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<th>Journal:</th>
<th>New Journal of Chemistry</th>
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<tr>
<td>Manuscript ID</td>
<td>NJ-ART-08-2019-004091.R1</td>
</tr>
<tr>
<td>Article Type:</td>
<td>Paper</td>
</tr>
<tr>
<td>Date Submitted by the Author:</td>
<td>25-Sep-2019</td>
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Alkaline earth ion exchange study in pure silica LTA zeolites using periodic first-principles calculations

Vancho Kocevski, a,c Shenyang Y. Hu b,c and Theodore M. Besmann a,c

Experiments show that Zeolites, such as Linde Type A (LTA), are promising materials for radioactive decontamination processes. In this work, the thermodynamic properties associated with alkaline earth ion (Ca\(^{2+}\), Sr\(^{2+}\) and Ba\(^{2+}\)) exchange in pure silica LTA was studied using periodic first-principles calculations. The adsorption energies of alkaline earth ions compared with that of Na\(^{+}\) were investigated. The driving force for the alkaline earth exchange and related isotherms were calculated, and analyzed as a function of the electron chemical potential. The results demonstrate that Na\(^{+}\) in a pure silica LTA can completely be removed by Ba\(^{2+}\) and almost completely be removed by Sr\(^{2+}\) from a stream, but cannot be effectively exchanged by Ca\(^{2+}\). We also showed that electron-donating dopants should suppress the Sr\(^{2+}\) and Ba\(^{2+}\) ion exchange, and that there is a substantial preference for incorporating Ba\(^{2+}\) over Sr\(^{2+}\). Lastly, the substantial difference between the adsorption energies of the ions in an assumed vacuum and those computed in water suggests that a solvation model is needed for accurate representation of ion adsorption in an LTA zeolite.

Models and Methodology

The studied LTA zeolite is an aluminosilicate with the formula Na\(_2\)\(\text{Al}_2\text{Si}_2\text{O}_8\cdot\text{H}_2\text{O}\) that contains a large amount of adsorption (exchange) sites. Its cubic framework is comprised of α-cages (supercages), formed by 3D interconnected β-cages ( sodalite cages) by double four-membered rings (see red shaded area in Fig. 1). The pore system in the LTA zeolite is formed by the 8-membered apertures (site 3 in Fig. 1) that interconnect the α-cages. The LTA zeolite has three unique adsorption sites, termed site 1, 2 and 3 with diameters of 4.4 Å, 3.6 Å and 6.9 Å, respectively (Fig. 1). Because of the large unit cell of 640 atoms, first-principles calculations are prohibitively expensive and thus we used pure silica LTA zeolite (ps-LTA zeolite), which has 72 atoms, as a model system. Ps-LTA zeolite has been synthesized using an organic structure-directing agent.
obtained by self-assembly \(^3\), and is thus available for experimental efforts to assess the results of the computational study.

We performed first-principles calculations using density functional theory (DFT), via the Vienna ab initio simulation package (VASP) plane-wave based code \(^{26,27}\). The generalized gradient approximation (GGA) of PBE \(^{28}\) and projector augmented wave (PAW) potentials \(^{29,30}\) were used to treat the exchange-correlation energy density functional and the ion-electron interactions, respectively. We also considered Van der Waals corrections, with dispersion interactions in the form of the DFT-D3 method \(^{31}\). The valence electronic configurations considered for construction of PAW potentials for Na, Ca, Sr, Ba, Si and O are 2\(p^3\)\(s^1\), 3\(p^6\)\(d^1\), 4\(s^2\)\(p^4\)\(s^2\), 5\(s^2\)\(p^6\)\(s^2\) and 2\(s^2\)\(p^4\), respectively. A plane wave basis set with an energy cut-off of 520 eV was used to expand the electronic wave functions, with a 10\(^{-8}\) eV energy convergence criteria. For sampling the Brillouin zone, we used a 3\(\times\)3\(\times\)3 \(k\)-point mesh. The ground state geometries at 0 K were optimized by relaxing the cell volume and atomic positions until the maximum forces on each atom were less than 0.001 eV/Å, while keeping the cubic framework constant. To obtain a more accurate model of ion exchange in aqueous solutions, we considered the systems to be surrounded by water in addition to the usual vacuum environment, employing the implicit solvation model VASPsol \(^{12,21}\).

