Environmental Remediation with Functional Aerogels and Xerogels

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Several different types of aerogels and xerogels are demonstrated as effective sorbents for the capture and/or immobilization of radionuclides and other contaminants in gaseous form [e.g., Hg(0), I2(g), Xe, Kr] as well as ionic form (e.g., Cd2+, Ce4+, Cs+, Cu2+, Fe3+, Hg2+, I−, IO3−, Kr, Pb2+, Rb+, Sr2+, 99Tc7+, U6+, Zn2+). These sorbents have unique properties, which include high specific surface areas, high pore volumes, a range of pore sizes, and functionalities that provide methods for binding radionuclides and other contaminants, generally through physisorption, chemisorption, or a combination thereof. This combination of properties and functionalities makes these types of materials ideal for use as sorbents for capturing radionuclides. The primary base materials that will be discussed in this paper include Ag0-functionalized silica aerogels, Ag0-impregnated aluminosilicate aerogels, Ag0-functionalized aluminosilicate aerogels, metal-impregnated (non-Ag) aluminosilicate aerogels and xerogels, sulfide-based aerogels, and carbon-based aerogel composites. For the capture of I2(g), the materials reported herein show some of the highest iodine loadings ever reported for inorganic sorbents. For the capture of ionic species, these materials also show promise as next-generation materials for active radionuclide remediation. This progress report describes materials fabrication, general properties, and environmental remediation applications.

1. Introduction

Porous sorbents including aerogels, xerogels, metal–organic frameworks (MOFs), and zeolites have received a lot of attention over the past several decades for environmental remediation applications. These sorbents have a variety of uses including the purification of gaseous and aqueous streams through chemisorption, physisorption, ion exchange, molecular sieving, and combinations thereof. All these materials have high specific surface areas (SSA), which are measured in terms of surface area per mass of material (i.e., m² g⁻¹), with values ranging from a few hundred m² g⁻¹ (e.g., zeolites) to several thousand m² g⁻¹ (e.g., MOFs). Table 1 presents examples of some SSA values and pore volumes (Vₚ) for different porous materials in these families.[13–10] To put this into perspective, some MOFs have more surface area of an American football field (5350 m²) per gram of material, e.g., DUT-32 with 6411 m² g⁻¹.[11]

The SSA parameter may be used to compare porous sorbents by normalizing the values on a mass basis, but it does not account for porous materials that are assembled using high-density moieties containing heavy metals such as those used in fabricating chalcogen-based aerogels (e.g., Ge4S104−, SnS42−, SnSe42−), called chalcogels.[12] Thus, in some cases, a correction factor can be used to renormalize the SSA values as a silica equivalent (SSAₑq) value using Equation (1) where SSAₘ is the measured specific surface area for the material of interest, mw₀ₐ is the molecular weight of SiO₂, and mwₐ is the molecular weight of the material of interest normalized to two anions.[13,14] As an example, PtGeS₅ (SSAₘ = 491 m² g⁻¹)[15] would be normalized to Pt₄Ge₆O₆S₃₂ where mwₐ = 200.3 g mol⁻¹ and the corresponding SSAₑq is 1636 m² g⁻¹

SSAₑq = SSAₘ × (mwₐ/mw₀ₐ)⁻¹

(1)

While previous reviews[16–21] have shown the applications where different porous materials can be used to capture and/or immobilize various contaminants, this paper focuses solely on functionalized aerogels and xerogels. Materials discussed herein include oxide-based and sulfide-based aerogels and xerogels as well as carbon-based aerogel composites that have been demonstrated to capture a range of environmental contaminants including those in gaseous form [e.g., Hg(0), I2(g), Xe, Kr] as well as some in ionic form (e.g., Cd2+, Ce4+, Cs+, Cu2+, Fe3+, Hg2+, I−, IO3−, Kr, Pb2+, Rb+, Sr2+, 99Tc7+, U6+, Zn2+) (see Figure 1). Descriptions of common synthesis methods utilized in the literature as well as some precursor selection guidelines will be provided for each class of sorbent.

2. Synthesis Methods

Methods for producing aerogels and xerogels vary widely based on the target chemistry, but the processes involved are

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to be removed through passive diffusion from the liquid medium. As the crosslinking and precipitation processes continue, the gel pieces are during this step, the more difficult this phase becomes. Therefore, rinses will increase the volume of waste produced. The larger the gel pieces are during this step, the more effectively byproducts are removed, but additional rinses will increase the volume of waste produced. The larger the gel pieces are during this step, the more difficult this phase becomes.

Following this stage, the water must be removed though a series of exchanges with an organic solvent; typically, this solvent is ethanol. Again, this is accomplished through passive diffusion to dilute the water present within the gel matrix, and mixing is recommended during this step to help agitate the gels. If the solvent is completely exchanged to an alcohol, this product is called an alcogel (Figure 2e). At this stage, the sample can be dried (e.g., in air, under vacuum) to create a xerogel (Figure 2f); this process can be destructive to the gel network and often results in significantly collapsed pore structures and reduced SSA values. Some things can be done to prevent pore structure collapse and that will be discussed in a later section. An alternative technique is to solvate exchange an alcogel to a polar organic solvent, such as hexane, prior to drying to reduce capillary forces.[24]

If the alcogel is then solvent exchanged with liquid CO₂, this product is called a supercritical fluid solvated gel (SCFSG), and it is a precursor to the final gel product. The SCFSG is a partially dehydrated gel that retains the structural integrity of the gel network but has a lower SSA than the xerogel. This is because the CO₂ is removed from the gel matrix through a combination of diffusion and capillary forces, which is more effective than passive diffusion. The SCFSG is then dried in air or under vacuum to create a xerogel.

Table 1. Summary of specific surface areas (SSA) and pore volumes (V_p) from the literature for a variety of aerogels, xerogels, chalcogels, metal–organic frameworks (MOFs), and zeolites. Materials are listed in descending order by SSA values.

| Material class | Material | SSA [m² g⁻¹] | V_p [cm³ g⁻¹] | Ref. |
|---------------|---------|-------------|--------------|------|
| Aerogel       | Carbon aerogel | 1040–1920  | 0.7–1.9      | [3]  |
|               | Silica aerogel  | 820–1110   | 2.6–4.7      | [1]  |
|               | Al-Si-O       | 940        | 2.4          | [2]  |
|               | Na-Al-Si-O    | 240–880    | 1.3–3.3      | [2]  |
|               | Resorcinol-formaldehyde | 360–830   | 0.4–3.1      | [3]  |
| Xerogel       | Carbon xerogel | 600–850   | 1.4–1.6      | [5]  |
|               | Silica xerogel | 420–970   | 0.2–1.2      | [4]  |
|               | Sn₅S₄         | 0.14       | –            | [6]  |
| Chalcogel     | Sn₂S₃ chalcogel | 460       | 3.9          | [6]  |
|               | PtGe₂S₅ chalcogel | 420       | 3.1          | [6]  |
| MOF           | DUT-32        | 6411       | 2.91         | [11] |
|               | MOF-5         | 2890       | 1.2          | [7]  |
|               | ZIF-8         | 1080       | 0.3          | [8]  |
| Zeolite        | Mordenite     | 570        | 0.3          | [10] |
|               | ZSM-5         | 410        | 0.1          | [10] |
|               | Zeolite A     | 120–240    | 0.2–0.5      | [9]  |
2.1. Making Oxide-Based Aerogels

2.1.1. Precursor Selection and Target Reactions

Table 2 lists a series of different species that can be used to fabricate oxide gels and/or for usage in sol-gel techniques that sometimes yield non-gel products.[22,25–41] Some of these reactants are liquids at room temperature, some are solids, and some are dissolved (or suspended) in a secondary liquid, which is typically an alcohol (e.g., methanol, ethanol, isopropanol). The hydrolysis rates of metal alkoxides vary widely where some compounds are quite stable in air (e.g., TEOS) while others can hydrolyze readily in air (e.g., aluminum tri-sec-butoxide or Al(OMe)₃, sodium ethoxide or NaOEt) and require storage and handling in an inert atmosphere such as a nitrogen glovebox. Depending on the target chemistry, sometimes several options are available for a given bond addition such as tetraethyl orthosilicate (TEOS) or tetramethyl orthosilicate (TMOS) for adding Si–O moieties to an oxide-gel network.

The reactions that occur in the addition of water to an alkoxide are summarized in Figure 2h–j for a Si-based alkoxide based on work by Brinker.[22] These reactions include hydrolysis, alcohol condensation, water condensation, alcoholysis, and esterification. The differences between these reactions include the bonds that are formed and the byproducts that are released as a result.

