# Inorganic Ion Exchangers and Sorbents for Groundwater, Process Water and Soil Remediation

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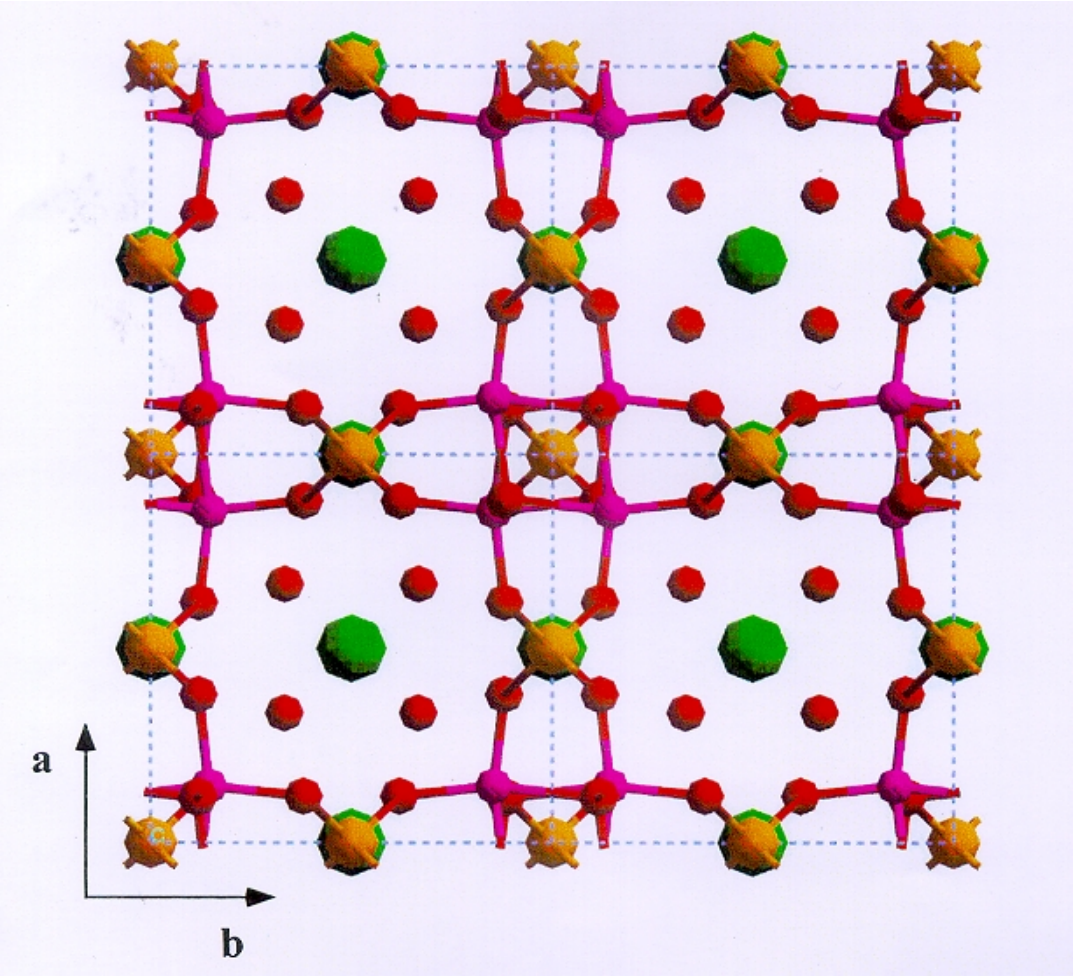
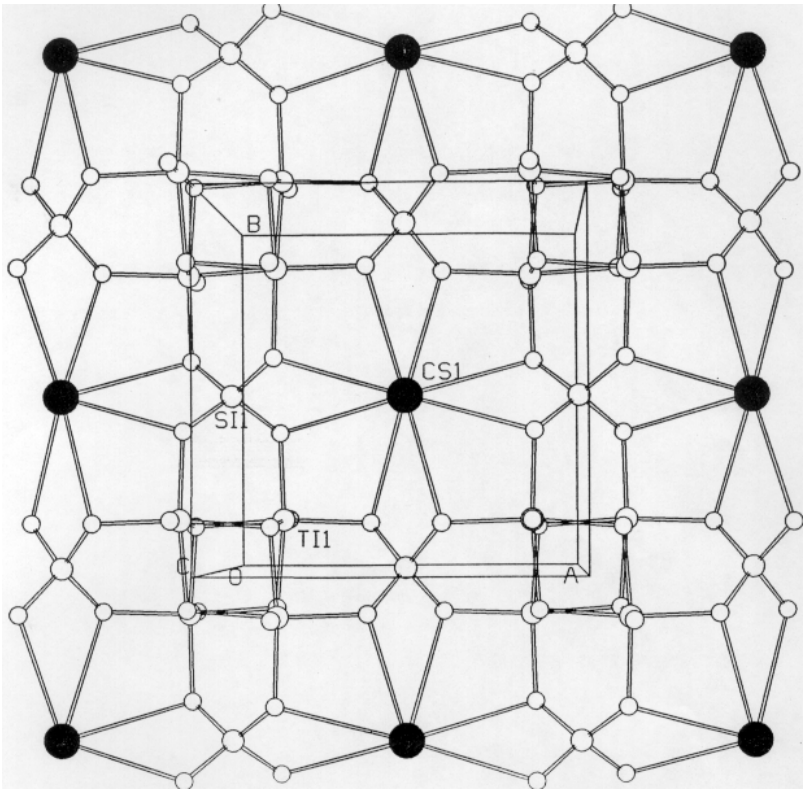
# Structure for the Potassium Pharmacosiderite, $HK_3Ti_4O_4(SiO_4)\bullet 4H_2O$