For each of the studied ions and adsorption sites we calculated the ion adsorption energy, \(E_{ads,0}\), from

\[
E^{A}_{ads,0} = E^{(LTA:A)} - E^{(LTA)} - \mu^{A}_{\text{sol}} \tag{1}
\]

where \(E^{(LTA:A)}\) and \(E^{(LTA)}\) are the DFT calculated total energies of the ps-LTA zeolite with and without adsorbed ion \(A\), respectively. The standard chemical potential of ion \(A\), \(\mu^{A}_{\text{sol}}\), is DFT calculated total energy of the single ion for the system in vacuum, while for the system in water it is set to be the scaled experimental standard chemical potential of the ion, as proposed by Persson et al. \(^{34}\). The standard chemical potentials used in this study are given in Table S1. Varying the ion concentration in water requires \(\mu^{A}_{\text{sol}}\) to be replaced with the solution chemical potential, \(\mu^{A}_{\text{sol}}\), defined as:

\[
\mu^{A}_{\text{sol}} = \mu^{A}_{\text{solv}} + k_{B}T\ln(x_{A}y_{A}), \tag{2}
\]

where \(\mu^{A}_{\text{solv}}\), \(x_{A}\) and \(y_{A}\) are the chemical potential, mole fraction and activity coefficient of ion \(A\) in water, respectively, \(k_{B}\) is the Boltzmann constant and \(T\) is the thermodynamic temperature. The \(y_{A}\) values were calculated using the Debye-Hückel equation, where the constants were found by fitting the reported experimental activity data of Kielland et al. \(^{35}\). The resulting constants are given in Table S2. Introducing \(\mu^{A}_{\text{solv}}\) allows the ion mole fraction at which ion \(A\) becomes preferred over ion \(A_{2}\) to be determined, which is found from the adsorption energy difference, \(\Delta E_{ads}\), defined as:

\[
\Delta E_{ads} = E_{ads}^{A_{1}} - E_{ads}^{A_{2}} = E_{ads,0}^{A_{1}} - E_{ads,0}^{A_{2}} - k_{B}T\ln\left(\frac{x_{A_{1}}y_{A_{1}}}{x_{A_{2}}y_{A_{2}}}\right). \tag{3}
\]

To predict the ability of ps-LTA’s zeolite to exchange Na\(^+\) ions for other ions of interest we need to determine the driving force for ion exchange, i.e., the ion exchange energy, \(\Delta E_{ie}\). The ion exchange reaction in zeolites can be described as:

\[
A_{1}(aq) + A_{2}(zeo) = A_{1}(zeo) + A_{2}(aq) \tag{4}
\]

with the absorption energies described in Eq. (1) the ion exchange energy, \(\Delta E_{ie}\), can be defined as:

\[
\Delta E_{ie} = E_{ads,0}^{A_{2}} - E_{ads,0}^{A_{1}} = E^{(LTA:A_{1})} - E^{(LTA:A_{2})} - \mu^{A_{1}}_{\text{sol}} + \mu^{A_{2}}_{\text{sol}} \tag{5}
\]

Note that because of the different charge between the ions, our systems are also differently charged. In such a case the ion exchange energy, \(\Delta E_{ie}\), should include the charge difference between ps-LTA zeolites with adsorbed Na\(^+\) and AE\(^+\) ions. The \(\Delta E_{ie}\) thus depends on the electron chemical potential, \(\epsilon\), i.e., the location of the Fermi level, as well as the charge difference between the systems, \(\Delta q\), from

\[
\Delta E_{ie} = \Delta E_{ie}^{0} + \Delta q \cdot \epsilon = \frac{E_{ads,0}^{A_{1}} - E_{ads,0}^{A_{2}}}{\gamma_{1} - \gamma_{2}} + (q_{1} - q_{2})\epsilon, \tag{6}
\]

where \(\Delta q\) = 1 as \(q_{1}\) = 2 for AE and \(q_{2}\) = 1 for Na. Similarly, the \(\Delta q\) and \(\epsilon\) also influence the adsorption energy difference, \(\Delta E_{ads}\), following:

\[
\Delta E_{ads} = \Delta E_{ads,0} - \Delta q \cdot \epsilon = \frac{E_{ads,0}^{A_{1}} - E_{ads,0}^{A_{2}}}{(\gamma_{1} - \gamma_{2})} + (q_{1} - q_{2})\epsilon. \tag{7}
\]