Catalyst additions to these processes can be used to speed up the gelation time by accelerating the hydrolysis and polycondensation reactions. An array of catalysts have been reported for oxide gels from acids (e.g., HCl, H₂SO₄, HF, HNO₃, and acetic acid or HOAc) to bases (e.g., KOH, NH₄OH), as well as salts (e.g., KF).[42,43] A good example of the differences in gelation times for uncatalyzed reactions versus catalyzed reactions (i.e., 0.05:1 catalyst:TEOS, by mole) was provided by Pope and Mackenzie[43] for comparing gelation times for TEOS hydrolyzed with 4 moles of water per mole of TEOS. They reported gelation times of 12 h for HF, 72 h for HOAc, 107 h for NH₄OH, or >1000 h if uncatalyzed.[43] It is important to fully remove the catalyst during solvent exchanging to prevent corrosion of autoclaves and other equipment at subsequent steps in the gel production process.

2.1.2. Loading Getters onto Aerogel Scaffolds

Getters can be added to oxide aerogel scaffolds using a variety of techniques including ion exchange, impregnation, and functionalization. For instance, materials can be soaked in a solution containing a salt with the desired metal cation such as using AgNO₃ for adding Ag⁺[44] soaked in a molten salt (e.g., AgNO₃, 50/50 AgNO₃/AgClO₃ by mass),[45] or by using (3-mercaptopropyl) trimethoxysilane (3MPTS) to add thiol (−SH) tethers followed by soaking in AgNO₃ (see Figure 3).[46] In the case of thiolation, the Ag links to the −SH tethers that are bound to an organic moiety connected to the silica backbone of the base aerogel material. The thiolation process is conducted by first hydrating the gels in a humid glass jar overnight, adding 3MPTS dropwise to the gels at ≈1.5 mL g⁻¹ of unhydrated sample (the mass before hydration), loading the gels into a high-pressure autoclave at 150 °C, loading the vessel with liquid CO₂ at 24 MPa, and allowing this to sit for up to 2 d in supercritical CO₂. Following the soak at 150 °C, the CO₂ can be vented as a gas and the gel material removed for the subsequent step of adding the getter (e.g., Ag⁺ with AgNO₃).

Ion exchange processes are commonly practiced for replacing cations within zeolite frameworks and this same approach can be applied to aerogel/xerogel chemistries. The selected getter loading process will depend on the gel chemistry, chemical compatibility with the available options, and the getter chemistry of choice. For instance, each getter will have different solubilities in different solvents, where some solvents could destroy (e.g., dissolve) the scaffold network; dissolving the getter additive in the base solvent can drastically change the pH of the solution.[46] For example, acidic solutions can dissolve silica networks.

2.2. Making Chalcogen-Based Aerogels

Chalcogenide aerogels, also called chalcogels, can be prepared through different, albeit similar, methods to oxide-based gels but generally with non-oxide precursors. These processes include 1) thiolysis of metal alkoxides with H₂S, 2) aggregation of nanoparticles, or 3) metathesis reactions (i.e., chemical linkage of chalcogenide clusters with interlinking metal ions). Several different example chemistries for each synthesis...
Figure 2. Process flow diagram for making g) aerogels or f-2) xerogels starting with a) precursor solutions; additional stages include b) mixing precursors, c) the sol, d) hydrogels, e) alcogels, and f-1) liquid CO₂ exchange; Adapted with permission. [2] Copyright 2017, American Chemical Society.

oxide reactions

(h) Hydrolysis/esterification, i) alcohol condensation/alcoholysis, and j) water condensation/hydrolysis processes where “R” denotes a charged organic group, e.g., CH₃⁺, C₂H₅⁺ (after Brinker[22]). Adapted with permission. [2] Copyright 2017, American Chemical Society.

sulfide reactions

(k) Thiolysis and l) condensation of Ge(OR)₄ metal alkoxide using H₂S where “R” denotes a charged organic group, e.g., CH₃⁺, C₂H₅⁺ (after Brock and Yu[23]).
such as CdSe or CdTe.

The thiolysis synthesis route for making chalcogels is similar to that described in Section 2.1 for producing oxide-based aerogels using metal alkoxides. In this case, the same metal alkoxides can be used but, instead of adding H$_2$O to hydrolyze the alkoxides and build an oxide-based network through −O− bridges, H$_2$S(g) is bubbled through the solution; the effect of adding H$_2$S is similar to that of adding H$_2$O, but adding H$_2$S results in −S− bridges. This process is shown schematically in Figure 2k,l, which is based off a description provided by Brock and Yu.[23]

The same process can also be used to create −Se− or −Te− bridges by exposing materials to H$_2$Se(g) or H$_2$Te(g), respectively, but these gases are extremely toxic. Alternative methods have been employed by adding metal salts and Se$_0$ or Te$_0$ to a material followed by heating to precipitate crystals with a matrix such as CdSe or CdTe.[66]

### Table 2. Summary of various alkoxide precursor options and chemistries that they provide for the gel network, sorted alphabetically based on network cation charge (M$^{n+}$) from high (n = 5) to low (n = 1) oxidation states. Information provided here include the bond addition to the network, the additive(s) used for these additives in the literature, and references where these materials have been used to fabricate gel materials or as additives in sol-gel processes.

| M$^{n+}$ (n = | Network cation | Bond addition(s) | Additive (formula) | Common (or IUPAC) name | Common abbrev. | Ref. |
|---|---|---|---|---|---|---|
| +5 | Nb$^{5+}$ | Nb−O | Nb(OC$_3$H$_7$)$_3$ | Niobium(V) ethoxide | NbOEt | [25] |
| | Ta$^{5+}$ | Ta−O | Ta(OC$_3$H$_7$)$_5$ | Tantalum(V) ethoxide | TaOEt | [26] |
| | V$^{5+}$ | O=V−O | VO(OC$_3$H$_7$)$_3$ | Vanadyl isopropoxide | VOPr | [27] |
| +4 | Ge$^{4+}$ | Ge−O | Ge(OC$_3$H$_7$)$_4$ | Tetraethyl orthogermanate | GeOEt | [28] |
| | Si$^{4+}$ | Si−O | Si(OC$_3$H$_7$)$_4$ | Tetraethyl orthosilicate | TEOS | [2] |
| | Sn$^{4+}$ | Sn−O | Sn(OC$_3$H$_7$)$_4$ | Tetramethyl orthosilicate | TMOS | [29] |
| | Ti$^{4+}$ | Ti−O | Ti(OC$_3$H$_7$)$_4$ | Titanium(IV) ethoxide | TiOEt | [31] |
| | Zr$^{4+}$ | Zr−O | Zr(OC$_3$H$_7$)$_4$ | Zirconium(IV) propoxide | ZrOPr | [32] |
| +3 | Al$^{3+}$ | Al−O | Al(OC$_3$H$_7$)$_3$ | Aluminum tri-sec-butoxide | Al(OBu$_3$)$_3$ | [2] |
| | B$^{3+}$ | B−O | B(OC$_3$H$_7$)$_3$ | Triethyl borate | TEOB | [33] |
| | Sb$^{3+}$ | Sb−O | Sb(OC$_3$H$_7$)$_3$ | Antimony(III) ethoxide | SbOEt | [35] |
| | Y$^{3+}$ | Y−O | Y(OC$_3$H$_7$)$_3$ | Yttrium(III) tris(isopropoxide) | YOPr | [36] |
| +2 | Ca$^{2+}$ | Ca−O | Ca(OC$_3$H$_7$)$_2$ | Calcium 2-methoxyethoxide | CaOMeEt | [37] |
| | Mg$^{2+}$ | Mg−O | Mg(OC$_3$H$_7$)$_2$ | Magnesium methoxide | MgOMe | [38] |
| | Cu$^{2+}$ | Cu−O | Cu(OC$_3$H$_7$)$_2$ | Copper(II) methoxide | CuOMe | [39] |
| +1 | K$^+$ | K−O | KO(OC$_3$H$_7$)$_2$ | Potassium ethoxide | KOEt | [40] |
| | Na$^+$ | Na−O | Na(OC$_3$H$_7$)$_2$ | Sodium methoxide | NaOMe | [41] |

### 2.2.2. Nanoparticle Aggregation

For nanoparticle aggregation, metal chalcogenides have been shown to interconnect if prepared through room-temperature reverse-micellar strategies or high-temperature arrested-precipitation. The chemistries demonstrated with this technology include CdS, CdSe, PbS, and ZnS. It was observed in the work by Mohanan and Arachchige[53] that these materials tended to have short-range order evidenced by semicrystalline nanoparticles observed with transmission electron microscopy (TEM). The SSA values for gels produced by Mohanan and Arachchige[53] with this technique ranged from 120–250 m$^2$ g$^{-1}$.

