The gallophosphate cloverite – A promising adsorbent for environmental remediation...?

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Abstract

Several recent molecular simulation studies proposed the gallophosphate zeotype cloverite, or cloverite-type materials, as promising adsorbents for the removal of various contaminants from water. This comment presents evidence that the cloverite models used in the simulations presented in those articles were most likely not charge-neutral. Use of such physically unrealistic adsorbent models is expected to have a negative impact on the meaningfulness of the simulation results. To provide a potential starting point for future simulation studies, a neutral model of guest-free cloverite is constructed and optimised with density functional theory

calculations.

Cloverite

The gallophosphate zeotype cloverite was reported by Estermann et al. in 1991. Its name is derived from the shape of the apertures of the largest pores in the structure, as they resemble four-leaf clovers. At the time of publication, these pore openings, which are lined by 20 TO₄ tetrahedra (where T = tetrahedrally coordinated atoms, in this case, Ga and P), were the largest reported for any zeotype structure (zeolite-like materials with pore openings constituted by up to 30 TO₄ tetrahedra have been reported more recently²). The largest cage of the cloverite structure, which lies at the intersection of channels lined by the 20-membered rings (20MRs) is also exceptionally large, with a body diagonal of ~30 Å. Another peculiarity of the cloverite structure is the interrupted nature of the framework: In each 20MR, there are four TO₄ tetrahedra having one "dangling" O atom, which is not connected to a neighbouring T atom,

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but forms a hydroxyl group that points towards the ring centre (**Figure 1**). As is the convention for interrupted frameworks, the structure commission of the International Zeolite Association (IZA) assigned a framework type code with a leading hyphen to the cloverite structure: -CLO.³

The crystal structure of cloverite, determined from single-crystal X-ray diffraction measurements, is cubic, space group $Fm\overline{3}c$, with a very large unit cell (a=52.712~Å). While the positions of framework atoms (including dangling O atoms) and fluoride anions incorporated in the double four-membered rings (d4r units) could be refined, a refinement of the positions of OSDA molecules and of hydrogen atoms of the hydroxyl groups remained elusive. This crystal structure is available from the IZA Structure Database (IZADB) in CIF format. The content of the conventional cubic unit cell is $Ga_{768}P_{768}O_{2976}(O_OH)_{192}F_{192}$, where O_OH is used as a label to distinguish dangling oxygen atoms from those belonging to Ga-O-P linkages. It has been postulated that the negative charge of -384~e per unit cell is balanced by protons of hydroxyl groups and quinuclidinium cations in equal amounts (192/192). Concurrent removal of OSDA cations and fluoride anions through calcination results in a neutral compound with accessible porosity.

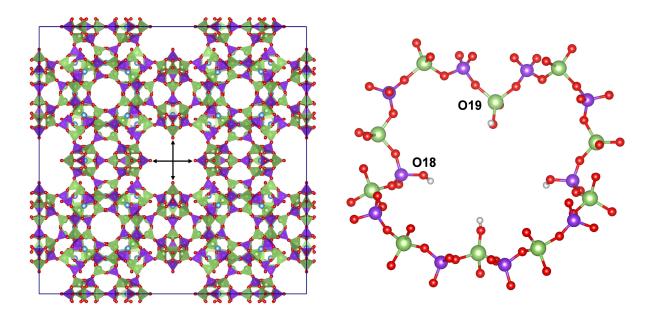


Figure 1: Left: Crystal structure of cloverite taken from the IZADB. Green and purple tetrahedra represent GaO₄ and PO₄ tetrahedra, respectively, light blue spheres correspond to fluorine atoms. Non-coordinated O atoms in one of the 20MRs are highlighted by arrows. **Right:** Single 20MR including charge-balancing protons. Figures prepared with VESTA.⁶

Subsequent experimental investigations focused on various properties of cloverite, such as its thermal stability and dehydration/defluorination behaviour,^{4,5} adsorption properties^{4,5,7} and its potential use in gas-phase catalysis.^{8,9} Although the framework remains intact after calcination, this detemplated form is unstable in the presence of water or other polar molecules,^{5,7} and can

only be stabilised by blocking the pores, for example, using silanes.¹⁰ The low stability of cloverite (together with the rather high cost of gallium) severely limits its potential applicability in separation and catalysis, despite the large pore openings. In 2010, an aluminophosphate analogue of cloverite was reported.¹¹ While it is more stable than the gallophosphate, the calcined form still shows significant decrease in crystallinity upon exposure to ambient air for several days. PKU-12, a germanosilicate having the -CLO topology, is also unstable in the presence of water.¹²