By defining the chemical potential of ions \(A_{1}\) and \(A_{2}\) at equilibrium, i.e., \(\Delta E_{ie} = 0\), the ion exchange isotherms for one to one exchange of Na\(^+\) ion with AE ions can be determined at standard state, \(T = 298\) K and \(c_{0} = 0.1\) M, as detailed in Kocovski et al. \(^{24}\), using the equation:

\[
X_{i}^{1} = \left(\frac{\epsilon^{A_{1}}}{\epsilon^{A_{2}}}\right)^{1/(\gamma_{2} - \gamma_{1})}, \tag{8}
\]

where

\[
X_{i}^{1} = \frac{\epsilon^{A_{1}}}{\epsilon^{A_{2}}} = e^{-\frac{E_{ads,0}^{A_{1}} - E_{ads,0}^{A_{2}}}{k_{B}T} \cdot \frac{\gamma_{1} - \gamma_{2}}{\gamma_{2} - \gamma_{1}}}, \tag{9}
\]

where \(X_{i}^{1}\) and \(X_{i}^{A_{1}}\) are the mole fraction of ion \(A_{1}\) on the i site of the zeolite and in solution, respectively, and \(\gamma_{1}\) is the partition function of the adsorbed ion A on site i. The ion-exchange isotherms as a function of the electron chemical potential can be calculated by replacing \(\Delta E_{ie}^{0}\) with \(\Delta E_{ie}\) in Eq. (8).

### Results and Discussion

#### Ion Adsorption

Initial information on the interaction between the AE\(^{2+}\) ions and ps-LTA zeolite were derived from the ion adsorption energies. Using Eq. (1) we calculated the adsorption energies, \(E_{ads,0}\), of AE\(^{2+}\) ions and Na\(^{+}\) at the three adsorption sites in ps-LTA zeolite in vacuum and water, using PBE and DFT-D3, respectively. The results are listed in Table 1. It is evident that the \(E_{ads,0}\) values calculated using DFT-D3 are always more negative compared to those calculated using PBE, which results from the stronger bonding from dispersion interactions in DFT-D3. Despite differences in the absolute values of \(E_{ads,0}\), calculated using PBE or DFT-D3 for sites 1 and 3, the energetic difference between
Sr$^{2+}$ or Ba$^{2+}$ and Na$^+$ are similar. On the other hand, for site 2 the differences calculated using DFT-D3 are less than those from PBE. The smaller size and larger charge of AE ions causes stronger bonding with adsorption site O atoms than for alkali ions$^{24}$, with the exception of Na$^+$, allowing the AE ions to bond at site 2. The ability to also adsorb ions on an additional site expands the ps-LTA capability to retain AE ions, increasing its possible utility in sequestering Sr and Ba radionuclides.

Table 1 Adsorption energies, $E_{ads,0}$, in eV, of ions in vacuum, and water, at the three adsorption sites, calculated by PBE and DFT-D3.

<table>
<thead>
<tr>
<th>ion</th>
<th>vacuum</th>
<th>water</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na$^+$</td>
<td>-8.039</td>
<td>-1.642</td>
</tr>
<tr>
<td>Ca$^{2+}$</td>
<td>-22.178</td>
<td>-0.960</td>
</tr>
<tr>
<td>Sr$^{2+}$</td>
<td>-21.118</td>
<td>-1.710</td>
</tr>
<tr>
<td>Ba$^{2+}$</td>
<td>-19.548</td>
<td>-2.129</td>
</tr>
</tbody>
</table>