In addition to this work, chalcogels produced through nanoparticle agglomeration can be ion exchanged to produce even new chemistries. In a study by Yao et al.,[64] CdSe gels were exchanged with Ag$^+$ using AgNO$_3$ dissolved in methanol to yield Ag$_2$Se aerogels. The starting CdSe gel had an SSA of 133 m$^2$ g$^{-1}$ and, after exchange, the Ag$_2$Se aerogel had an SSA of 111 m$^2$ g$^{-1}$.

### 2.2.3. Metathesis Reactions: Chemical Linkage of Clusters and Interlinking Metals

Producing chalcogels using the chalcogenide clusters and interlinking metal ions is a fairly recent discovery[13,14] that opens up
more options and chemical flexibility than previous methods for making new chalcogel chemistries ranging from simple to complex. The available list of clusters is still growing as new chemistries can be synthesized following existing procedures. Some of the more well-studied chemistries include Ge-(S,Se), Sn-(S,Se), Mo-S, and W-S systems. In most cases, the chalcogenide clusters are not commercially available and must be synthesized. For instance, one of the salts used to provide Ge_4S_{10}^{4−}, [(CH_3)4N]_2GeS_{10}, is made hydrothermally from (CH_3)4NOH, Ge powder, and S powder where the product solution can be filtered and a solvent added (e.g., acetone) to induce precipitation/crystallization toward the target compound. Common solvents for dissolving these precursors include water and formamide. Two examples, which are shown in Figure 4 are the synthesis of CoNiMoS_4 and SnS_3 chalcogels described elsewhere,[6,53,68,69] For CoNiMoS_4, separate solutions of Ni(NO_3)_2, CoCl_2, and (NH_4)_2MoS_4 are dissolved in formamide, combined and mixed, and then casted into polypropylene vials to undergo gelation. For SnS_3, chalcogel synthesis, Na_4Sn_2S_6·14H_2O and Sn(II) acetate are separately dissolved in formamide, combined and mixed, and then cast to undergo gelation.

### 3. Iodine Capture with Metal-Functionalized Aerogels and Xerogels

#### 3.1. Silver-Functionalized Silica Aerogel

Silver-functionalized silica aerogels (Ag_0^SA) are a relatively new class of iodine sorbents that are being evaluated by Matyáš et al.[46,70] to replace silver mordenite (Ag_0^Z) in nuclear fuel reprocessing off-gas schemes proposed by the U.S. Department of Energy Office of Nuclear Energy (DOE-NE); note that DOE-NE currently considers Ag_0^Z as the baseline technology for I_2(g) capture. The Ag_0^SA sorbent has documented decontamination factors (DFs) upward of 10000 in laboratory tests of dissolve off-gas streams, where DF is a metric for determining the effectiveness of the sorbent to remove a contaminant of interest from a stream (sometimes containing other species that might compete with the binding sites).[46,71] The DF parameter is defined in Equation (2) where CE is the capture efficiency (e.g., if 99.99% is captured, CE = 0.9999 and DF = 10000).[16] The process for synthesizing these materials consists of several steps: 1) commercially available silica aerogel granules are heat-treated to remove hydrophobic silyl functional groups from the aerogel surfaces, 2) a thiol (i.e., −SH) layer is added to the gel using the process mentioned above with 3MPTS (thiolation; see Section 2.1.2), 3) silver ions (i.e., Ag^+), Sn^2+, and Pb^2+ are added to the gel through chemisorption to the sulfur in the thiol groups (i.e., Ag-impregnation; −S-Ag), and 4) the silver is reduced under a flowing stream of H_2/Ar gas (i.e., Ag-functionalization; −SH + Ag^0, see Figure 3. Upon I_2(g) capture, AgI crystals are formed within the composite sorbent.

\[
DF = 1/(1 − CE)
\]

Some of the benefits of the Ag_0^SA over the Ag_0^Z include a higher capacity for iodine (i.e., ≈480 mg g^{−1}, ≈3–4× greater than Ag_0^Z)[56,70,71] and a higher functionality after aging in NO_3 atmosphere and high-humidity environments (both of which could

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Table 3. Summary of different types of commonly studied chalcogel chemistries. Note that solvents used are not included herein and the reader is referred to the primary literature for the full synthesis procedures.

| Method                  | Chemistry (family) | Primary precursors(s)ᵃ | Interlinking metal(s) | Ref(s) |
|-------------------------|--------------------|------------------------|-----------------------|--------|
| Alkoxide thiolation     | Ge-S               | Ge(OCH_3)3, H_2S       | Ge^6+                 | [48]   |
|                         | La-S               | La(Ni(OCH_3)3), H_2S   | La^3+                | [49]   |
|                         | Nb-S               | Nb(OCH_3)3, H_2S       | Nb^3+                | [50]   |
|                         | Ti-S               | Ti(OCH_3)3, H_2S       | Ti^4+                | [50]   |
|                         | W-S                | W(OCH_3)3, H_2S        | W^6+                 | [51]   |
|                         | Zn-S               | Zn(OCH_3)3, H_2S       | Zn^2+                | [52]   |
| Nanoparticle aggregation| CdS                | Cd(NO_3)_2, Na_2S      | Cd^2+                | [53]   |
|                         | CdSe               | Cd(NO_3)_2, Na_2Se     | Cd^2+                | [53]   |
|                         | PbS                | Pb(NO_3)_2, Na_2S      | Pb^2+                | [53]   |
|                         | ZnS                | Zn(OAc)_2, Na_2S       | Zn^2+                | [53]   |
| Metathesis reactions    | Pt(Ge,Sn)(S,Se)    | Ge(S,S,Se)^{10−}, Sn(S,S,Se)^{6−}, Sn(S,S,Se)^{4−} | Pt^{2+}               | [13−15] |
|                         | (Mo,W)-M-S         | (Mo,W)S^{2−}, Co^{2+}, Ni^{2+} | [54,55] |
|                         | (K,Na)             | AsS_{3}^{3−}, SbS_{3}^{3−}, Fe^{3+}, K^{+}, Na^{+} | [56,57] |
|                         | (Sn,As)-Fe (S,Te)  | Sn_{2}(S,Se)^{6−}, Sn_{2}(S,Se)^{4−}, SbSe_{2}^{−} | [12,58] |
|                         | Zn-Sn-S            | Sn_{2}S_{4}^{2−}, Sn_{2}S_{4}^{4−}, Sn_{2}S_{4}^{6−} | Zn^{2+}               | [59]   |
|                         | Fe-Sn-S            | Fe_{2}S_{2}^{2−}, Sn_{2}S_{4}^{4−}, Fe_{2}S_{2}^{4−}, Sn_{2}S_{4}^{6−} | [60]   |
|                         | Fe-M-Sn-S          | Fe_{2}S_{2}^{2−}, Sn_{2}S_{4}^{4−}, Zn^{2+}, Sn^{2+}, Ni^{2+}, Co^{2+} | [61]   |
|                         | Mo-Co-M-S          | MoS_{2}^{−}, Co^{2+}, Pb^{2+}, Cd^{2+}, Pd^{2+}, Cr^{3+}, Bi^{3+} | [62]   |

ᵃOAc denotes acetate (or CH_3COO^−).

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**Figure 3.** Cartoon showing Ag^0 moieties attaching to thiol tethers using 3MPTS (see Section 2.1.2). Reproduced with permission.[16] Copyright 2016, Elsevier.
be observed in a nuclear fuel reprocessing facility. Additionally, Ag0SA has thiol groups that help prevent oxidation of Ag0, a process that renders the sorbent less effective, and it can be consolidated into a multiphase waste form containing AgI particles encapsulated within a glassy silica matrix.