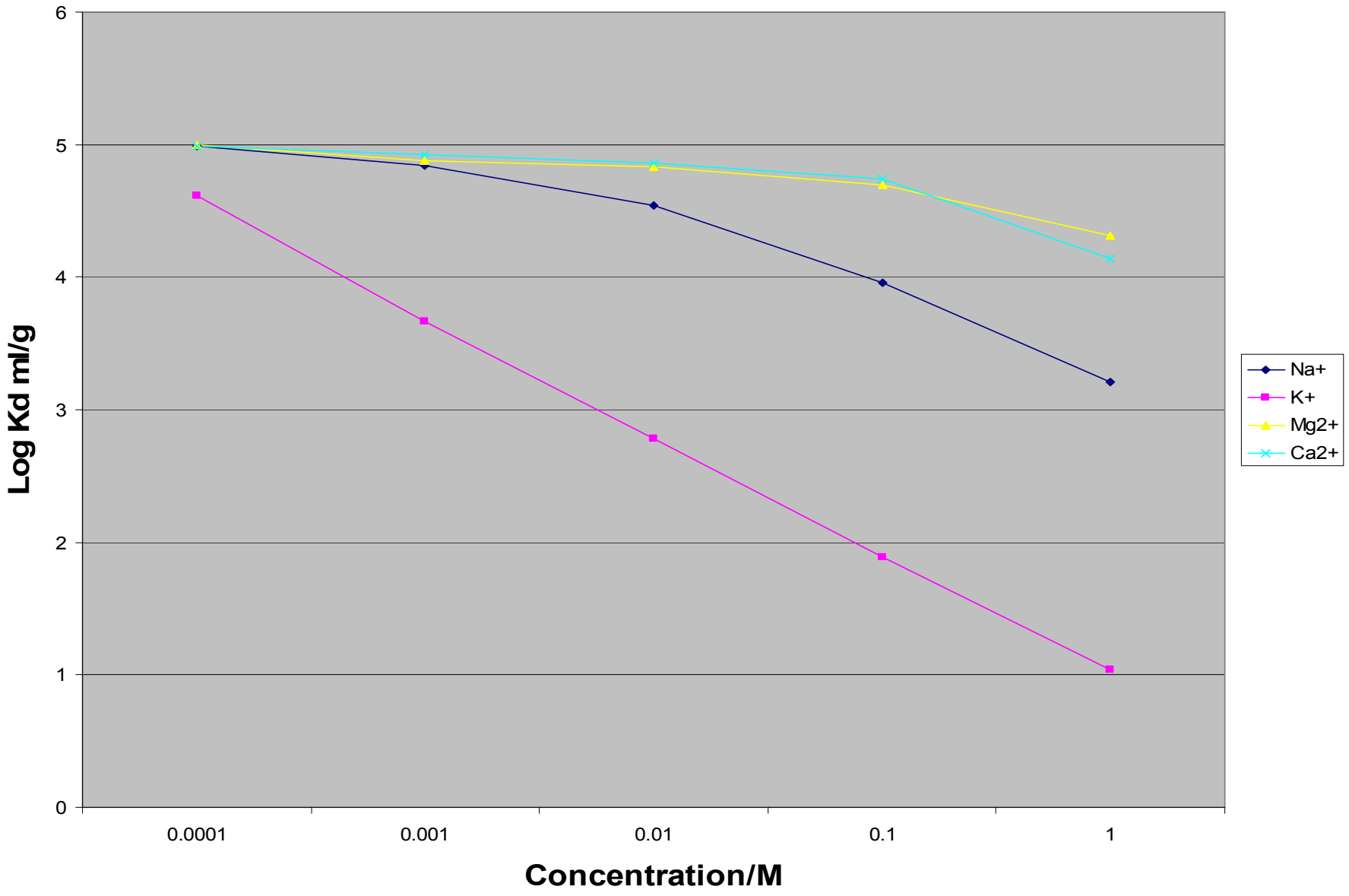


# Structure of $\mathbf{NaH_{0.75}Cs_{0.25}Ti_2O_3SiO_4}$

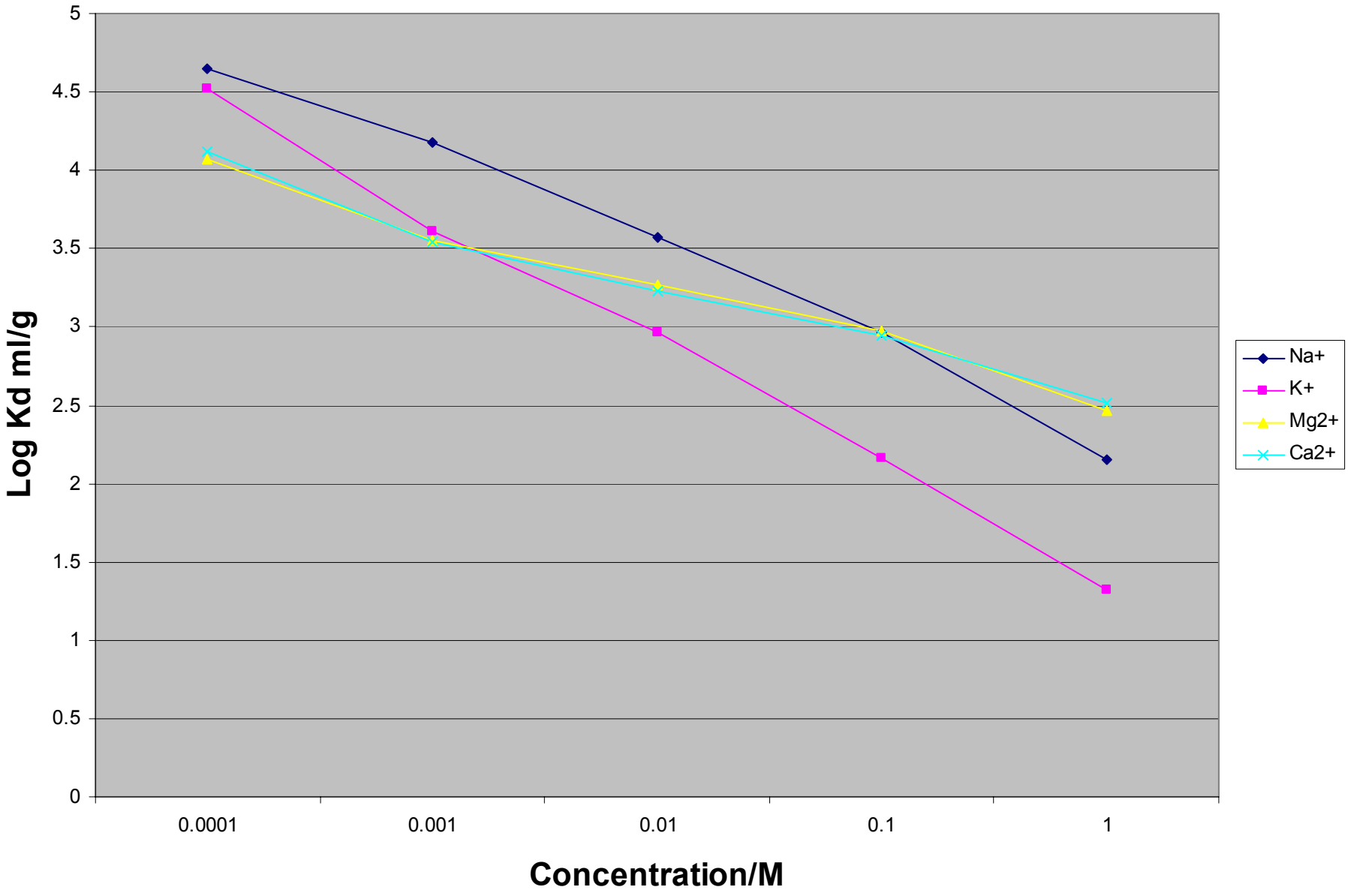
$Cs^+$ fits perfectly into the center of the tunnel while $Na^+$ occupies sites in the framework cavities. Eight silicon oxygens coordinate the $Cs^+$ at distances equal to the sum of the ionic radii.