The most noticeable results in Table 1 are: i) the absorption energies $E_{ads,0}$ of AE ions in vacuum is much more negative than those in water, which can be explained by the more positive standard chemical potential of AE ions in vacuum as shown in Table S1; ii) the difference of absorption energy $E_{ads,0}$ for Na$^+$ and the AE ions in water is much smaller than that in vacuum because they have comparable chemical potentials in water; and iii) the negative absorption energy $E_{ads,0}$ of Na, Ca, Sr, and Ba ions at site 1, 2, and 3 in water increases in the order of Ca, Na, Sr and Ba ions which is different from that in vacuum. The $E_{ads,0}$ for Ba$^{2+}$ is more negative than for Na$^+$ for each of the three adsorption sites, with exchange among these ions highly favored. On the other hand, the $E_{ads,0}$ for Ca$^{2+}$ is always more positive than that of Na$^+$ at each of the adsorption sites (Table 1), thus an exchange between Na$^+$ in ps-LTA and Ca$^{2+}$ in water is not energetically favored. However, complete exchange of Na$^+$ with Ca$^{2+}$ in an LTA has been experimentally observed$^{26,37}$. This discrepancy between the experiment and calculation may arise from using ps-LTA as a model system instead of the LTA zeolite, specifically neglecting the effect of replacing Si with Al as is the case in the zeolite.

The case for Sr$^{2+}$ is slightly more complex as $E_{ads,0}$ for Sr$^{2+}$ is more negative than for Na$^+$ on site 1, while for other site two the average value $E_{ads,0}$ of Sr$^{2+}$ and Na$^+$ calculated from PBE and DFT-D3 are similar. The results show that the exchange between Na$^+$ for Sr$^{2+}$ at site 1 in the ps-LTA zeolite is energetically favored. With $E_{ads,0}$ for Ba$^{2+}$ more negative than for Sr$^{2+}$ also implies that Ba$^{2+}$ ions will be preferentially adsorbed. However, the adsorption energy of ions strongly depends on the chemical potential of ion in the medium which is a function of ion concentration and temperatures. Therefore, the chemical potentials of ions in the medium will dramatically affect the ion exchanges and equilibrium concentration of AE ions, i.e., the capacity in LTA. The big difference between the adsorption energies calculated in vacuum and water reinforced our previous finding that a more accurate representation of ion-zeolite interaction requires consideration of the water environment$^{24}$. While the greatest accuracy requires modeling water molecules and balancing anions, the required size of such a model exceeds current DFT capability.

### Ion Exchange

The driving force for exchanging Na$^+$ with an AE$^{2+}$ ion can be analyzed from the dependence of the adsorption energy difference, $\Delta E_{ads}$ (Eq. 3), on the molar ratio of the ions, $x$(AE)/$x$(Na) in water, at 298 K. The ion exchange occurs if $\Delta E_{ads}$ is positive (as shown in Fig. S1). The $x$(AE)/$x$(Na) values at which $\Delta E_{ads} = 0$ eV for all adsorption sites are listed in Table 2. It is found that a very high Ca$^{2+}$ concentration ($x$(Ca$^{2+}$)/$x$(Na$^+$) > 10$^{2}$) is required to exchange Na$^+$ with Ca$^{2+}$ because of a more positive adsorption energy of Ca$^{2+}$ compare to that of Na$^+$. The opposite is true for Ba$^{2+}$ exchange with Na$^+$ requiring only very low Ba$^{2+}$ concentrations ($x$(Ba$^{2+}$)/$x$(Na$^+$) < 10$^{-3}$). In the case of Sr$^{2+}$, the $x$(AE)/$x$(Na) ratio at which $\Delta E_{ads} = 0$ eV is ~10$^{-4}$ for each of the three sites, such that small variations in concentration can drive Na$^+$/Sr$^{2+}$ ion exchange in either direction. Site 1 adsorption for Sr$^{2+}$ is favored until the Na$^+$ concentration is 23 times greater than that of Sr$^{2+}$. The results are less clear for site 2, where for Sr$^{2+}$ and Ba$^{2+}$ ions DFT-D3 computes lower $x$(AE)/$x$(Na) values as compared to site 1, and which also differ from PBE calculated values. The latter arises from the difference in values for $E_{ads,0}$ calculated using PBE and DFT-D3 for site 2.