In a recent paper by Matyáš et al., X-ray photoelectron spectroscopy analysis on base sorbents and sorbents loaded with I2(g) revealed some key insights into the way that this sorbent works. For instance, when the sorbents were exposed to a 1 vol% NO(g) atmosphere during an aging experiment, the Ag0 nanoparticle sizes increased and free sulfate was observed on the surfaces of the material due to oxidized thiol groups (i.e., S2+ → S6+). These changes to the material prevented full utilization of the Ag0 for I2(g) capture. In some cases, Ag2SO4 was observed, providing evidence that the thiol layers help act as a buffer to prevent oxidation of the Ag0, because the Ag2SO4 crystals tend to surround the Ag0 nanocrystals and act as a barrier to further Ag0 oxidation. Unfortunately, this barrier layer lowers the Ag0 accessibility during iodine capture experiments, resulting in decreased I2(g) sorption capacity. Studies demonstrated that the sorbent could be regenerated under a reducing gas stream to revert the oxidized Ag+ back to Ag0 and oxidized SO4(2-) back to S6+. After aging, the Ag0SA showed a reduced I2(g) sorption capacity of 43 relative%, but this was in comparison to a 85 relative% reduction for the Ag0Z,

\[ K_d = \left( \frac{c_i - c_t}{c_t} \right) \left( \frac{V}{m} \right) \] (3)

\[ c_i \approx 0.044 \text{ mmol L}^{-1} \]

3.2.2. Silver-Loaded Aluminosilicates for Iodine Capture

Silver-loaded aluminosilicate aerogels were developed as follow-on work to the silver-functionalized silica aerogels. For this work, Na-Al-Si-O and (Na-free) Al-Si-O aerogels were fabricated from metal alkoxides including TEOS, Al(OBUt)3, NaOMe, and NaOEt (see Table 2 for definitions) with the target compositions of NaAlSiO4 and AlSiO1.5, respectively. For some formulations, an H2OAc catalyst was implemented to reduce gelation times. A series of different parameters were evaluated during the synthesis.
including the Na-precursor, cosolvent alcohols (e.g., methanol, ethanol, isopropanol) utilized to suspend the Na and Al precursors, batch size, mixing times, and the mixing environment (i.e., in air or within a nitrogen glovebox). Following gelation, gels were removed from the casting vials, diced, and rinsed with 50/50 ethanol/DIW (10×), followed by solvent exchanges to pure ethanol (10×), exchanged in liquid CO2 (10×), then the vessel was taken to the supercritical CO2 state, and the CO2 was vented as a gas, yielding aerogels. Several batches resulted in high SSA values ranging from 517 to 882 m² g⁻¹ for the Na-Al-Si-O aerogels and up to 942 m² g⁻¹ for Al-Si-O aerogels. Examples of each alcogel and aerogel are shown in Figure S2 (Supporting Information).

Following gel synthesis, different approaches were utilized to load Ag into the gel network including: 1) soaking as-made (AM) gels in AgNO₃ solutions followed by drying (Ag-impregnation), 2) reducing the Ag⁺ in gels that underwent Ag-impregnation to Ag⁰ under a flowing stream of 2.7%H₂/Ar gas (Ag-reduction), and 3) thiolating gels that experienced Ag-impregnation and Ag-reduction (Ag-functionalization). The appearances of these materials afterward were notably different in color (note that pictures of the materials can be found in the original work).[2] During chemical analysis of the gels after Ag-impregnation, the Na concentrations in the Na-Al-Si-O base gels were really low, and nearly 0 mass% in some cases. After additional Ag-exchange testing, the Ag⁺ was found to replace the Na⁺ in the gel network. After analyzing the Al-Si-O gels (those without Na), it was clear that the Ag-content was much lower at 12 at% versus 35 at% for Ag-functionalized gels (starting from Na-Al-Si-O gels containing Na). Analyses with TEM and powder X-ray diffraction (PXRD) on functionalized gels revealed discrete and consistently sized Ag⁰ nanoparticles present within the gels, which ranged between ~3 and 14 nm in diameter (see Figure 5).

Iodine loadings were conducted in a polymer autoclave containing the sample and 99.99% pure iodine crystals at 150 °C over the course of 24 h. To remove physisorbed iodine, the iodine was removed from the container, and the samples were placed back into the oven without the iodine for ~1 h.

Figure 6a provides visual appearances for the thiolated and Ag⁰-functionalized Na-Al-Si-O aerogels both inside and outside the H₂/Ar Ag-reduction apparatus. The PXRD patterns of the as-made, Ag-functionalized, and iodine-loaded Na-Al-Si-O aerogels are provided in Figure 6b. The AM aerogel had a broad diffraction peak centered around 29° 2θ, which is indicative of an amorphous network without long-range order. The Ag-functionalized aerogel did not have the same diffraction peak as the as-made aerogel, but rather had some broad peaks lower.

Figure 5. a–e) TEM images and f–i) powder X-ray diffraction patterns from Ag-functionalized Na-Al-Si-O aerogels and an Al-Si-O aerogel (AS-1-SH-Ag⁰). These data show that the Ag present within these gels is crystalline Ag⁰. Adapted with permission.[2] Copyright 2017, American Chemical Society.
centered around 38°–46° 2θ and 65° 2θ, which corresponded well with crystalline Ag0 (Fm3m, ICSD No. 53761)[77] with an average crystallite size of 3.2 nm. The PXRD pattern for the iodine-loaded aerogel showed very strong diffraction peaks for AgI as verified by a match with pure AgI and contained a mixture of hexagonal (P63mc, ICSD No. 62790)[78] and cubic (F43m, ICSD No. 61542)[79] crystalline morphologies.

The iodine-loading capacities for these materials were rather high based on mass uptake and confirmed with scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDS) analysis showing high Ag-utilization (I:Ag molar ratio). This means that the iodine loadings were consistent with the Ag-loadings. The loadings based on mass uptake on a Is1 mm−1 basis (mass of iodine per mass of starting sample) are shown along with the mass% of iodine measured in the sample via SEM-EDS analysis for comparison in Figure 6c. Also included for comparison are data collected for Ag0Z. The iodine loadings (mIs m−1) for Ag-impregnated (Ag+) and Ag-reduced (Ag0), thiolated/Ag-impregnated (SH-Ag+), thiolated (SH), and silver mordenite as a comparison (shown as AgZ). d) Comparison of SSA values for samples at different stages during the synthesis process including as-made (AM), heat-treated at 350 °C for 30 min (HT), SH, Ag+, Ag0, SH-Ag+, and thiolated/Ag-reduced (SH-Ag0 or Ag-functionalized); included are TEM micrographs showing the as-made Na-Al-Si-O and Ag-exchanged (Ag-Al-Si-O) aerogels. Adapted with permission.[2] Copyright 2017, American Chemical Society.

Figure 6. a) Pictures of thiolated/Ag-impregnated and Ag-functionalized Na-Al-Si-O aerogels within the Ag-reduction chamber (under flowing H2/Ar); pictures of thiolated/Ag-impregnated, Ag-functionalized, and iodine-loaded Na-Al-Si-O aerogels; a refinement of Ag (ICSD No. 53761)[77] is shown in addition to the PXRD pattern of 99.999% pure AgI. c) Iodine uptake of various samples including thiolated/Ag-functionalized (SH-Ag0), Ag-reduced (Ag0), thiolated/Ag+ -impregnated (SH-Ag+), thiolated (SH), and silver mordenite as a comparison (shown as AgZ). d) Comparison of SSA values for samples at different stages during the synthesis process including as-made (AM), heat-treated at 350 °C for 30 min (HT), SH, Ag+, Ag0, SH-Ag+, and thiolated/Ag-reduced (SH-Ag0 or Ag-functionalized); included are TEM micrographs showing the as-made Na-Al-Si-O and Ag-exchanged (Ag-Al-Si-O) aerogels. Adapted with permission.[2] Copyright 2017, American Chemical Society.
The most detrimental process step for lowering the SSA values is the heat-treatment process (350 °C for 30 min in air) at the front end that is used to strengthen the gel network so that it does not collapse during the thiolation and/or Ag⁺-impregnation steps. This heat treatment was also adopted for unthiolated gel processing. This step could be avoided but would likely result in gel damage during subsequent steps such as the Ag⁺-impregnation step. The second most detrimental step resulting in lowered SSA values was the thiolation process.

Following the 2017 study,[2] additional comparisons were made in a 2020 study[80] between Ag-loaded aluminosilicate aerogels, heat-treated aerogels, and xerogels. A critical difference between the 2020 study[80] and the 2017 study[2] is that the new work utilized a simplified process. For instance, no Ag reduction (using H₂/Ar) and no thiolation were implemented, and xerogels were introduced into the process. Based on the 2017 study,[2] iodine loadings were still determined to be high when the Ag⁺ was exchanged into the base material (0.517 m² g⁻¹) without reducing the silver to Ag⁰.

