

**Highly Selective Removal of Cesium and Strontium  
Utilizing a New Class of Inorganic Ion Specific Media – 9267**

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**ABSTRACT**

Radionuclides such as Cesium-137 and Strontium-90 are key drivers of liquid waste classification at light water reactors and within the DOE tank farm complexes. The treatment, storage, and disposal of these wastes represents a major cost for nuclear power plant operators, and comprises one of the most challenging technology-driven projects for the DOE Environmental Management (EM) program.

Selective removal of specified isotopes through ion exchange is a common and proven treatment method for liquid waste, yet various aspects of existing technologies leave room for improvement with respect to both cost and effectiveness. We demonstrate a novel class of inorganic ion-exchangers for the selective removal of cesium and strontium, the first of a growing family of patent-pending, potentially elutable, and paramagnetic ion-exchange materials [1]. These highly selective inorganic ion-exchangers display strong chemical, thermal and radiation stability, and can be readily synthesized from low-cost materials, making them a promising alternative to organic ion-exchange resins and crystalline silicotitanate (CST). The introduction of this new family of highly specific ion-exchange agents has potential to both reduce the cost of waste processing, and enable improved waste-classification management in both nuclear power plants (for the separation of Class A from B/C wastes) and DOE tank farms (for the separation of low level waste (LLW) from high level waste (HLW)).

**INTRODUCTION**

Selective removal of cesium and strontium is critical for waste treatment and environmental remediation. Cesium-137 (half-life 30 years) is a strong beta-gamma emitter, and Strontium-90 (half-life 29 years) is a beta emitter and a large source of Cerenkov radiation, resulting in shielding challenges. Both elements are found in the Reactor Coolant System of light water reactors at nuclear power plants, and are present in both spent nuclear fuel and in the liquid HLW found in tank farms at DOE sites. Cesium and strontium are major contributors to both activity and heat load; technologies to separate these isotopes from waste are attractive to managers seeking to control the classification of waste types.

Technologies for removing cesium and strontium have been an active field of research. Notable separation technologies developed for liquid wastes include: (i) solvent extraction, (ii) fractional crystallization, (iii) inorganic ion exchange, and (iv) organic ion exchange. Selection of the appropriate separation technology is typically specific to the application. For example, most liquid waste processing systems at nuclear power plants use ion-exchange media. Additionally, the waste treatment plant (WTP) at Hanford uses highly selective organic ion-exchange resins to remove cesium from HLW. These types

of organic ion-exchangers use molecular recognition to selectively bind—and effectively remove—cesium and strontium. However, in spite of their advantages, these organic ion-exchangers must be synthesized using multi-step organic synthesis processes, and typically have lower exchange capacity compared with their inorganic counterparts. These characteristics can seriously limit the scope of applications for these materials.

An alternative to organic ion-exchangers is emerging for nuclear waste remediation. Inorganic ion-exchangers offer a superior chemical, thermal and radiation stability that is simply not achievable with organic compounds. They can be used to remove both cesium and strontium with a high level of selectivity under a broad pH range. Inorganic ion-exchangers can operate at acidic pH where protons inhibit ion exchange in alternative technologies such as CST. They can also be used at high pH, a condition typically present in many DOE tank farms. For example, inorganic ion-exchangers have shown significant strontium uptake from pH 1.9 to 14. In addition, inorganic ion-exchange materials can be produced using a simple, straightforward process that uses fewer steps than the process used for the production of organic ion-exchange materials (multi-step organic synthesis).

## OVERVIEW OF EXISTING ION EXCHANGE MATERIALS

Ion-exchangers are materials (e.g., resins or sorbents) that exchange ions between two electrolytes or between an electrolyte solution and a complex. Typically, the materials are used to purify, separate, and decontaminate aqueous and other ion-containing solutions of a specific ion [2].