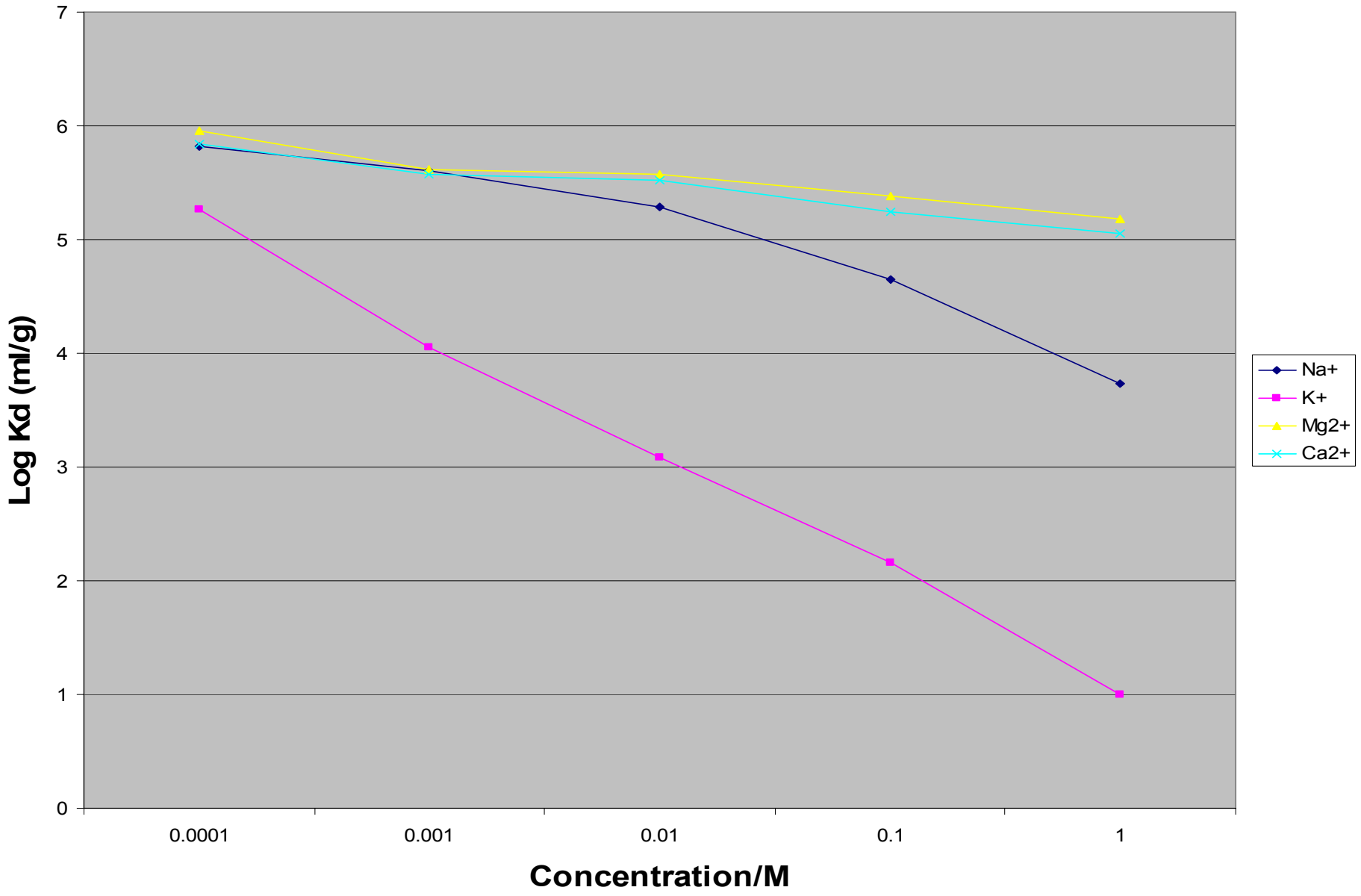
# $Cs^+$ Kds for the Al-PILC



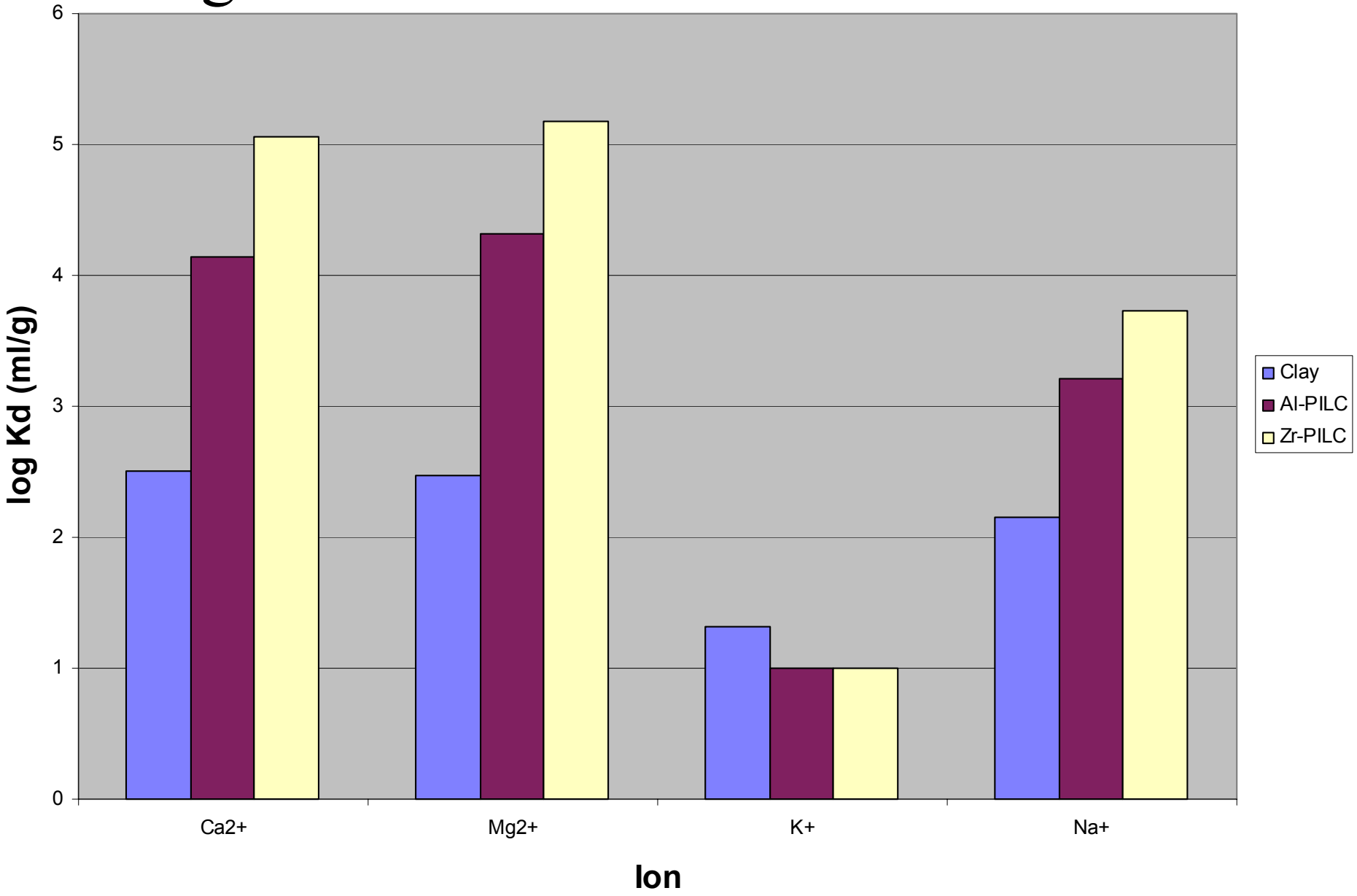