Here, similar base materials in the alcogel state (see Figure 2e) were either converted to aerogels in a critical point dryer (Figure 2f) or dried in a vacuum desiccator to yield xerogels (Figure 2f-2). Another difference in this study was that the aerogels retained nearly the full SSA (i.e., 531 m² g⁻¹) as the aerogel counterparts (598 m² g⁻¹) due to some process improvements based on the 2017 study.[2] These improvements included a longer aging time for the alcogels (several months vs a few days) and ethanol removal under vacuum within a desiccator instead of drying them in air, where drying in air is a more energetic process. After Ag⁺-exchange, the xerogels retained higher SSA values (i.e., 240 m² g⁻¹) compared to the aerogels that were not heat treated (i.e., 120 m² g⁻¹) and even the heat-treated aerogels (i.e., 150 m² g⁻¹). Note that the heat treatment process was performed only on some of the aerogels to improve the mechanical rigidity of the base material (as discussed previously).

The more important comparison is in the iodine uptake values for these materials. The aerogels, heat-treated aerogels, and xerogels showed iodine uptake values of 0.405, 0.377, and 0.327 m³ %, respectively. These values are not as high as those achieved in the 2017 study,[2] but the base materials differed in 2020 study[80] this difference was attributed to batch-to-batch variability and differences in aging times used between the different sets of experiments.

The main goal of the 2020 study[80] was to evaluate whether or not the iodine uptake of Ag-loaded aerogels and xerogels differed significantly. Eliminating extra processing steps during gel synthesis drastically simplified the process and allowed for the scale-up of sorbent production volumes. Since aerogel production requires an autoclave, this adds additional pressure hazards to the process, but also makes scale-up more difficult and expensive than it is for xerogel production. Finally, the xerogels are quite mechanically robust, especially compared to the base aerogels and even the heat-treated aerogels.

3.2.2. Ag-Free Aluminosilicate Aerogels and Xerogels for Iodine Capture

A follow-up study[47] to the Ag-loaded aluminosilicate study was conducted to evaluate non-Ag getters in aluminosilicate aerogels and xerogels. The main driver for this study was to find alternative getters to Ag because Ag is a hazardous material controlled in the United States by the Environmental Protection Agency under the Resource Conservation and Recovery Act,[81] complicating the waste form disposal process. Also, Ag is also a precious metal, making large-scale sorbent production an expensive venture.

In this study, several different getters materials were evaluated based on thermodynamic predictions from metal-iodide complexation (∆G°r,0) using Gibb’s free energies compared to the metal-oxide complexation (∆G°r,0) with HSC Chemistry (v9, Outotec, Finland). Calculations performed as part of that study showed that only 14 species in the database showed a more favorable metal-iodide complexation over the metal-oxide complexation including (Ag⁺, Pb²⁺, Hg⁺, Ag⁺, Hg²⁺, Tl⁺ (T ≥ 400 °C), Eu²⁺ (25 °C ≤ T ≤ 400 °C), Pb²⁺ (25 °C ≤ T ≤ 100 °C), Pd²⁺ (T), Pt²⁺ (25 °C ≤ T ≤ 150 °C), and Pt⁴⁺ (T = 25 °C).

Some of these species were incorporated into the sodium aluminosilicate scaffold using ion exchange processes with different solvent systems and the final selection of getters included Cs⁺, Cu²⁺, K⁺, Li⁺, Rb⁺, Sb³⁺, and Sn⁴⁺ (in addition to Ag⁺), based on promising data in the literature.[2,6,8,69,82-85] The ion exchange process was typically depicted by the exchanged gel showing a loss of Na⁺ to the solution during the exchange as the target cations were loaded into the scaffold. The most effective materials at capturing iodine based on gravimetric uptake (measured by mass uptake) and chemical uptake (quantified by EDS analysis) were Cu²⁺ (CuSO₄), Sn⁴⁺ [Sn(II) acetate], and Sn⁴⁺ [i.e., colloidal SnO₂, Sn(IV) acetate] [in addition to Ag⁺ (AgNO₃)] (see Figure 7); note that the species in parenthesis

![Figure 7. Comparison of chemical uptake based on EDS data (mₚ,EDS) and gravimetric uptake (mₚ,gr)]. The left side of the figure (shaded in gray) shows data where negative gravimetric uptake and positive chemical uptake were observed. Reproduced with permission.[47] Copyright 2020, American Chemical Society.
are the salts added during ion exchange. More work is needed to fully understand the mechanisms of these exchanges for the different getter systems.

4. Chalcogen-Based Aerogels (Chalcogels) for Radionuclide Capture

The two primary theories to explain the high affinity of chalcogens for capturing I$_2$(g) and heavy metals are centered around physisorption and chemisorption. From a physisorption perspective, the selective affinity of the chalcogen-based aerogel backbone for I$_2$(g) can be explained by Pearson's hard/soft acid-base (HSAB) principle.$^{[86,87]}$ The HSAB principle evaluates electron-pair donating Lewis bases and electron-pair accepting Lewis acids to predict complexation behaviors of cations and ligands.$^{[86]}$ To compare species, the chemical hardness ($\eta$) can be calculated using the ionization energy ($I$) and electron affinity ($\chi$) for a given species “s” using Equation (4). If two species have similar chemical hardness values, where one is a Lewis acid and the other is a Lewis base, the HSAB principle predicts that these two species will share an affinity. Table 4 presents some different values for a range of Lewis acids and bases as well as some neutral species.$^{[80-90]}$ These data suggest that the chalcogen affinity for I$_2$(g) would rank in the order of $\text{Se} > \text{S}$, but to date, only S-based chalcogens have been evaluated for this application

$$\eta = 1/2 (I_s - \chi_s) \quad (4)$$

The chemisorption capture route is based on evidence from the formation of metal-iodide complexes with chalcogen constituents following the capture of I$_2$(g). Previous studies$^{[6,68,69,82]}$ revealed Sn-based and Sb-based chalcogens from iodide species including SnI$_4$, SnI$_4$(S$_8$)$_2$, and SbI$_4$, which were easily detectable by comparing the iodine breakthrough into the NaOH solution and those values were compared to the iodine concentration when the sample was not present. Solutions were analyzed using inductively coupled plasma mass spectrometry (ICP-MS) to determine the iodine concentration. The compositions evaluated using this setup include PtGe$_2$S$_5$,$^{[15]}$ Sn$_2$S$_3$,$^{[6,68,69]}$ CoNiMo$_2$S$_8$,$^{[6]}$ NiMoS$_4$,$^{[82]}$ CoMoS$_4$,$^{[82]}$ Sb$_2$Sn$_3$S$_{12}$,$^{[82]}$ Zn$_2$Sn$_3$S$_8$,$^{[82]}$ and KCoS$_4$.$^{[82]}$ For consistency with other sorbents discussed herein, the $m_1$,$m_1$ loading capacities for iodine are provided in Table 5 for these chemistries.$^{[15,68,82]}$

Additionally, iodine capture was evaluated using a dilute I$_2$(g) stream environment of 4.2 ppm (by volume) in air as the carrier gas. These experiments were conducted using a DYNACAL iodine permeation tube with a permeation rate of 22.89 ng s$^{-1}$ at 100 $^\circ$C. This stream was connected to a separate furnace at 150 $^\circ$C through a heated transfer line where chalcogel sorbents resided; the vent line for this system was placed in 0.1 m NaOH solution that was replaced periodically; this setup can be seen in Figure 9a. Iodine capture efficiency was determined by comparing the iodine breakthrough into the NaOH solution as a function of time, with the sorbent in the column, and those values were compared to the iodine concentration when the sample was not present. Solutions were analyzed using inductively coupled plasma mass spectrometry (ICP-MS) to determine the iodine concentration. The compositions evaluated using this setup include PtGe$_2$S$_5$,$^{[15]}$ CoNiMo$_2$S$_8$ (see Figure 9c),$^{[6]}$ and Sn$_2$S$_3$ (see Figure 9d).$^{[6]}$ In all cases, the uptake over the test duration was > 99 mass% with Sn$_2$S$_3$ showing the highest uptake over the full test duration demonstrated at >99.5% and increasing with time (see Figure 9b). In a separate study by Subrahmanyam et al.$^{[91]}$ (NH$_4$)$_2$MoS$_4$ chalcogens were also demonstrated to have a high affinity for iodine vapors.