The efficiency of Sr$^{2+}$/Na$^+$ ion exchange can also be analyzed from Sr$^{2+}$ uptake point of view, considering a Sr$^{2+}$ solution that is passed through ps-LTA with a Na$^+$ normalized concentration of 1. In such case, the Sr$^{2+}$ concentration needs to be <0.042 for the ion exchange driving force to be zero, resulting in a 95.8 % Sr$^{2+}$ capacity in the ps-LTA. This value is in agreement with the 99.9 % Sr$^{2+}$ capacity measured in a LTA zeolite$^{20}$ and the 94 % capacity predicted in the phase-field modeling$^{25}$. Given the lack of consideration of finite temperature in our calculations, namely the vibrational contribution to the energy, and/or from the use a simplified model of LTA, i.e., ps-LTA, these remain small differences in determined values.

Table 2 $x$(AE)/$x$(Na) ratio at which the adsorption energy difference, $\Delta E_{ads} = 0$ eV, at the three adsorption sites, calculated with PBE and DFT-D3. The $\Delta E_{ads}$ as a function of the $x$(AE)/$x$(Na) ratio is shown in Fig. S1.

<table>
<thead>
<tr>
<th>ion</th>
<th>site 1</th>
<th>site 2</th>
<th>site 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca$^{2+}$</td>
<td>7.89·10$^{-3}$</td>
<td>1.86·10$^{-3}$</td>
<td>4.13·10$^{-3}$</td>
</tr>
<tr>
<td>Sr$^{2+}$</td>
<td>4.50·10$^{-2}$</td>
<td>4.08·10$^{-2}$</td>
<td>1.47·10$^{-2}$</td>
</tr>
<tr>
<td>Ba$^{2+}$</td>
<td>4.15·10$^{-3}$</td>
<td>1.13·10$^{-3}$</td>
<td>1.02·10$^{-3}$</td>
</tr>
</tbody>
</table>

The different charges of the systems cause the ion exchange energy, $\Delta E_{ads}$, to also depend on the electron chemical potential, $\epsilon_f$, as discussed in Sec. II (Eq. 6). Shown in Table 3 is the $\epsilon_f$ at which $\Delta E_{ads} = 0$ eV for each of the sites, calculated using PBE and DFT-D3, and the dependence of $\Delta E_{ads}$ on $\epsilon_f$ is shown in Fig. S2. Negative $\Delta E_{ads}$ values provide a thermodynamic driving force for exchanging the Na$^+$ with AE$^{2+}$. Evidently, change in the $\epsilon_f$ does not influence $\Delta E_{ads}$ values of Ca$^{2+}$ at any of the 3 sites, due to the positive $\Delta E_{ads}$. A DFT-D3 calculated very small increase, ~0.07 eV, in $\epsilon_f$ can prevent the exchange of Na$^+$ with Sr$^{2+}$ on site 1, as does a slightly larger $\epsilon_f$, 0.14 eV, for site 2. In the case of Ba$^{2+}$, an increase of ~0.5 eV in $\epsilon_f$ is needed to eliminate the thermodynamic driving force for ion exchange on site 1. Also, DFT-D3 for Ba$^{2+}$ ion computes larger $\epsilon_f$ values as compared to PBE. Increasing $\epsilon_f$ implies that electrons need to be donated to the ps-LTA, which is possible to control by doping the ps-LTA framework with an n-dopant, e.g., replacing Si with P or replacing O with F. It can also be
accomplished by introducing electron donors in the aqueous solution that interact with the ps-LTA framework, e.g., decreasing the pH. On the other hand, introducing p-dopants, such as Al, or increasing the pH of the aqueous solution would promote AE\(^{2+}\) ion adsorption.

Table 3  Electron chemical potential, \(\varepsilon_i\) (in eV), at which the ion exchange energy, \(\Delta E_{\text{ads}}\), is 0 eV, at the three adsorption sites, calculated with PBE and DFT-D3. The cells denoted with "n/a" indicate that at \(\varepsilon_i = 0\), \(\Delta E_{\text{ads}} > 0\) eV. \(\Delta E_{\text{ads}}\) as a function of \(\varepsilon_i\) is shown in Fig. S2.