# $Cs^+$ Kds for the Los Trancos Clay



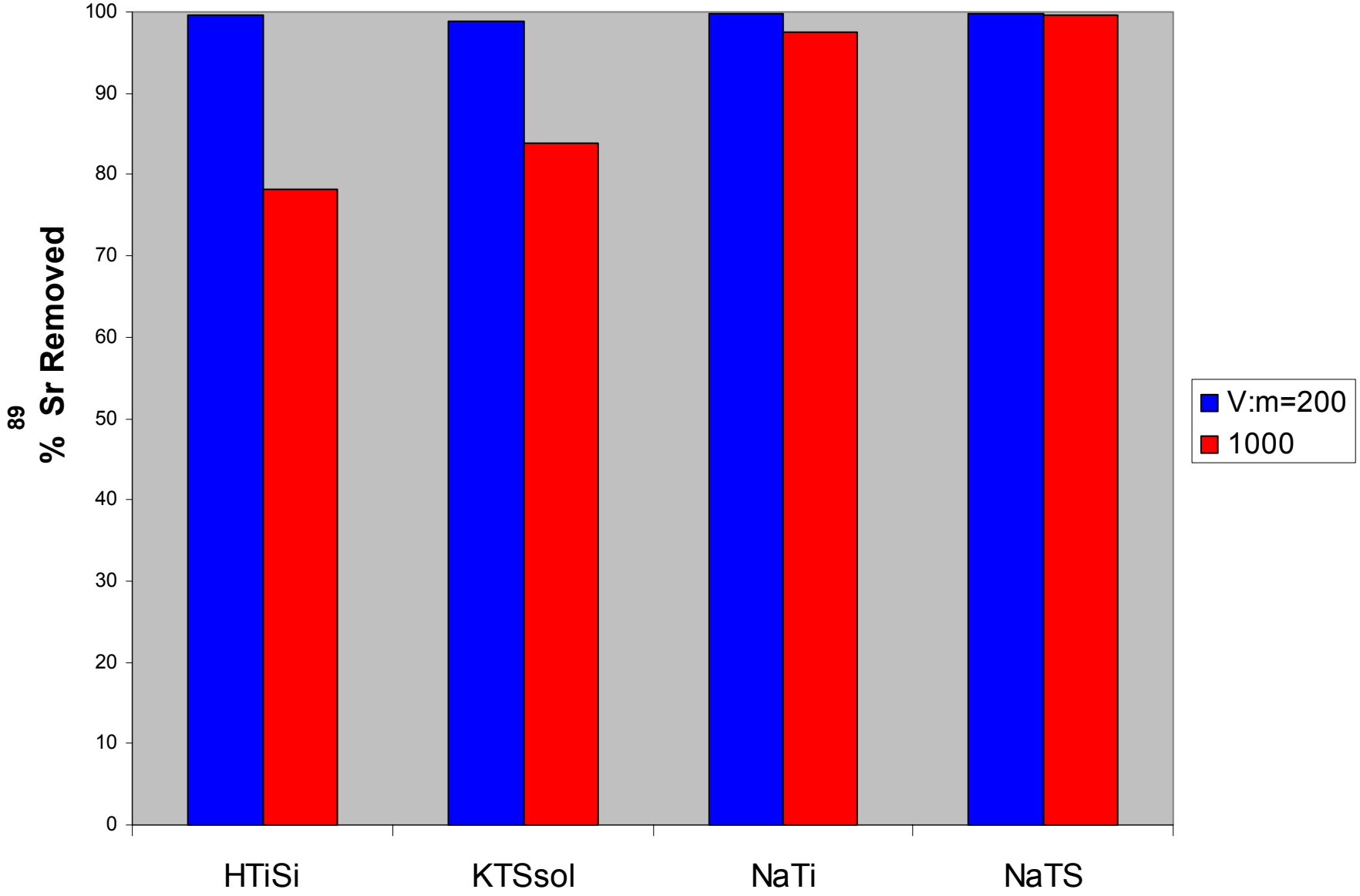