Ion exchange materials work by exchanging mobile ions from an external solution for ions that are electrostatically bound to the functional groups contained within a solid matrix (the ion exchange material). When the functional groups are negatively charged (acidic), the materials are called cation exchangers; when the functional groups are positively charged (basic), the materials are called anion exchangers. Ion exchange materials typically have greater affinity for certain ionic species than for others, making it possible to capture the higher-affinity species (e.g.,  $^{90}\text{Sr}$  and  $^{137}\text{Cs}$ ) from solution in exchange for lower-affinity species (e.g., H). Physically, ion exchangers for industrial use typically comprise small (1-2 mm diameter) beads that form a matrix or support structure. Each bead typically has a highly developed structure of pores on the surface, through which ions can diffuse and become integrated in the underlying matrix.

Both organic and inorganic ion exchange materials have been developed for the selective removal of cesium and strontium in both LLW and HLW. These materials are available in a variety of forms with widely different chemical and physical properties. In general, an ion exchanger is chosen based upon its suitability for a given application.

- *Organic ion exchange resins:* Organic ion exchange resins are commonly used in nuclear waste treatment during the purification of liquids from primary circuits or fuel pools. These resins include polystyrenes, phenolic resins, polysaccharides (such as cellulose), proteins (such as casein, keratin and collagen) and carbonaceous materials (such as charcoals, lignites and coals).
  - *Advantages:* Organic ion exchange resins have several advantages. They are widely available at very low cost, are mechanically strong, and can be treated or stabilized with other additives to improve their uniformity, stability, or sorption selectivity. For example, charcoals can be doped with chemicals to improve their capacity or selectivity, and cellulose can be modified to incorporate phosphate, carbonic, or other acidic functional groups.
  - *Disadvantages:* The materials have lower exchange capacity compared with inorganic exchangers, and are susceptible to both excessive swelling and peptide formation. They

have lower radiation and thermal stabilities than their inorganic counterparts. In addition, many organic exchangers are non-selective and are unstable outside a moderately neutral pH range. Lastly, radiation damage limits their ability to be sufficiently recharged following radioisotope elution, making the materials less desirable for multiple capture/release cycles.

- *Inorganic ion exchange sorbents:* A variety of inorganic materials have emerged in recent years as ion exchangers, including clays [3], zeolites [2,3], and hexacyanoferrates (Prussian Blue) [4]. Inorganic ion exchange materials are commonly used for the treatment of liquid waste streams for which very high chemical cleanliness is not required (e.g., for reclassification of HLW to LLW).
  - *Advantages:* In general, inorganic exchangers are highly selective, making it possible to utilize ion exchange in the event that very high concentrations of competing ions are present. They also exhibit better thermal and radiation stability compared to organic exchangers. Zeolites, in particular, can be manufactured/engineered with a wide variety of chemical properties and pore sizes and are stable at high temps. Titanates are especially good for absorbing  $\text{Sr}^{2+}$  in highly alkaline solutions with extremely high salt concentrations such as those found in nuclear waste [2,5,6].
  - *Disadvantages:* Inorganic media are generally less mechanically and chemically stable than their organic counterparts. Synthetic zeolites, in particular, are relatively high in cost, have limited chemical stability at extreme pH ranges, and their ion specificity is susceptible to interference from similar sized ions. Titanates and silicotitanates are less effective for Sr capture in acidic conditions (pH <4-5) because protons inhibit the ion exchange [7]. Only doped antimony silicates have been shown to be effective at highly acidic pH levels (pH <= 1) [8]. Lastly, while hexacyanoferrates have been shown effective for removal of cesium in solution, they are less effective for the removal of strontium.