<table>
<thead>
<tr>
<th>ion</th>
<th>PBE</th>
<th>DFT-D3</th>
<th>PBE</th>
<th>DFT-D3</th>
<th>PBE</th>
<th>DFT-D3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca(^{2+})</td>
<td>8.79·10(^{-4})</td>
<td>1.86·10(^{-4})</td>
<td>4.13·10(^{-4})</td>
<td>2.34·10(^{-4})</td>
<td>4.86·10(^{-4})</td>
<td>1.19·10(^{-4})</td>
</tr>
<tr>
<td>Sr(^{2+})</td>
<td>4.50·10(^{-4})</td>
<td>4.08·10(^{-4})</td>
<td>1.47·10(^{-4})</td>
<td>2.48·10(^{-4})</td>
<td>4.97·10(^{-4})</td>
<td>6.69·10(^{-4})</td>
</tr>
<tr>
<td>Ba(^{2+})</td>
<td>4.15·10(^{-4})</td>
<td>1.13·10(^{-4})</td>
<td>1.02·10(^{-4})</td>
<td>1.71·10(^{-4})</td>
<td>8.70·10(^{-4})</td>
<td>3.75·10(^{-4})</td>
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</table>

Isotherms

The ion exchange equilibrium can be further investigated by evaluating the ion exchange isotherms, as defined by Eq. (8) for \(T = 298\) K and \(c_0 = 0.1\) M. Ion exchange isotherms for Ca\(^{2+}\), Sr\(^{2+}\) and Ba\(^{2+}\) in water calculated using PBE and DFT-D3 are plotted in Fig. 2. The results show that Ca\(^{2+}\) ion exchange is not possible at any of the adsorption sites, reflecting the high positive ion exchange energy values (Table S3). On the other hand, complete exchange of Na\(^+\) for Ba\(^{2+}\) is possible at all three adsorption sites, due to the large negative ion exchange energies calculated by either PBE or DFT-D3 (Table S3). In the case of Sr\(^{2+}\), both PBE and DFT-D3 calculate only partial ion exchange is possible on the three adsorption sites. Unlike Ca\(^{2+}\) and Ba\(^{2+}\), the ion exchange energies for Sr\(^{2+}\) have smaller and more similar values (Table S3), distributed around the 0 by ±0.07 eV, implying a possibility for only partial ion exchange. Having the possibility to completely or to a high extent exchange Na\(^+\) for Ba\(^{2+}\) or Sr\(^{2+}\) is requirement for sequestering these radionuclides from nuclear wastewater using the ps-LTA zeolite.

Fig. 2  Ion exchange isotherms calculated using (a) PBE, and (b) DFT-D3 for ions on sites 1 (solid line), 2 (dashed-dotted line) and 3 (dashed line).

By replacing the \(\Delta E_{\text{ads}}\) in Eq. (8) with \(\Delta E_{\text{ads}}\), the ion exchange isotherms can also be plotted as a function of \(\varepsilon_i\). Focusing only on site 1, the most probable adsorption site for AE\(^{2+}\) and therefore that of greatest importance. Fig. 3 shows the ion exchange isotherms for Sr\(^{2+}\) and Ba\(^{2+}\) for a range of \(\varepsilon_i\). Values. From Fig. 3a and 3b it is clear that the ion exchange of Na\(^+\) for Sr\(^{2+}\) is no longer possible when \(\varepsilon_i > 0.4\) eV, when calculated with both PBE and DFT-D3. In the case of Ba\(^{2+}\), partial exchange becomes dominant for \(\varepsilon_i > 0.4\) in PBE and for \(\varepsilon_i > 0.5\) eV in DFT-D3 calculations. Increasing in \(\varepsilon_i\) further suppresses the Ba\(^{2+}\) ion exchange, and not possible for \(\varepsilon_i > 0.8\) eV and for \(\varepsilon_i > 0.9\) eV in PBE and DFT-D3 calculations, respectively.