# $Cs^+$ Kds for the Zr-PILC



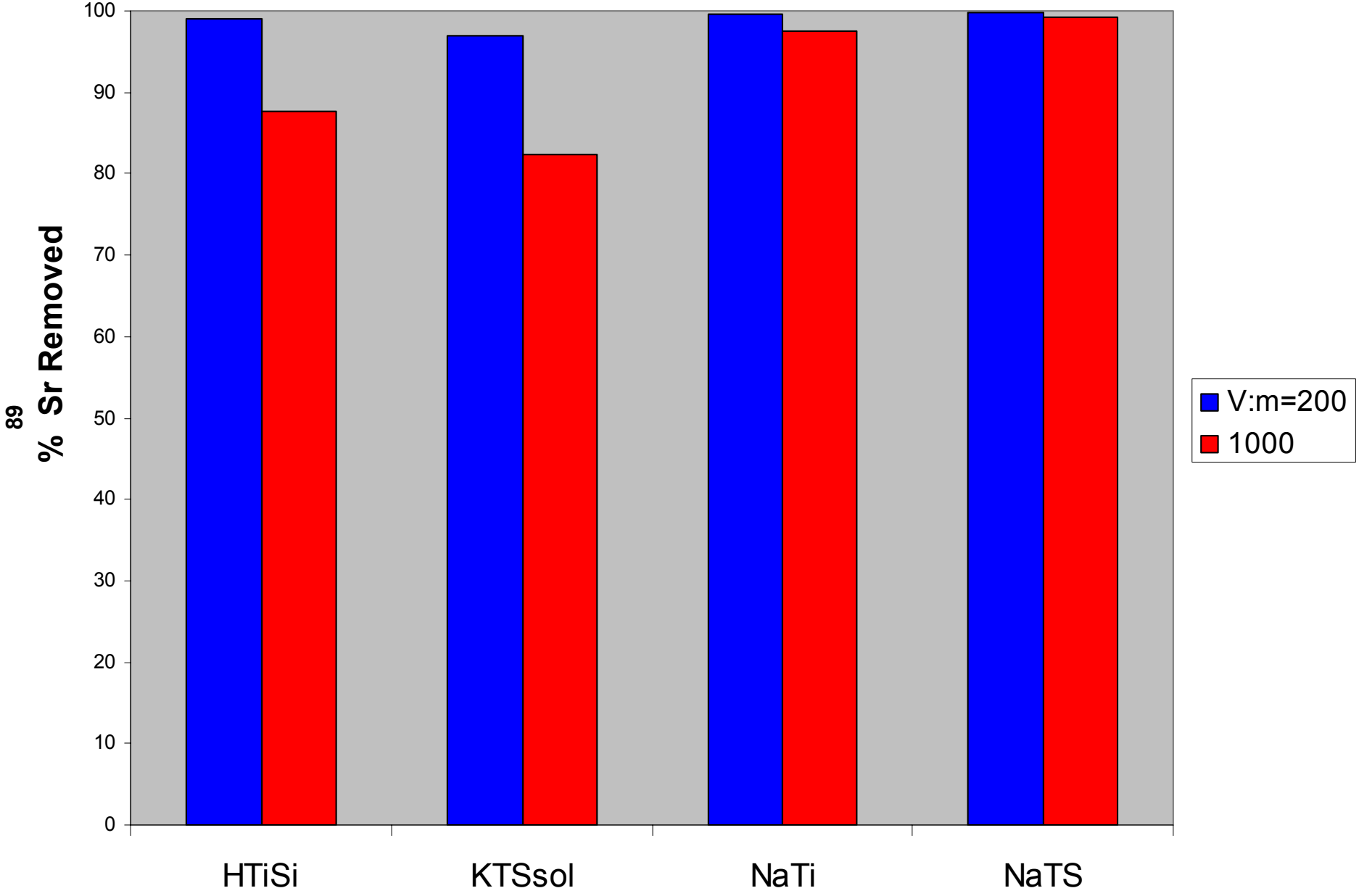
# Log $Cs^+$ Kds in 1M Metal Ion Solution