## INTRODUCTION OF A NOVEL CLASS OF INORGANIC ION-EXCHANGERS

A class of patent-pending new, potentially elutable materials based upon layered metal sulfides with ion-exchangeable interlayer cations has been developed. An example of such materials,  $\text{K}_{2x}\text{Mn}_x\text{Sn}_{3-x}\text{S}_6$  ( $x = 0.5-0.95$ ) or KMS-1, has been shown to be an exceptionally efficient Sr-ion-remover over a wide range of pH (>96% Sr removal when pH=3.2-14) [1]. Based on its high selectivity for Sr, the material is especially effective in strongly alkaline environments that contain an excess of  $\text{Na}^+$  ions, such as those found in liquid wastes at DOE tank farms. These materials can be easily synthesized using readily available compounds using either a solid-state or hydrothermal synthesis techniques:

- Using solid-state synthesis, a mixture of Sn (1.9 mmol, 226 mg), Mn (1.1 mmol, 60 mg), S (16 mmol, 512 mg), and  $\text{K}_2\text{S}$  (2 mmol, 220 mg), was sealed under vacuum ( $10^{-4}$  Torr) in a silica tube and heated ( $50^\circ\text{C}/\text{h}$ ) to  $500^\circ\text{C}$  for 60 h, followed by cooling to R.T. Removal of excess flux yielded a dark-brown polycrystalline material (0.4 g, ~80% yield based on Sn).
- Using hydrothermal techniques, elemental Sn (60 mmol, 7.140 g), Mn (30 mmol, 1.656 g), S (180 mmol, 5.784 g),  $\text{K}_2\text{CO}_3$  (30 mmol, 4.157 g), and water (40 ml) were mixed in a Teflon-lined stainless-steel autoclave. The autoclave was sealed and placed in a  $200^\circ\text{C}$  box furnace. After 4 d, the autoclave was cooled to RT; filtration, washing, and drying produced a brown polycrystalline product (14.30 g, yield »81%).

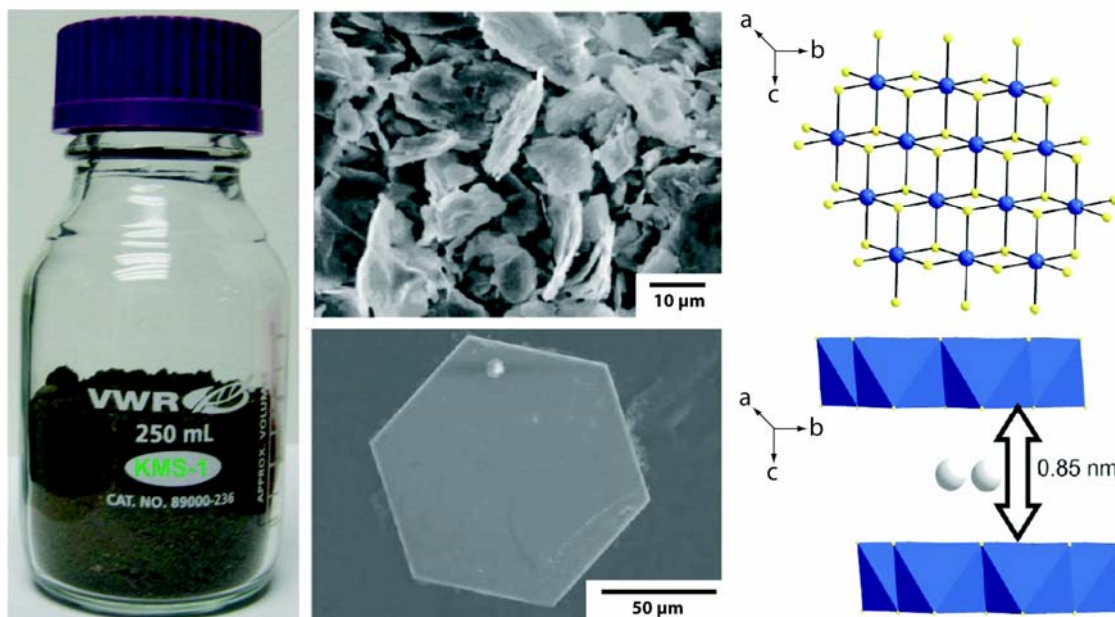


Fig. 1. Macroscopic, microscopic, and structural images of KMS-1. Image adapted from [1]

These methods of preparation produced a layered-structure of  $K_{1.9}Mn_{0.95}Sn_{2.05}S_6$  in which Mn and Sn form edge-sharing Mn/Sn-S octahedra. In this structure, Mn and Sn atoms occupy the same crystallographic position and all S ligands are three-coordinated;  $K^+$  ions are disorderly positioned between layers, allowing them high mobility to exchange with other ions (e.g.,  $Sr^{2+}$ ).