Recent simulation studies of cloverite

In several recent simulation studies, grand-canonical Monte Carlo (GCMC) simulations were employed to predict adsorption isotherms of organic or inorganic contaminants in different zeolites. As high uptakes were predicted for cloverite in gallophosphate form or, in one case, another -CLO-type structure, this framework was proposed as a particularly promising system for contaminant removal in the context of environmental remediation. The following studies are discussed in more detail in this comment:

- o In one paper, abbreviated SN2020 for convenience, the adsorption of three drug molecules, ciprofloxacin, diclofenac, and chloramphenicol, was investigated. The conclusions of this paper state: "According to the molecular simulation results in this research, CLO zeolite has proved to be the satisfactory zeolite suited for adsorption of diclofenac, ciprofloxacin and chloramphenicol [...]."
- More recently, a similar approach was used to study the adsorption of various chlorinated hydrocarbons like hexachlorobenzene (HCB). In the abstract of this paper, abbreviated JC2024, it is highlighted that "[i]t was found that CLO (a cubic microporous gallophosphate) demonstrated the highest adsorption capacity for HCB among 245 zeolites, with a loading capacity of 65.84 wt%."
- Two computational investigations of ion adsorption addressed the adsorption of metal cations like Pb²⁺ (CMS2021)¹⁴ and of inorganic anions like AsO₄³⁻ (JML2022).¹⁵ A representative quote from the conclusions of JML2022 reads: "According to the molecular simulation results, the CLO zeolite has proved to be the best zeolite for adsorption of anions (PO₄³⁻, NO₃-, CrO₄²⁻, AsO₄³⁻)."

While this comment addresses exclusively the modelling of the structure of cloverite, some aspects of the simulation setup, such as the unclear relationship between fugacity and concentration in the aqueous phase, have also been the subject of some scrutiny (see, for example, the present author's PubPeer comment regarding JML2022: https://pubpeer.com/publications/9A405AF8B5714665C857948C5AB54C).

Non-neutral models of cloverite

In the first place, it may seem questionable whether a rather unstable and expensive zeotype like the gallophosphate cloverite can play any role in large-scale applications, especially in the view of its instability towards hydration. However, it would appear overly dogmatic to limit the scope of computational screening investigations to those materials for which a practical applicability has already been established, as the inclusion of less conventional materials may result in new insights and potentially spark further experimental research. Hence, the main point of criticism elaborated in this comment is not the fact *that* cloverite was included in the investigations, but rather *how* it was modelled. Although neither of the four papers provides input structures of the adsorbent models used in the simulations, the following issues can be identified based on the information provided in text, figures, and tables:

- In the abstract of SN2020, the composition of cloverite is stated as F₂₄Ga₉₆P₉₆O₃₇₂(OH)₂₄. ¹³ Presence of 192 T atoms (Ga+P) indicates that this sum formula refers to one eighth of the conventional cubic unit cell. A summation of the formal charges indicates that this structure is not charge-balanced, with a total charge of -24 e per formula unit (-192 e per cubic cell). On the other hand, an inspection of the figures of SN2020 (notably Figure 3 A and Figure S1) indicates that neither the fluorine atoms nor the hydrogen atoms saturating the "dangling" oxygen atoms were present in the cloverite structure used in the simulations. This would result in a sum formula Ga₉₆P₉₆O₃₉₆, which also is not neutral (-24 e per formula unit). Incidentally, a cloverite model having this composition is included in the structure database that is part of the commercial software DS BIOVIA *Materials Studio*, which was used in the simulations reported in SN2020.
- CMS2021 does not state a cell composition, but Figure S50 shows dangling, unsaturated oxygen atoms and no fluorine atoms, rendering it plausible to assume that a model with sum formula Ga₉₆P₉₆O₃₉₆ was used, as in SN2020.¹⁴ The same reasoning can be applied for the case of JC2024, notably on the basis of Figure 9.¹⁶
- o Although the sum formula is not given in JML2022, a density of 1.129 g cm⁻³ is stated in Table S1.¹⁵ This is exactly the density of the purely siliceous model of the -CLO framework that is included in the IZADB. This purely hypothetical all-silica -CLO model has, again, dangling oxygen atoms and is therefore not neutral. As all T sites are occupied by the same element, silicon, the structure can be described in a smaller unit cell having composition Si₁₉₂O₃₉₆ (charge: −24 e).

