strontium exchange processes. The formation of Mn^{3+} is supported by x-ray photoelectron spectroscopy data (see SI Fig. 8 and 9 and SI Table 2).

To assess the strontium removal capacity of KMS-1, we performed Sr^{2+} ion-exchange equilibration studies. The Sr^{2+} ion

Fig. 1. Structure and morphology. (*A*) SEM image of a typical crystal of K$_{1.9}$Mn$_{0.95}$Sn$_{2.05}$S$_6$ (KMS-1) with a hexagonal plate-like shape obtained with a hydrothermal reaction. (*B*) SEM image of polycrystalline K$_{2x}$Mn$_x$Sn$_{3-x}$S$_6$ (*x* = 0.5–0.95) obtained by a solid-state reaction. (*C*) Part of the layer framework of K$_{1.9}$Mn$_{0.95}$Sn$_{2.05}$S$_6$ viewed down the *c*-axis. The Mn-Sn and S atoms are represented by blue and yellow balls, respectively. (*D*) View of the structure, with a polyhedral representation of the layers, along the *c*-axis.

exchange-equilibrium data are shown in Fig. 3*A*. These data can be fitted with the Langmuir isotherm model expressed as

$$q = q_{\mathrm{m}} \frac{bC_e}{(1 + bC_e)}, \qquad [1]$$

where *q* (mg/g) is the amount of the cation adsorbed at the equilibrium concentration C_e (ppm), q_m is the maximum adsorption capacity of the adsorbent, and *b* (liters/mg) is the Langmuir constant related to the free energy of the adsorption.

The maximum Sr^{2+} exchange capacity q_m of KMS-1 (*x* = 0.95) was found to be 77 ± 2 mg/g (or 0.9 mmol/g), which compares well with those of the best strontium adsorbents [Sr^{2+} capacities = 1.0–2.0 mmol/g (7)].

The affinity of the material for Sr^{2+} can be expressed in terms of the distribution coefficient K_d (for definition, see *Materials and Methods* and ref. 17). In Fig. 3*B* are presented the plots of K_d^{Sr} and percent strontium uptake vs. the initial strontium concentration (0.45–79.5 ppm) in the solution. It can be seen that the percent Sr^{2+} removal (83.3–99.4%) is high over a wide range of initial concentrations. Remarkably, the maximum K_d^{Sr} value of

Fig. 2. X-ray powder diffraction patterns for the pristine K$_{2x}$Mn$_x$Sn$_{3-x}$S$_6$ (*x* = 0.5–0.95) and Sr^{2+}-exchanged materials.

Fig. 3. Equilibrium ion-exchange data. (*A*) Sr^{2+}-adsorption isotherms for K$_{2x}$Mn$_x$Sn$_{3-x}$S$_6$·2H$_2$O (*x* = 0.95). The line represents the fitting of the data with the Langmuir isotherm model. (*B*) Plot of Sr uptake and K_d^{Sr} vs. the initial concentration of Sr^{2+}.

1.58 × 10^5 ml/g (Table 1) obtained lies among the highest reported in the literature for Sr^{2+} adsorbents (18).

Taking into account that the pH of nuclear waste and contaminated ground water may vary from strongly acidic to extremely alkaline, we have also studied the effect of pH on Sr^{2+} adsorption. Sr^{2+} ion exchange experiments of KMS-1 with solutions of various pH (1.7–10) indicated significant Sr^{2+} uptake in the entire pH range tested (Fig. 4*A*). The capability of KMS-1 to absorb strontium from acidic solutions is particularly impressive. Specifically, the strontium adsorption at pH ∼ 4.3 did not deviate significantly from the maximum possible (≈95.9% of its maximum theoretical) and remained significant (37.2% of the maximum one) even at pH ∼ 1.7. We have also conducted ion-exchange experiments with trace concentrations of Sr^{2+} (4–6 ppm) at pH ∼ 0.4, 1.2, 2.1, and 3.2 (V:m ∼ 1,000 ml/g) that showed K_d values of 202, 383, 517, and 2.49 × 10^4 ml/g respectively (Fig. 4*B* and Table 1). These K_d^{Sr} values revealed a remarkable strontium affinity of KMS-1 under strongly acidic conditions. For comparison, the commercial strontium adsorbent Na$_2$Ti$_9$O$_{20}$·xH$_2$O (NaTi) displays a K_d of 5,000 ml/g at pH ∼ 4 and 32 ml/g at pH ∼ 2 (for a more detailed comparison, see below) (19).