This material exhibits excellent thermal and time-based stability in atmospheric and aqueous environments. Figure 2a shows powder x-ray diffraction (PXRD) patterns for a sample of pristine KMS-1 and its thermogravimetric analysis (TGA) residue prepared at 600°C. There is clear similarity between the two samples, indicative of good thermal stability. Figure 2b shows PXRD patterns of freshly prepared KMS-1 and a sample of KMS-1 after exposure to the atmosphere for approximately two months. Broadening of the (006) peak resulted from atmospheric hydration.

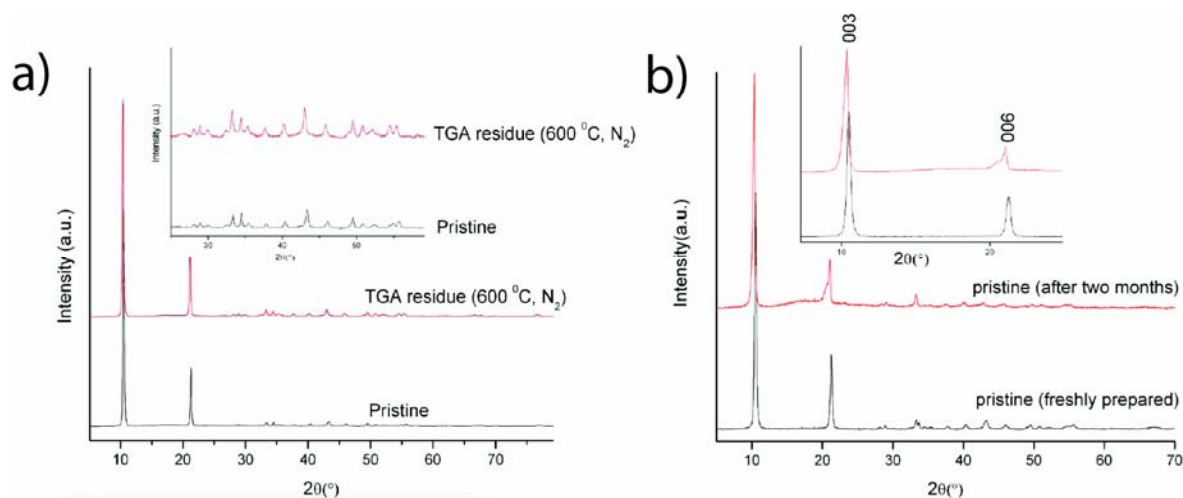


Fig. 2. Thermal and time-based stability of KMS-1. Image adapted from [1]

## MATERIAL PERFORMANCE

**Strontium Removal:** Polycrystalline samples of KMS-1 demonstrate remarkable  $\text{Sr}^{2+}$  removal properties, in which nearly all  $\text{K}^+$  ions are replaced with  $\text{Sr}^{2+}$  ions in just a few hours (confirmed by EDS). Figure 3a shows PXRD measurements of KMS-1 before and after the  $\text{Sr}^{2+}$  ion exchange process. Following  $\text{Sr}^{2+}$  exchange, the (003) and (006) Bragg peaks shifted to lower  $2\theta$  values, indicative of higher d-spacing and topotactic ion exchange—that is, ion exchange by internal atomic displacement in the crystal lattice—in the material. Thermal analysis revealed a final Sr:Mn =  $\sim 0.5$ ; this value is lower than the value predicted by charge-balance requirements (Sr:Mn = 1.0) due to oxidation of  $\text{Mn}^{2+}$  to  $\text{Mn}^{3+}$  during the Sr exchange process (data not shown).