One way to increase the mechanical integrity of a sorbent is to embed the active sorbent in a passive matrix (e.g., a polymer-based scaffold) to create a composite material. Here, the passive matrix essentially dilutes the capacity of the active sorbent on a per-mass basis since a part of the composite is made up of a passive matrix that either does not interact with the contaminant(s) of interest or only interacts slightly. In a previous study,$^{[84]}$ this approach was used with Sn$_2$S$_3$ chalcogel powders to make chalcogel-polyacrylonitrile (PAN) composites for iodine capture (Figure 9e). Some benefits from this approach are that the PAN matrix is very porous, stable under elevated temperatures, mechanically robust, and very lightweight, adding minimal mass to the active chalcogel sorbent. In this study, Sn$_2$S$_3$-PAN composites were made containing 30, 50, and 70 mass% chalcogel in the PAN. The iodine capacity scaled quite linearly with the amount of Sn$_2$S$_3$ present in the composite.$^{[92]}$ and the

with PXRD. The formation of these iodide species allows for a better understanding of how the iodine is interacting with these types of chalcogens.

Chalcogens have very porous networks and appear very similar to oxide-based counterparts when observed with SEM and TEM (see Figure 8). In some cases, crystalline diffraction has been observed with selected area diffraction (SAD), and this is presumed to be surface oxidation of the materials.

### Table 4. Tabulated values of $I_s$, $A_s$, $\chi_s$, and $\eta_s$ for various species, “s,” sorted by electronegativity.

| Acid/base | Species | $I_s$ | $A_s$ | $\chi_s$ | $\eta_s$ | Ref. (s) |
|-----------|---------|------|------|---------|---------|--------|
| Acid      | K$^+$   | 31.63| 4.34 | 17.99   | 13.65   | $^{[87,88]}$ |
|           | Zn$^{2+}$ | 39.7 | 17.96| 28.8    | 10.8    | $^{[87]}$ |
|           | HCl     | 12.7 | -3.3 | 4.7     | 8.0     | $^{[89]}$ |
|           | Hg$^{2+}$ | 34.2 | 18.75| 26.5    | 7.7     | $^{[87]}$ |
|           | U$^{4+}$ | 45.77| 31.06| 38.415  | 7.4     | $^{[90]}$ |
|           | CO$_2$(g)| 13.8 | 6.9  | 6.9     | 6.9     | $^{[87]}$ |
|           | Cu$^+$  | 20.3 | 7.72 | 14.0    | 6.3     | $^{[87]}$ |
|           | Hf(g)   | 10.5 | 0.0  | 5.3     | 5.3     | $^{[89]}$ |
|           | HNO$_3$ | 11.03| 0.57 | 5.8     | 5.2     | $^{[89]}$ |
|           | I$_2$(g) | 9.3  | 2.6  | 6.0     | 3.4     | $^{[87]}$ |
| Neutral   | CH$_3$I | 9.5  | 0.2  | 4.9     | 4.7     | $^{[89]}$ |
|           | Cl$_2$| 11.4 | 2.6  | 7.0     | 4.6     | $^{[89]}$ |
| Base      | S       | 10.36| 2.08 | 6.22    | 4.12    | $^{[87]}$ |
|           | Se      | 9.75 | 2.02 | 5.89    | 3.86    | $^{[87]}$ |
|           | Te      | 9.01 | 1.97 | 5.49    | 3.52    | $^{[87]}$ |
loading rates changed with different Sn$_2$S$_3$ loadings (Figure 9f). These results demonstrate both the passive nature of the PAN matrix and the need for PAN minimization to maximize the iodine capacity in the final composite sorbent.

### 4.2. Chalcogels for the Capture of Uranium and Technetium

Studies were done to evaluate the uptake of uranium-238 (i.e., $^{238}$UO$_2$$^{2+}$) and technetium-99 (i.e., $^{99}$TcO$_4$$^{-}$) ions from solution using the following chalcogel chemistries: Co$_{0.7}$Bi$_{0.3}$MoS$_4$ (CoBiMoS), Co$_{0.7}$Cr$_{0.3}$MoS$_4$ (CoCrMoS), Co$_{0.5}$Ni$_{0.5}$MoS$_4$ (CoNiMoS), PtGe$_2$S$_5$ (PtGeS), and Sn$_2$S$_3$ (SnS).

For these experiments, ≈0.05–0.1 g of each chalcogel were loaded into separate 20 mL glass vials with 9 mL DIW; a blank vial was also loaded with 9 mL of DIW. This was followed by the addition of 1 mL solution containing either $10^{-5}$ M $^{99}$TcO$_4$$^{-}$ added as NaTcO$_4$ or $10^{-5}$ M $^{238}$UO$_2$$^{2+}$ added as UO$_2$(NO$_3$)$_2$ for final concentrations of $10^{-6}$ M for each target radionuclide. Sample vials were sealed and mixed end-over-end for 7 d. Then the supernatant was collected through a syringe with a 0.45 µm filter, and the analyte concentrations were analyzed with ICP-MS. Capture efficiencies and $K_d$ values were measured using Equations (3) and (5) (see Section 3), respectively, where $m$ is the mass of sorbent material ($V/m = 1000$ mL g$^{-1}$) and other variables were defined in Section 3.

**Efficiency**

$$\text{Efficiency} = 100 \times \frac{C_i - C_f}{C_i}$$  

The efficiency data and $K_d$ values from these tests are shown in Table 6. The values revealed a wide range of values for the different chalcogel chemistries where CoBiMoS, PtGeS, and Sn$_2$S$_3$ worked well for both $^{99}$TcO$_4$$^{-}$ and $^{238}$UO$_2$$^{2+}$ at ≥87.3% fractional uptake and $K_d$ values of ≥$1.5 \times 10^3$. The highest values were observed for PtGeS for both species with $K_d$s of 3.6 × 10$^4$ for $^{99}$TcO$_4$$^{-}$ and 9.4 × 10$^4$ for $^{238}$UO$_2$$^{2+}$ along with efficiencies of 98.0% and 99.4%, respectively. The lowest uptake values were found with CoCrMoS at 57.3% and 68.1% efficiencies for
99TcO\textsuperscript{4-} and 238UO\textsubscript{2}\textsuperscript{2+}, respectively. These data provide a demonstration that chalcogels could prove useful for the remediation of these radionuclides from aqueous solutions.

### 4.3. Chalcogels for the Capture of Heavy Metals

Recent work showed promise for chalcogels for heavy metal remediation; many of these heavy metals could be considered as byproducts to radiological processes and, thus are included in the current review. In a study by Subrahmanyam et al.\cite{91} (NH\textsubscript{4})\textsubscript{2}MoS\textsubscript{4} chalcogels were demonstrated to have a high affinity for Hg vapors, forming crystalline HgS upon capture with a final composition of Hg\textsubscript{1.9}MoS\textsubscript{4} after complete exchange of the NH\textsubscript{4} with Hg. In a study by Pala and Brock,\cite{93} ZnS chalcogels were used to remove Pb\textsuperscript{2+} and Hg\textsuperscript{2+} from aqueous solutions. Oh et al.\cite{59} showed that Zn\textsubscript{2}Sn\textsubscript{x}S\textsubscript{2}S\textsubscript{x} (x = 1, 2, 4) chalcogels can be used to remove Hg\textsuperscript{2+}, Pb\textsuperscript{2+}, Cd\textsuperscript{2+}, Cu\textsuperscript{2+}, Zn\textsuperscript{2+}, and Fe\textsuperscript{2+} from aqueous solutions with very high $K_d$ values ranging from $7 \times 10^3$ (Fe\textsuperscript{2+}) to $2.8 \times 10^7$ (Hg\textsuperscript{2+}).

### 4.4. Chalcogels for the Capture of Noble Gases

Noble gases are byproducts of nuclear fission, namely, Xe and Kr. Under 40 CFR 190.94 the U.S. Environmental Protection Agency requires the capture 85Kr evolved from a nuclear fuel reprocessing facility, if one were to be built in the United States. The concentration of Xe present within irradiated nuclear fuel is nominally $10 \times$ the total Kr concentration and this combined with the unreactive nature of noble bases makes the selective capture of Kr even more challenging. The traditional option for capturing noble gases has been cryogenic distillation,\cite{95–99} but new MOF sorbents\cite{100–102} have shown promise as alternatives to distillation.