We performed competitive Sr^{2+}-Na$^+$ experiments (with trace concentrations of ≈1.5–5 ppm of strontium and 1.90 × 10^3 to 2.17 × 10^5-fold excess of sodium) to examine the selectivity of KMS-1 for Sr^{2+} over Na$^+$ under environmentally relevant highly alkaline conditions (pH ∼ 13–14). Sodium is the most abundant cation in highly alkaline nuclear waste (1). The results (Table 1) showed quantitative (≈99.8%) removal of Sr^{2+} from a solution of 0.1 M NaOH (pH ∼ 13, Sr^{2+}:Na$^+$ = 1:1,887, reaction time of ≈24 h) with an enormous K_d of 4.50 × 10^5 ml/g. Even with much higher Na$^+$ concentration (5 M) and pH ∼ 14—i.e., conditions usually present in nuclear waste—KMS-1 retained their exceptional selectivity for strontium with high K_d^{Sr} values of 2.62 (Sr^{2+} initial concentration of ≈2.1 ppm) to 5.84 × 10^3 (Sr^{2+} initial concentration of ≈1.5 ppm) ml/g obtained in 24-h reactions. The KMS-1 continued to absorb Sr^{2+} even after 4 days' reaction[¶] with

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[¶]The strontium adsorption rate at pH ∼ 14 and 5 M Na$^+$ is remarkably fast at the beginning and decelerates as the reaction proceeds. The kinetics of ion exchange is typically controlled by film diffusion or particle diffusion (see ref. 26). In our system, in the first few minutes the sorption is probably controlled by film diffusion, where the slow step is the diffusion of Sr through the liquid diffusion layer surrounding the sorbent particles. Other factors affecting the kinetics of strontium adsorption by KMS-1 may be the structure stability and crystallinity of KMS-1. The layered structure of KMS-1 was largely retained after at least 2 h of contact of the solid with the highly alkaline solution (pH ∼ 14). Within this reaction time, the strontium adsorption was very fast with KMS-1 absorbing ≈50% and 64% of their 24-h Sr^{2+} uptake within 5 min and 2 h, respectively. However, the loss of the crystallinity of KMS-1 and their partial decomposition, which were observed with further increasing the reaction time (SI Fig. 12), presumably result in lowering the strontium adsorption rate. The final form of the material after 4 days of ion exchange contains almost no Sn and S, and Na-Mn in a ratio of 1:2. No Mn ions leached out from KMS-1 during the reaction. This decomposition form of KMS-1 also contains ≈1% wt of Sr, which is strongly bound because it could not be removed with copious washing with water.

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Table 1. Selected data for Sr^{2+} ion exchange experiments of KMS-1

Exchanging cations	Sr^{2+}/Na^+ ratio	Conditions	Initial concentration, ppm	Final concentration, ppm	% removal	K_d, ml/g
Sr^{2+}	—	pH ~ 3.2, $V{:}m$ ~ 971 ml/g	4.09	0.15	**96.3**	**2.49×10^4**
Sr^{2+}	—	pH ~ 7, $V{:}m$ ~ 1,000 ml/g	4.60	0.03	**99.3**	**1.52×10^5**
$Sr^{2+}+Na^+$ (0.1 M)	1/1,887	pH ~ 13, $V{:}m$ ~ 971 ml/g	4.65	0.01	**99.8**	**4.50×10^5**
$Sr^{2+}+Na^+$ (5 M)	$1/2.17 \times 10^5$	pH ~ 14, $V{:}m$ ~ 1,000 ml/g	2.15	0.17	**92.1**	**1.16×10^4**
$Sr^{2+}+Ca^{2+}+Mg^{2+}+Na^++Cs^+$	—	pH ~ 11, $V{:}m$ ~ 990 ml/g	3.70 (Mg)	0.48 (Mg)	**94.5 (Sr)**	6.64×10^3 (Mg)
			11.14 (Ca)	1.17 (Ca)		8.40×10^3 (Ca)
			4.60 (Sr)	0.24 (Sr)		**1.83×10^4 (Sr)**
			9.17 (Cs)	3.17 (Cs)		1.87×10^3 (Cs)
			25.96 (Na)	22.42 (Na)		156.5 (Na)

The % Sr removal and strontium distribution coefficient values are in boldface type.