Based on the evidence collected, it seems reasonable to surmise that all four investigations used models of cloverite (or, in the case of JML2022, of a purely siliceous -CLO-type framework) that were not charge-neutral. When simulating the adsorption of neutral, non-polar

guest molecules, it may be a permissible first approximation to ignore electrostatic interactions altogether. In such cases, the non-neutrality of the adsorbent model and the presence of dangling oxygen atoms may not cause any major artefacts. However, the adsorption of polar molecules and, even more so, of cations or anions will be strongly impacted, if not dominated, by electrostatic interactions. For such cases, use of charge-imbalanced adsorbent models is expected to result in spurious electrostatic contributions to the total energy. In particular, the dangling, undercoordinated oxygen atoms will act as negatively polarised sites that would provide an artificially strong electrostatic interaction with cations or positively polarised areas of guest molecules. Clearly, these spurious contributions will negatively affect the physical meaningfulness of the simulation results and may result in qualitatively wrong predictions, for example, by systematically favouring non-neutral adsorbents over neutral ones. Without going into further details of the four studies, we may note that the reported loadings of 728 Pb2+ cations (positive excess charge: +2,184 e) or 420 phosphate anions (negative excess charge: -1,260 e) per conventional -CLO unit cell, taken from CMS2021 and JML2022, respectively, appear physically unrealistic, especially when considering that, apparently, no additional charge-balancing species were included in the simulations. In the commenter's opinion, this points to significant problems with the representation of electrostatic interactions, which may not necessarily be caused, but certainly exacerbated by the use of non-neutral adsorbent models.

A charge-balanced cloverite model

In order to obtain a charge-balanced model of the gallophosphate cloverite, the structure refined by Estermann et al. was taken from the IZADB.¹ The fluorine atoms occupying the *d4r* units were removed, and all dangling oxygen atoms were saturated by hydrogen atoms. This structure was then optimized using dispersion-corrected density functional theory (DFT) calculations, employing two different exchange-correlation functionals, namely, the Perdew-Burke-Ernzerhof functional¹⁷ together with a Grimme-type D3¹⁸ dispersion correction (PBE-D3) and the rev-vdW-DF2 functional proposed by Hamada.¹⁹ Both of these approaches performed well in a previous benchmarking study on all-silica zeolites and aluminophosphate zeotypes.²⁰ Further details of the DFT calculations are provided in the Appendix.

Table 1 compares some important structure parameters of the DFT-optimised structures to those of the experimental structure. The cell parameter *a* is 1.8%/1.0% (PBE-D3/rev-vdW-DF2) larger than the experimental one. This tendency is unsurprising when considering, first, that cell parameters of guest-free zeolites/zeotypes are often larger than those of assynthesised systems²¹ and, second, that a tendency to overestimate the cell parameters has been established for both functionals (although it is less pronounced than for many other

dispersion-corrected DFT approaches).²⁰ Regarding bond distances, it is noteworthy that the average Ga-O and P-O bond distances in the DFT-optimised structures are about 0.04 Å longer than in the experimental structure, regardless of the choice of functional. Nevertheless, they fall well into the range of typical Ga-O/P-O bond distances compiled in a survey of experimental zeolite and zeotype structures.²² Compared to bonds within Ga-O-P linkages, bonds to the oxygen atom of the hydroxyl group are somewhat compressed for gallium, but expanded for phosphorus. The O-H distances amount to 0.971/0.974 Å (PBE-D3/rev-vdW-DF2) for the (Ga-)O-H group and 0.974/0.977 Å for the (P-)O-H group. As the hydrogen atoms were placed on a mirror plane in the starting structure in order to retain the $Fm\bar{3}c$ symmetry, it has to be conceded that the final, optimised positions are likely to depend on the starting positions and may not correspond to global minima. However, it is not expected that the exact orientation of the hydroxyl groups would strongly affect the properties computed using such a DFT-optimised model, e.g., in adsorption simulations.