**Ion Exchange-Equilibrium Studies:** Ion-equalization studies were also performed to measure and confirm the ion exchange removal properties of KMS-1. Fig 3b shows the amount of cation adsorbed  $q$  (in mg/g) as a function of the equilibrium concentration  $C_e$  (in ppm). The maximum ion exchange capacity of KMS-1  $q_m$  was determined to be approximately 77 ( $\sim 0.9$  mmol/g), which is similar to that observed for the best  $\text{Sr}^{2+}$  adsorbents. The data was also fitted to a Langmuir isotherm model, as shown in the figure.

The distribution coefficient ( $K_d$ ) of  $\text{Sr}^{2+}$  to KMS-1 was measured as an indicator of affinity; the distribution coefficient describes the sorption/desorption propensity of a compound for a material [8]. Figure 3c shows the percentage uptake and  $K_d$  of  $\text{Sr}^{2+}$  removal as a function of initial concentration. In general, higher  $K_d$  values were observed for lower initial concentrations of  $\text{Sr}^{2+}$ . Interestingly, the maximum  $K_d$  observed ( $=1.58 \times 10^5$  ml/g) is among the highest reported in the literature for an  $\text{Sr}^{2+}$  adsorbent [9].

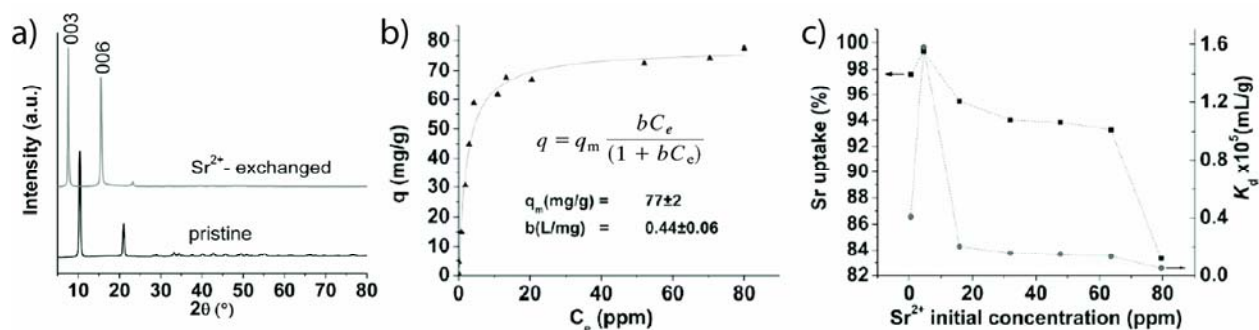


Fig. 3. Ion exchange data for KMS-1 and strontium. a) X-ray powder diffraction patterns for pristine KMS-1 and KMS-1 after  $\text{Sr}^{2+}$  ion adsorption. b)  $\text{Sr}^{2+}$  adsorption isotherms in KMS-1 data and model. c) Plot of  $\text{Sr}^{2+}$  percentage uptake and distribution coefficient vs. initial concentration of  $\text{Sr}^{2+}$ . Image adapted from [1]

**Strontium Removal in Solutions of Varying pH:** An important quality in ion exchange materials for nuclear waste processing is the ability to adsorb  $\text{Sr}^{2+}$  in solutions with widely ranging pH. Experiments on the ability of KMS-1 to adsorb  $\text{Sr}^{2+}$  showed that the material can efficiently adsorb  $\text{Sr}^{2+}$  in both acidic conditions (pH = 3.2) and alkaline conditions (pH = 14) with removal percentages  $>92\%$  (Table 1). At pH = 7 and pH = 13, removal percentages were  $>99\%$ . Sr removal was even significant (removal percentage  $>37\%$ ) in extremely acidic environments (pH = 1.7).