A paper by Subrahmanyam et al.\cite{103} revealed that chalcogels could be used to capture Xe from the noble gas mixture. Here, four different chalcogels were utilized including (NH\textsubscript{4})\textsubscript{0.03}MoS\textsubscript{4} (MoS\textsubscript{x}), Na\textsubscript{0.3}Sb\textsubscript{2}S\textsubscript{3} (SbS-I), K\textsubscript{0.15}Na\textsubscript{0.3}Sb\textsubscript{2}S\textsubscript{2.5} (SbS-II), and Na\textsubscript{0.1}Sb\textsubscript{2}S\textsubscript{3} (SbS-III) with SSA values of 128–290 m\textsuperscript{2} g\textsuperscript{-1}. The MoS\textsubscript{x} (NH\textsubscript{4})\textsubscript{3}MoS\textsubscript{4} chalcogels were demonstrated to have a high affinity for Hg vapors, forming crystalline HgS upon capture with a final composition of Hg\textsubscript{1.9}MoS\textsubscript{4} after complete exchange of the NH\textsubscript{4} with Hg. In a study by Pala and Brock,\cite{93} ZnS chalcogels were used to remove Pb\textsuperscript{2+} and Hg\textsuperscript{2+} from aqueous solutions. Oh et al.\cite{59} showed that Zn\textsubscript{2}Sn\textsubscript{x}S\textsubscript{2}S\textsubscript{x} (x = 1, 2, 4) chalcogels can be used to remove Hg\textsuperscript{2+}, Pb\textsuperscript{2+}, Cd\textsuperscript{2+}, Cu\textsuperscript{2+}, Zn\textsuperscript{2+}, and Fe\textsuperscript{2+} from aqueous solutions with very high $K_d$ values ranging from $7 \times 10^3$ (Fe\textsuperscript{2+}) to $2.8 \times 10^7$ (Hg\textsuperscript{2+}).

### Table 5. Summary of chalcogel chemistries evaluated for I\textsubscript{2}(g) uptake in saturated environment showing the gel chemistry (sorted alphabetically), the sample identification (ID) from the original work, the measured SSA value for that chalcogel, the SSA\textsubscript{eq} value [see Equation (1)], the I\textsubscript{2}(g) loading based on mass uptake within the vacuum desiccator, and the corresponding reference for the original work.

| Chalcogel Sample ID | SSA \textsuperscript{[m\textsuperscript{2} g\textsuperscript{-1}]} | SSA\textsubscript{eq} \textsuperscript{[m\textsuperscript{2} g\textsuperscript{-1}]} | I\textsubscript{2}(g) loading \textsuperscript{[mmol \textsubscript{S} g\textsuperscript{-1}]} | Ref. |
|---------------------|-----------------|-----------------|-----------------|-----|
| CoMoS\textsubscript{6} | 360 848 | 2.00 | [82] |
| KCoS\textsubscript{x} | 350 848 | 2.00 | [82] |
| NiMoS\textsubscript{6} | 490 1154 | 2.25 | [82] |
| PtGe\textsubscript{2}S\textsubscript{3} | 360 1200 | 2.39 | [15] |
| Sn\textsubscript{2}S\textsubscript{3} | 270 999 | 2.13 | [68] |
| Zn\textsubscript{2}Sn\textsubscript{2}S\textsubscript{4} | 400 1244 | 2.25 | [82] |

Figure 9. a) Experimental setup for 4.2 ppm iodine capture experiments using DYNACAL permeation tube, b) a summary of the capture as a function of time for PtGe\textsubscript{2}S\textsubscript{3}, CoNiMo\textsubscript{2}S\textsubscript{8}, and Sn\textsubscript{2}S\textsubscript{3},\cite{6,15} c) a close-up picture of the CoNiMo\textsubscript{2}S\textsubscript{8} chalcogel after the uptake test, and d) a close-up picture of the PtGe\textsubscript{2}S\textsubscript{3} chalcogel after the uptake test; Adapted with permission.\cite{6} Copyright 2013, American Chemical Society. e) Schematic showing chalcogel-PAN composite synthesis process and f) iodine loading as a function of time for two composites and the pure PAN (no chalcogel added); Reproduced with permission.\cite{68} Copyright 2014, American Chemical Society.
chalcogel showed the highest uptake for both Xe and Kr as shown in Figure 10a,b, respectively. Calculations were conducted using the ideal adsorbed solution theory (IAST) to look at Xe/Kr selectivities among the four chalcogels and the MoS$_x$ chalcogel exhibited the highest value of 6.0 compared to selectivities of 2.0–2.8 for all Sb-S chalcogels. It is hypothesized that the differences in selectivities between the Mo-S and Sb-S chalcogels are possibly due to the differences in metal ion oxidation state (i.e., Mo$^{4+}$ vs Sb$^{3+}$) as well as crystal radii.

5. Heavy Metal Capture with Carbon-Based Aerogel Composites

For removal of heavy radionuclides from aqueous solutions, different carbon-based functionalized aerogel composites have been developed to improve adsorption capacities while maintaining high porosities and high SSA values while also allowing for the incorporation of various getters in the structures.$^{[104–110]}$

Table 7 shows the adsorption capacities of radionuclides by various sorbents in the literature.$^{[105–108]}$ Also included in Table 7 are additional data for similar compounds without aerogels included for comparison.$^{[111,112]}$

Coleman et al.$^{[104]}$ developed a granulated activated carbon (GAC)-silica aerogel composite for uranium removal from aqueous solution. Hydrophobic GAC-aerogel composites were synthesized and modified with phosphoric acid, phosphonate, or Ca(NO$_3$)$_2$, and their uranium adsorption capacities were evaluated in 100 ppb uranium and pH 7 surrogate solution.$^{[104]}$ The results showed that GAC-aerogel composites were better adsorbents compared to normal GAC.

Chen et al.$^{[105]}$ developed a Fe$^0$-polyaniline-graphene aerogel composite (Fe$^0$-PANI-GA) for U$^{6+}$ removal from acidic solutions. Graphene aerogel is composed of cross-linked graphene sheets with robust porous structures that can incorporate getters and has been studied for removal of heavy metal ions.$^{[113]}$ Zero-valent iron (Fe$^0$) is an effective adsorbent for heavy metal ions due to more reactive sites on the surface.$^{[114,115]}$ and polyaniline contains abundant primary and secondary amino groups that help assist the adsorption of heavy metal ions.$^{[116]}$ The Fe$^0$-PANI-GA composite was more effective for removal of U$^{6+}$ compared to GA or PANI-GA alone in acidic solution, and the maximum sorption capacity was 350 mg g$^{-1}$ in pH 5 solution at room temperature (see Table 7)$^{[105]}$.

Liu et al.$^{[110]}$ developed Na$_2$Ti$_3$O$_7$-carbon aerogel for removal of Rb$^+$ and Cs$^+$ cations from aqueous solution. The adsorption mechanism involves replacement of Na$^+$ with Rb$^+$ and Cs$^+$ cations in Na$_2$Ti$_3$O$_7$ and complexation of hydroxyl functional groups from Na$_2$Ti$_3$O$_7$-carbon aerogel with Rb$^+$ and Cs$^+$ cations.$^{[110]}$ The maximum adsorption capacity of Na$_2$Ti$_3$O$_7$-carbon aerogel for Rb$^+$ and Cs$^+$ cations were 1.11 mmol g$^{-1}$ (94.9 mg g$^{-1}$) and 1.45 mmol g$^{-1}$ (193 mg g$^{-1}$), respectively, from a solution of pH 5.5.$^{[110]}$

Li et al.$^{[106]}$ used a combination of microorganisms and aerogels to develop an adsorbent of fungal hypha-graphene oxide aerogel composite for uranium removal from aqueous solution.