The ion exchange between Sr\(^{2+}\) and Ba\(^{2+}\) ions shown in Fig. 4, indicate \(\Delta E_{\text{ads}}\) is negative, and therefore existence of a thermodynamic driving force for exchanging Ba\(^{2+}\) with Sr\(^{2+}\) yielding ion exchange isotherms. Evidently, for ion exchange to be spontaneous, a very large x(Sr)/x(Ba) ratio is required (Fig. 4a), i.e., \(10^3\) - \(10^{14}\) depending on the site and potential used. The large \(\Delta E_{\text{ads}}\) values influence the ion exchange isotherms, allowing only partial exchange on site 3 as calculated using PBE (Fig. 4b). This indicates that when using only a ps-LTA zeolite to capture Ba\(^{2+}\) and Sr\(^{2+}\), the protocol should require that Ba\(^{2+}\) is removed first, with removal of Sr\(^{2+}\) in a subsequent step. The larger \(\Delta E_{\text{ads}}\) computed by DFT-D3 results from the stronger induced bonding between the larger Ba\(^{2+}\) and the ps-LTA zeolite as compared to Sr\(^{2+}\). This in turn decreases the Ba\(^{2+}\) adsorption energy with respect to Sr\(^{2+}\), increasing \(\Delta E_{\text{ads}}\). Also, there is an evident trend with the \(\Delta E_{\text{ads}}\) decreasing from site 3, to site 1 and to site 2, computed by either PBE or DFT-D3.

Fig. 3  Ion exchange isotherms for various values of the electron chemical potential, \(\varepsilon_i\), for Sr\(^{2+}\) calculated using (a) PBE, and (b) DFT-D3, and Ba\(^{2+}\) calculated using (c) PBE, and (d) DFT-D3. The color change from red to yellow and blue to green shows the increase in \(\varepsilon_i\) for the systems containing Sr\(^{2+}\) and Ba\(^{2+}\), respectively.

Fig. 4  (a) adsorption energy difference, \(\Delta E_{\text{ads}}\), and (b) ion exchange isotherms for exchanging Ba\(^{2+}\) with Sr\(^{2+}\) on site 1 (solid line), site 2 (dashed-dotted line) and site 3 (dashed line), calculated using PBE, and DFT-D3. The \(\Delta E_{\text{ads}}\) and isotherms calculated using PBE and DFT-D3 are shown in red and blue, respectively.

Conclusions

In vacuum, the adsorption energies of alkaline earth ions were significantly more negative than the energy of Na\(^+\) adsorption. The difference in energies was substantially lessened, coming close to
zero, when the ions were solvated in water. We show that this discrepancy results from the large difference in the chemical potential of the alkaline earth ions and Na$^+$ in vacuum. This emphasizes that the solvation model is necessary for a more accurate representation of ion adsorption on zeolites. Moreover, we showed that Na$^+$ exchange with Ba$^{2+}$ is possible on all three adsorption sites as reflected by the large difference in Na$^+$ and Ba$^{2+}$ adsorption energies. On the other hand, Ca$^{2+}$/Na$^+$ ion exchange is not possible, unless the $x$(Ca$^{2+}$)/x(Na$^+$) ratio is considerably large (> 10$^3$), differently from the experiments. We argue that this discrepancy arises from using the ps-LTA as a model in our calculations. In the case of Sr$^{2+}$, the Na$^+$ ion exchange is only partially possible, with calculated normalized concentration of Sr$^{2+}$ in the zeolite of 0.9983. The calculated value is slightly lower than the experimentally observed one, which we argue is a result of not taking vibrational contributions to the energy into account when using ps-LTA as a computational model. The results demonstrate that ps-LTA can be successfully used for sequestering Ba$^{2+}$ and Sr$^{2+}$ radionuclides.

Furthermore, we showed that the ps-LTA electron chemical potential has a considerable influence on the ion exchange. This means that defects in the ps-LTA framework or the introduction of electron donors in the aqueous solution can suppress the Na$^+$ ion exchange with alkaline earth ions. Also, we demonstrate that when using PBE calculations, exchanging Ba$^{2+}$ with Sr$^{2+}$ is only partially possible on site 3, but not on the remaining adsorption sites, while when considering DFT-D3, Ba$^{2+}$/Sr$^{2+}$ exchange was not possible on any of the adsorption sites. In aqueous solution, a very large $x$(Sr$^{2+}$)/x(Ba$^{2+}$) ratio (>10$^7$) is required to overcome the Ba$^{2+}$ adsorption and for Sr$^{2+}$ to preferentially adsorb on the ps-LTA.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This work is supported by the U.S. Department of Energy, Office of Science, Basic Energy Sciences, under Award No. DE-SC0016574 (Center for Hierarchical Waste Form Materials). This research used computational resources provided by the National Energy Research Scientific Computing Center (NERSC) and the HPC cluster Hyperion, supported by the Division of Information Technology at University of South Carolina.

Notes and references