*Strontium Removal in Solutions with Competitive Cations:* Another useful property in determining the merit of an ion exchange material for  $\text{Sr}^{2+}$  is its ability to select for strontium in the presence of other cations. Table 1 describes the relative  $K_d$  for  $\text{Sr}^{2+}$  to KMS-1 in a mixture of competitive cations ( $\text{Na}^+$ , 1.1 mM;  $\text{Ca}^{2+}$ , 0.28 mM;  $\text{Mg}^{2+}$ , 0.15 mM;  $\text{Cs}^+$ , 0.069mM;  $\text{Sr}^{2+}$ , 0.02 mM). The results showed that the ability of KMS-1 to remove Sr is only slightly reduced by the presence of competitive cations and the affinity for Sr was greater than that of all other cations in the mixture ( $K_d = 1.83 \times 10^4$  ml/g). The order of the ion affinity showed that the layered metal sulfides exhibited greatest affinity for the softer ions (e.g., strontium and calcium) and ions with a 2+ vs. 1+ charge.

*Comparison of KMS-1 With Other Known Ion Exchange Materials:* Figure 4 shows the dissociation constant of  $\text{Sr}^{2+}$  as a function of pH for six ion exchange materials: (i) sodium titanate (NaTi), (ii) sodium silicotitanate (CST), (iii) cryptomelane-type manganese oxide (CRY-1), (iv) Sandia octahedral molecular sieves (SOMS), and (v) doped antimony silicates. Compared to the other adsorbents, KMS-1 provides the greatest  $K_d$  for Sr ( $K_d > 10^4$  mL/g) for a wide range of pH. It outperforms commercial adsorbents NaTi and CST, as well as CRY-1

**Table I.** Distribution Coefficients for Strontium Ion Exchange with KMS-1.

Exchanging cations	$\text{Sr}^{2+}/\text{Na}^+$ ratio	Conditions	Initial concentration, ppm	Final concentration, ppm	% removal	$K_d$ , ml/g [8]
$\text{Sr}^{2+}$	—	pH ~ 3.2, V:m ~971 ml/g	4.09	0.15	<b>96.3</b>	<b><math>2.49 \times 10^4</math></b>
$\text{Sr}^{2+}$	—	pH ~ 7.0, V:m ~1,000 ml/g	4.60	0.03	<b>99.3</b>	<b><math>1.52 \times 10^5</math></b>
$\text{Sr}^{2+} + \text{Na}^+$ (0.1 M)	1/1,887	pH ~ 13, V:m ~971 ml/g	4.65	0.01	<b>99.8</b>	<b><math>4.50 \times 10^5</math></b>
$\text{Sr}^{2+} + \text{Na}^+$ (5 M)	$1/2.17 \times 10^3$	pH ~ 14, V:m ~1,000 ml/g	2.15	0.17	<b>92.1</b>	<b><math>1.16 \times 10^4</math></b>
$\text{Sr}^{2+} + \text{Ca}^{2+} + \text{Mg}^{2+} + \text{Na}^+ + \text{Cs}^+$	—	pH ~ 11, V:m ~990 ml/g	3.70 (Mg) 11.14 (Ca) 4.60 (Sr) 9.17 (Cs) 25.96 (Na)	0.48 (Mg) 1.17 (Ca) 0.24 (Sr) 3.17 (Cs) 22.42 (Na)	<b>94.5 (Sr)</b>	$6.64 \times 10^3$ (Mg) $8.40 \times 10^3$ (Ca) <b><math>1.83 \times 10^4</math> (Sr)</b> $1.87 \times 10^3$ (Cs) $1.56 \times 10^2$ (Na)

under highly acidic conditions, and it performs nearly as well as the commercial adsorbents in alkaline conditions. In the figure, SOMS appear to exhibit high  $K_d$  for a variety of pH values as well, but SOMS are much less selective for  $\text{Sr}^{2+}$  than KMS-1, and are, therefore, less efficient for  $\text{Sr}^{2+}$  removal in mixed-cation environments. These characteristics demonstrate that KMS-1 compounds are ideal compounds for  $\text{Sr}^{2+}$  removal in conditions associated with nuclear waste remediation.