≈92.1% removal of Sr^{2+} (Sr^{2+} initial concentration of ≈2.1 ppm) and a K_d^{Sr} of 1.16×10^4 ml/g, which is in very good comparison with those (3.70×10^3 to 2.26×10^5 ml/g) of the most efficient inorganic adsorbents (20, 21).

We also tested the effect of a mixture of competitive cations (Na^+, 1.1 mM; Ca^{2+}, 2.8×10^{-1} mM; Mg^{2+}, 1.5×10^{-1} mM; Cs^+, 6.9×10^{-2} mM) on the Sr^{2+} (0.02 mM) ion exchange in alkaline solutions (pH ~ 11, $V{:}m$ = 990 ml/g). The results (Table 1) revealed that the strontium affinity of KMS-1 is hardly affected by the presence of the competitive cations as is apparent by the high K_d^{Sr} value (1.83×10^4 ml/g) obtained under these conditions. The selectivity order determined by the comparison of K_d values is $Sr^{2+} > Ca^{2+} > Mg^{2+} > Cs^+ \gg Na^+$. This order shows the preference of the sulfide materials for the softer ions

(e.g., Sr^{2+} vs. Ca^{2+})[‖] and the ions with the highest charge (i.e., 2+ vs. 1+ cations).

Finally, it would be useful to compare the Sr^{2+} affinity and selectivity of KMS-1 with those of the state-of-the art inorganic adsorbents. In Fig. 4C, the dependence of reported K_d^{Sr} values of various materials (including KMS-1) with the pH of the solution is represented. KMS-1 outperforms commercial adsorbents like sodium silicotitanate (7, 8, 20) and sodium titanate (6–8, 19, 20, 22), as well as others like CRY-1 (cryptomelane-type manganese oxide) (23), under strongly acidic conditions. The KMS-1 contain soft basic sites, the S^{2-} ligands, which display small affinity for hard proton ions. Instead, the strontium exchange of the majority of oxygen-containing materials strongly interferes with proton ions having high affinity for the hard O^{2-} ligands. At the same time, KMS-1 is nearly as effective as the commercial exchangers in highly alkaline environments (pH ~ 14). Sandia octahedral molecular sieves (SOMS) also seem efficient under acidic and alkaline conditions (24), but their selectivity for strontium is dramatically reduced even with the presence of low Na^+ concentrations (24). Sb silicate (SbSi) is the only inorganic adsorbent highly selective for strontium in pH as low as 1 (8), but its ability to be efficient at pH ≥ 14 (pH of many nuclear waste types) is questionable because of its appreciable dissolution at pH ≥ 13 (25).

Conclusion

The KMS-1 compounds are capable of highly selective interactions with Sr^{2+} or $SrOH^+$ [this is the main form of Sr^{2+} at pH > 12.8 (19)] and strong discrimination against hard ions such as Na^+ and H^+. They possess this function despite the fact that their layers have no special features for structural preference (e.g., pore or window openings or rings of sizes specific for Sr). To the best of our knowledge, they represent the only examples ever reported of nonoxidic inorganic ion exchangers showing exceptional selectivity for strontium. The KMS-1 compounds with their soft negatively charged sulfide layers, therefore, point to a new paradigm in terms of the chemical classes that can be considered as selective adsorbents under extreme pH conditions for the effective treatment of radioactive wastes. The importance of metal sulfides in this area is poised to grow.