Table 1: Unit cell parameters and average T–O bond distances of cloverite. Experimental values are from the work of Estermann et al., ¹ DFT values are from this work.

	Experiment	DFT, PBE-D3	DFT, rev-vdW-DF2
a / Å	51.712	52.671	52.340
d _{aver} (Ga−O) / Å	1.813±0.034	1.854±0.012	1.852±0.012
<i>d</i> (Ga−O_OH) / Å	1.820	1.789	1.789
d _{aver} (P−O) / Å	1.506±0.027	1.549±0.010	1.549±0.010
d(P-O_OH) / Å	1.494	1.594	1.592

Concluding remarks

In summary, an analysis of the information provided in some earlier molecular simulation studies points to a use of non-neutral models of cloverite in those works. It seems thus likely that the results reported for polar or charged guest species are affected by spurious electrostatic interactions. A neutral model of the gallophosphate cloverite was constructed and optimised using dispersion-corrected DFT calculations; it should constitute a suitable starting point for future molecular simulation studies of this material. An extension of the same approach to -CLO-type structures with other compositions or other interrupted zeolite frameworks should be straightforward. Looking beyond the specific case of cloverite, one feels compelled to reiterate that care must be taken when using structural data from structure databases for simulations of adsorption (or other) properties. Although significant efforts have been made to develop "computation-ready" structure databases, for example, in the field of MOFs,^{23–25} even these may still contain structures that require modifications to allow for

physically meaningful simulations, with identified issues including missing hydrogen atoms or charge-balancing ions. ^{26,27} In general, crystal structure databases are not designed to provide structures that are directly usable in simulations. It is therefore pivotal to include a "sanity check", either by the user or via a suitably designed algorithm, prior to using structures from such databases in any kind of molecular simulation. For the specific case of the IZADB, it can be stated that the all-silica models of fully connected frameworks, optimised with a distance least-squares algorithm (DLS-76), should not require further modifications, whereas models of interrupted frameworks have to be treated with care. The same is true for the experimental crystal structures contained in this database, which often contain disorder, for example, of extra-framework cations or water molecules. Finally, it is recommended that researchers either supply structures of adsorbent models or describe the origin of the initial models and, where applicable, all modifications unambiguously and in sufficient detail in order to allow for a reliable reproduction of the simulation results.

Appendix: Details of DFT calculations

The structure of cloverite as refined by Estermann et al. was taken from the IZA Database. 3 Fluorine atoms were removed, and the two non-coordinated oxygen atoms (labelled O18 and O19 according to the original publication, **Figure 1**) were saturated with hydrogen atoms. These hydrogen atoms were put on the mirror plane perpendicular to a on which the O18 and O19 atoms also reside (Wyckoff position 96i). The structure was then converted to the primitive cell prior to full DFT optimisations using the CP2K code, version 2023.1.28 As described in the main text, separate optimisations were performed using the PBE-D3^{17,18} and rev-vdW-DF2¹⁹ functionals. The DFT calculations used "molecularly optimised" double-zeta basis sets (DZVP-MOLOPT-SR) proposed by VandeVondele and Hutter²⁹ and Goedeker-Teter-Hutter pseudopotentials devised by Krack,³⁰ employing a cutoff energy of 600 Ry. Due to the size of the unit cell, only the Γ point was included in the sampling of the first Brillouin zone. The optimisations enforced the $Fm\bar{3}c$ symmetry of the cloverite structure (keyword KEEP SPACE GROUP in the block CELL OPT of the CP2K input file). Using a BFGS optimiser, the optimisations were considered converged when the maximal step size (displacement between optimisation steps) was below 10^{-4} a_0 ($a_0 = 0.52918$ Å), the maximal residual force was below 10^{-5} Hartree/ a_0 , and the residual pressure was below 10 bar. The final structures were converted back to the conventional cell setting using the DS Biovia Materials Studio suite.

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Supporting Information

Supporting information archive contains CIF files of the gallophosphate cloverite optimised with DFT calculations as well as CP2K input files.

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