## COMMERCIALIZATION

On-going work includes the creation of a wide range of layered metal sulfide ion-exchangers, of which KMS-1 is one such example. The goal is to address the specific, problematic radionuclides that present

the greatest challenge to waste management and remediation (e.g., Cs, Sr, U, Co, Ni, Fe). Surrogate testing is being pursued under conditions similar to those found at target commercial and DOE waste sites. Future developments will involve working closely with nuclear power plants to support the testing of our ion-exchange materials on small samples of actual customer waste, including on-site customer testing at a larger scale. Real-world performance will be studied, possibly validated through an independent audit by the Electric Power Research Institute (EPRI), and will be presented at upcoming conferences. Future studies will also include further analyses of the manufacturing and scaled production costs of these materials.

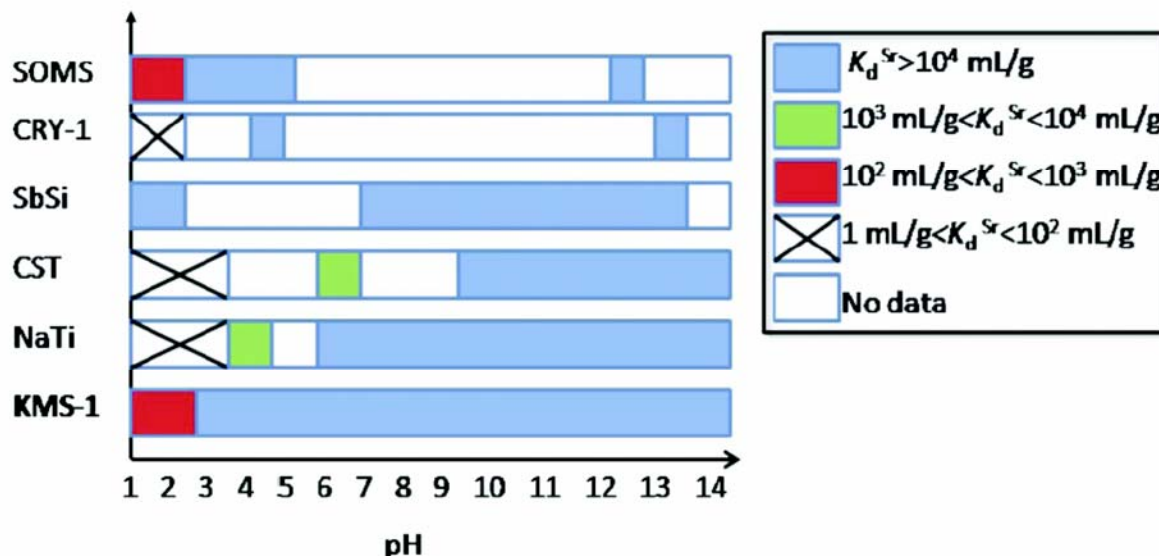


Fig. 4. Comparison of KMS-1 to other adsorbents. Image adapted from [1]

## CONCLUSION

Layered metal sulfides such as KMS-1 are highly specific, high capacity and potentially elutable inorganic ion-exchangers suitable for the removal of cesium and strontium from liquid radioactive wastes. Future testing and verification studies will involve the development of further modified media for other isotopes and applications. These paramagnetic inorganic compounds have several advantages over existing commercial products, including exceptional selectivity, high chemical, thermal, and radiation stability, option of magnetic filtration, and straightforward synthesis. Producing these ion specific media in a cost effective manner will be demonstrated in the next phase of development. These new materials are poised to play a significant role in the treatment of liquid wastes present at both commercial and DOE EM sites, allowing for improved waste classification and management in commercial nuclear power plants (for the separation of Class A from B/C wastes) and DOE tank farms (for the separation of LLW from HLW).

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