# Percent $^{89}$Sr Removal from NCAW Simulant



# Percent $^{89}$Sr Removal from DSSF-7 Simulant



# Inorganic Ion Exchangers and Sorbents for Groundwater, Process Water and Soil Remediation

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# Hanford Waste Problems

- Hanford site
  - leaders in Pu production for nuclear weapons
  - PUREX process
- 55 million gallons of high level waste in 177 steel-lined tanks
- tanks contain 3 phases:
  - alkaline sludge, salt cake, and supernate
- 66 tanks are known to leak
  - groundwater and rivers

# Objectives

To provide in usable forms, a broad spectrum of inorganic ion exchangers, that can be utilized for a range of applications involving remediation of groundwater, plumes, tanks wastes and soils.

- Why Use Inorganic Ion Exchangers?
  - Resistance to organic solvents and strong oxidizers
  - Radiation and temperature stable
  - High selectivities and distribution ratios
    - inherent structural features
  - Tune ion exchange properties:
    - alter synthetic parameters (time, temperature, starting reagents…)
    - substitute different metals ions into framework or vary exchangeable cation

Sodium Titanosilicate

$Na_2Ti_2O_3(SiO_4)$

Discovered by a team at Sandia National Laboratory

Reported to sequester $Cs^+$ from Alkaline 5 M $NaNO_3$ solutions.

Considered for removal of $^{137}Cs$ from nuclear wastes at Hanford.

# Altered Clays and Mica

- We have propped open montmorillonite clays with alumina and zirconia polymers. As shown below, and in Oak Ridge Seep D groundwater, these altered clays have a high affinity for $Cs^+$. They may be used in groundwaters and process waters or in soil remediation.
- Sodium mica has an extremely high affinity for $Cs^+$. When about 0.8-1.0 meq/g has been taken up the layers collapse and trap the $Cs^+$ permanently. These micas are ideal as barrier materials for $Cs^+$ in soils.

# Groundwater & Process Water

- Our Ion Exchangers have successfully removed $Cs^{+}$ and $Sr^{2+}$ from INEEL ICPP Process water, Hanford N-Springs groundwater and Oak Ridge Seep D groundwater.