Fig. 4. Comparison of KMS-1 with known sorbents. (A) Sr^{2+} uptake by $K_{2x}Mn_xSn_{3-x}S_6{\cdot}2H_2O$ (x = 0.75) as a function of pH. The dashed line indicates the maximum theoretical Sr capacity (58 mg of Sr/g) calculated for $K_xMn_xSn_{3-x}S_6{\cdot}2H_2O$ (x = 0.75). (B) Representation of K_d^{Sr} obtained with ion-exchange reactions in acidic solutions (pH ~ 0.4–3.2). The initial Sr^{2+} concentration was ≈4 ppm in all reactions with the exception of the reaction at pH ~ 0.4 with an initial strontium concentration of ≈6 ppm. (Inset) K_d^{Sr} at pH 0.4, 1.2, and 2.1. (C) Diagram representing the dependence of K_d^{Sr} for various materials on the pH. A K_d value greater than 10,000 ml/g is considered excellent (see ref. 19). The data for materials NaTi (sodium titanate), CST (sodium silicotitanate), CRY-1 (cryptomelane-type manganese oxide), SOMS (Sandia octahedral molecular sieves), and SbSi were obtained from the following references: NaTi, refs. 6, 8, 19, 20, and 22; CST, refs. 8 and 20; CRY-1, ref. 23; SOMS, ref. 24; and SbSi, ref. 8.

‖According to the ion-exchange selectivity rules (see ref. 26, pp 158–159), the ion exchanger prefers the cation with the smallest hydrated sphere; i.e., that causing the least swelling. TGA (SI Fig. 11) and XRD (SI Fig. 10) analyses on strontium- and calcium-exchanged KMS-1 materials ions indicated similar hydration (≈5 H_2O) of the intercalated cations and larger c-axes for the Sr^{2+}-exchanged samples, respectively. Therefore, the preference of the material for softer ions explains its selectivity for Sr^{2+} over Ca^{2+} and not hydration-swelling effects.

Materials and Methods

Polycrystalline $K_{2x}Mn_xSn_{3-x}S_6 \cdot yH_2O$ ($x = 0.5$–0.95; $y = 2$–5) (KMS-1) can be synthesized by solid-state reaction of Sn (1.9 mmol), Mn (1.1 mmol), K_2S (2 mmol), and S (16 mmol) at 500°C or by hydrothermal reaction of Sn (60 mmol), Mn (30 mmol), K_2CO_3 (30 mmol), and S (180 mmol) at 200°C. The yield for both preparation methods was found to be ≈80%. Single crystals of KMS-1, suitable for x-ray analysis, were obtained by a hydrothermal reaction of K_2S (0.40 mmol), $MnCl_2$ (0.20 mmol), Sn (0.40 mmol), and S (0.40 mmol) at 220°C. Energy dispersive spectroscopy (EDS) and inductively coupled plasma (ICP)–atomic emission (AES) analyses were used to determine the composition of KMS-1. The purity of various samples was verified by x-ray powder diffraction.

A typical ion-exchange experiment of KMS-1 with Sr^{2+} is as follows. In a suspension of KMS-1(0.07 mmol, 40 mg) in water (20 ml), an excess of $SrCl_2 \cdot 6H_2O$ (1.0 mmol) was added as a solid. The mixture was kept under magnetic stirring or constant shaking for ≈12 h. Then, the dark brown polycrystalline material was isolated by filtration, washed several times with water, acetone, and ether, and dried in air. The distribution coefficient K_d, used for the determination of the affinity and selectivity of compounds KMS-1 for Sr^{2+}, is given by the equation $K_d = (V[(C_0 - C_f)/C_f])/m$, where C_0 and C_f are the initial and equilibrium concentration of M^{n+} (ppm), V is the volume (ml) of the testing solution, and m is the amount of the ion exchanger (g) used in the experiment.

The Sr^{2+} uptake from solutions of various concentrations was studied by the batch method at $V{:}m \sim 1{,}000$ ml/g, at room temperature and 24-h contact. The solids were then separated by centrifugation and filtration [through filter paper (Whatman No. 1)]. The Sr^{2+} content of the solutions was determined with ICP-AES. The data obtained were used for the determination of Sr^{2+} adsorption isotherms. Competitive ion-exchange experiments of KMS-1 were also carried out with the batch method at $V{:}m$ ratio (1,000 ml/g), at room temperature and contact time of 1–7 days.

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