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Table 6. Summary of solution uptake of $^{99}$TcO$_4^−$ and $^{238}$UO$_2^{2+}$ with chalcogels including the efficiency (Eff. %); [see Equation (3)] and the $K_d$ values [see Equation (4)]. Reproduced with permission.$^{[6]}$ Copyright 2013, American Chemical Society.

| Sample ID | $^{99}$Tc uptake | $^{238}$U uptake |
|-----------|-----------------|-----------------|
|           | Eff. [%] | $K_d$ [mL g$^{-1}$] | Final pH | Color | Eff. [%] | $K_d$ [mL g$^{-1}$] | Final pH | Color |
| CoBiMoS   | 94.0     | $1.68 \times 10^3$ | 2.31    | Very blue | 94.9     | $1.81 \times 10^3$ | 2.26    | Faintly blue |
| CoCrMoS   | 57.3     | $2.88 \times 10^2$ | 2.78    | Faintly pink | 68.1     | $3.15 \times 10^2$ | 2.72    | Barely pink |
| CoNiMoS   | 62.2     | $1.62 \times 10^2$ | 4.72    | Pale blue | 88.2     | $8.08 \times 10^2$ | 9.06    | Pale blue |
| PtGeS     | 98.0     | $3.61 \times 10^4$ | 4.80    | Faintly orange | 99.4     | $9.43 \times 10^4$ | 4.44    | Faintly orange |
| SnS       | 87.3     | $1.49 \times 10^3$ | 5.47    | Faint yellow | 99.1     | $2.31 \times 10^4$ | 5.53    | Faintly yellow |
| Blank     | –        | –                | 5.59    | Clear | –        | –                | 5.18    | Clear |

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Figure 10. a) Xe and b) Kr adsorption isotherms recorded at 273 K up to 1 bar. Adapted with permission.$^{[103]}$ Copyright 2017, American Chemical Society.
solutions. Fungal hypha contain a large amount of phospho-
nate, hydroxyl, and amine groups on the cell wall that have
strong chelation with uranium ions.\textsuperscript{[106]} The sorption capacity
of fungal hypha-graphene oxide aerogel composites for U\textsuperscript{6+}
ions in a solution of pH 5 was 288 mg g\textsuperscript{-1}.\textsuperscript{[106]}

Chen et al.\textsuperscript{[107]} developed konjac glucomannan/graphene oxide
composites for U\textsuperscript{6+} removal from simulated waste-
water. Konjac glucomannan is a renewable natural resource
that can adsorb radionuclides, but with a relatively low adsorp-
tion capacity. By combining with graphene oxide and aerogel,
its absorption capacity can be increased significantly.\textsuperscript{[107]} The
maximum adsorption capacity of U\textsuperscript{6+} from pH 5 solution at
313 K was 513 mg g\textsuperscript{-1}.\textsuperscript{[107]}

Zhao et al.\textsuperscript{[108]} removed cerium, a surrogate of plutonium and
minor actinides, from an aqueous solution using SiO\textsubscript{2}-ZrO\textsubscript{2}-
calcium alginate aerogels and showed that Ca and Zr sites
were occupied by Ce\textsuperscript{4+} cations with the maximum adsorption
capacity of 232 mg g\textsuperscript{-1}. Calcium alginate is a natural biological
polymer that can be extracted from brown algae.

Zhu et al.\textsuperscript{[109]} demonstrated that low cost and non-toxic
cotton-carbon aerogel with high cellulose content can be used
as an adsorbent for removal of Sr\textsuperscript{2+} cations from pH 5–7 solu-
tions. The maximum removal efficiency of cotton-carbon aerogel for Sr\textsuperscript{2+} removal was 60.2\% from a solution of pH 6,
and cotton-carbon aerogel was reusable for five adsorption and
desorption cycles.\textsuperscript{[109]}

6. Summary and Conclusions

This progress report provides a review of recent work in the
area of functional aerogels and xerogels for environmental
remediation applications. The materials discussed herein
include sorbents for liquid and/or gaseous streams. Sorbents
discussed include metal-functionalized silica-based aerogels
and xerogels, sulfide-based aerogels, and carbon-containing
aerogel composites for target species such as Cd\textsuperscript{2+}, Ce\textsuperscript{4+}, Cs\textsuperscript{+},
Cu\textsuperscript{2+}, Fe\textsuperscript{3+}, Hg\textsuperscript{2+}, Hg\textsubscript{(g)}, I\textsuperscript{-}, IO\textsubscript{3}\textsuperscript{-}, Kr, Pb\textsuperscript{2+}, Rb\textsuperscript{+}, Sr\textsuperscript{2+}, \textsuperscript{99}Tc\textsuperscript{2+}, U\textsuperscript{6+},
Xe, and Zn\textsuperscript{2+}. These sorbents have a range of specific surface
areas, porosities, and capacities for these contaminants.

Depending on the application, different materials are more
suitable than others. For instance, some aerogels are quite
fragile and friable; these might not be ideal for applications
requiring high-flow gas streams or extreme-pH aqueous envi-
nronments. For such environments, additional techniques can
be implemented such as embedding the active sorbent in a
passive matrix, as was done with the chalcogel-PAN composites;
this added mass of the inactive matrix will decrease the
capacity of the overall composite, but with the added benefit of
increased mechanical integrity.

Overall, oxide-based aerogels and xerogels are likely less
expensive to make than chalcogens, due to the commercially
availability of a wide range of alkoxide precursors and a very
limited availability of chalcogen precursors; additionally,
commercially available chalcogen precursors also tend to be rather
expensive. The added benefit of chalcogens, however, is that
they are oftentimes inherently “functionalized” for these types
of applications where the as-made sorbents can be used to
capture species of interest. In contrast, oxide-based gels often
require the addition of a getter species, e.g., Ag\textsuperscript{+}/Ag\textsuperscript{0}.

The primary conclusion of this work is that plenty of open
spaces exist on this topic in the literature and new applications
are being discovered regularly. Additional topics of interest
and challenges in this area are plentiful, some of which are
described below. For instance, future work should focus on
finding non-hazardous metal getters. Silver is a hazardous
material as well as a precious metal. With recent work showing
promise for other getters such as Cu, Sn, and Sb, this provides
an opportunity for cheaper and less hazardous sorbents. A limi-
tation with aerogel production is the requirement for critical
point drying using autoclaves and supercritical fluids. This can
be avoided if xerogels are pursued instead. Plus, xerogels can

| Type                  | Sorbents                  | Target species | Species capacity [mg g\textsuperscript{-1}] | Solution pH | Temperature [K] | Ref.   |
|-----------------------|---------------------------|----------------|--------------------------------------------|-------------|----------------|-------|
| **With aerogels**     |                           |                |                                            |             |                |       |
| Graphene aerogel      | U                         | 131            | 5.5                                        | 298         | [105]          |       |
| PANI/graphene aerogel | U                         | 242            | 5.5                                        | 298         | [105]          |       |
| Fe\textsuperscript{3+}-PANI-graphene aerogel | U           | 350            | 5.5                                        | 298         | [105]          |       |
| Fungal hypha-graphene oxide aerogel | U            | 288            | 5                                          | 293         | [106]          |       |
| Konjac glucomanann/graphene oxide aerogel | U           | 513            | 5                                          | 313         | [107]          |       |
| SiO\textsubscript{2}-ZrO\textsubscript{2}-calcium alginate aerogels | Ce          | 232            | 7                                          | 308         | [108]          |       |
| Graphene oxide/polypyrrole | U            | 147            | 5                                          | 298         | [117]          |       |
| Na\textsubscript{2}TiO\textsubscript{3}-carbon aerogel | Rb          | 94.9           | 5.5                                        | 298         | [110]          |       |
| Na\textsubscript{2}TiO\textsubscript{3}-carbon aerogel | Cs          | 193            | 5.5                                        | 298         | [110]          |       |
| **Without aerogels**  |                           |                |                                            |             |                |       |
| Carbonaceous nanofiber | U                         | 125            | 4.5                                        | 298         | [111]          |       |
| Carbonaceous nanofiber | Eu                        | 91             | 4.5                                        | 298         | [111]          |       |
| Graphene oxide        | U                         | 56             | 3.8                                        | 298         | [112]          |       |
| Graphene oxide/\alpha-MnO\textsubscript{2} | U              | 185            | 3.8                                        | 298         | [112]          |       |
| Graphene oxide        | Th                        | 154            | 3.8                                        | 298         | [112]          |       |
| Graphene oxide/\alpha-MnO\textsubscript{2} | Th              | 498            | 3.8                                        | 298         | [112]          |       |
be made with minimal SSA loss, as was discussed herein, and they tend to have significantly higher mechanical stability than the aerogel counterparts. A large-scale production process for making xerogels would greatly improve the workflow.

Very little work has been done looking at gel-polymer composites for these applications and this type of approach could be used to further push the limits of environmental remediation applications, e.g., under conditions where gels (without added support) might not fare well from a mechanical integrity perspective. The added disadvantage of the polymer being part of the composite is that the sorbent cannot be easily consolidated into a waste form if the polymer remains, unless it is selectively removed (e.g., by burning it off) beforehand. However, the composite sorbent could be loaded into a secondary matrix for disposal, such as a cement or grout.

This leads into the final point, which is that the fate of the contaminant-loaded sorbent need be considered. Very little has been done to attempt consolidation of contaminant-loaded gels into a waste form suitable for long-term disposal. This remains an area that is wide open for future research. Since these sorbents are porous, at a minimum, they could be hot pressed into a dense monolithic waste form. However, it would be preferred if the contaminants could be removed and the base sorbent recycled for future use.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

aerogels, environmental remediation, silver functionalization, xerogels

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