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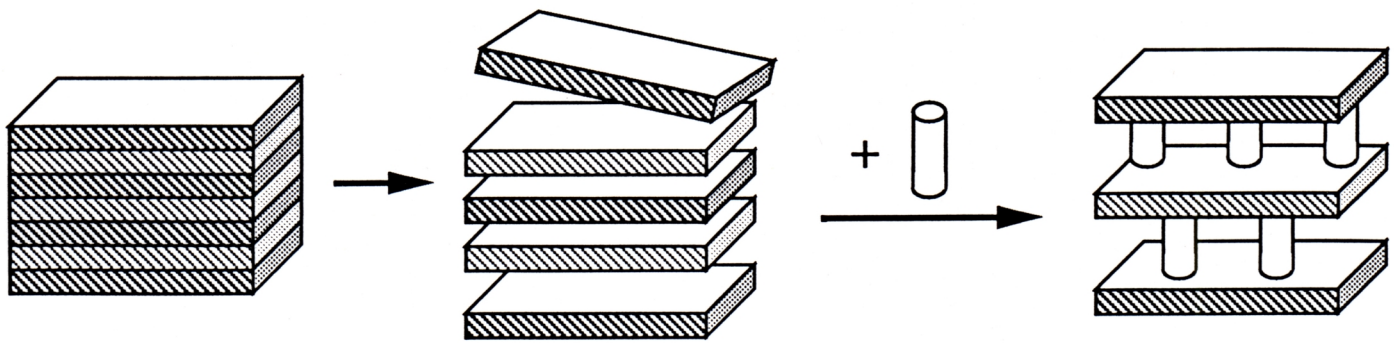
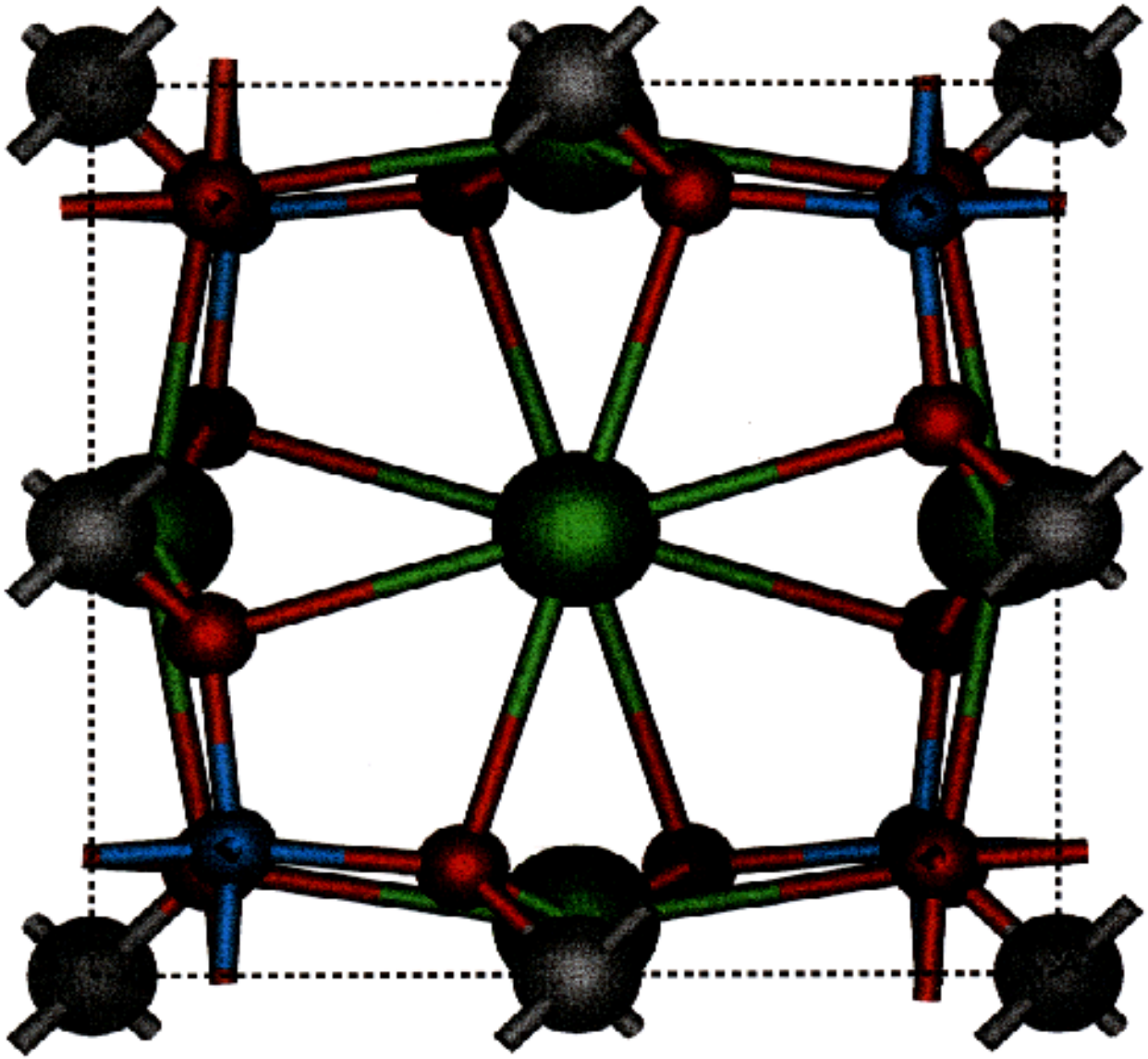
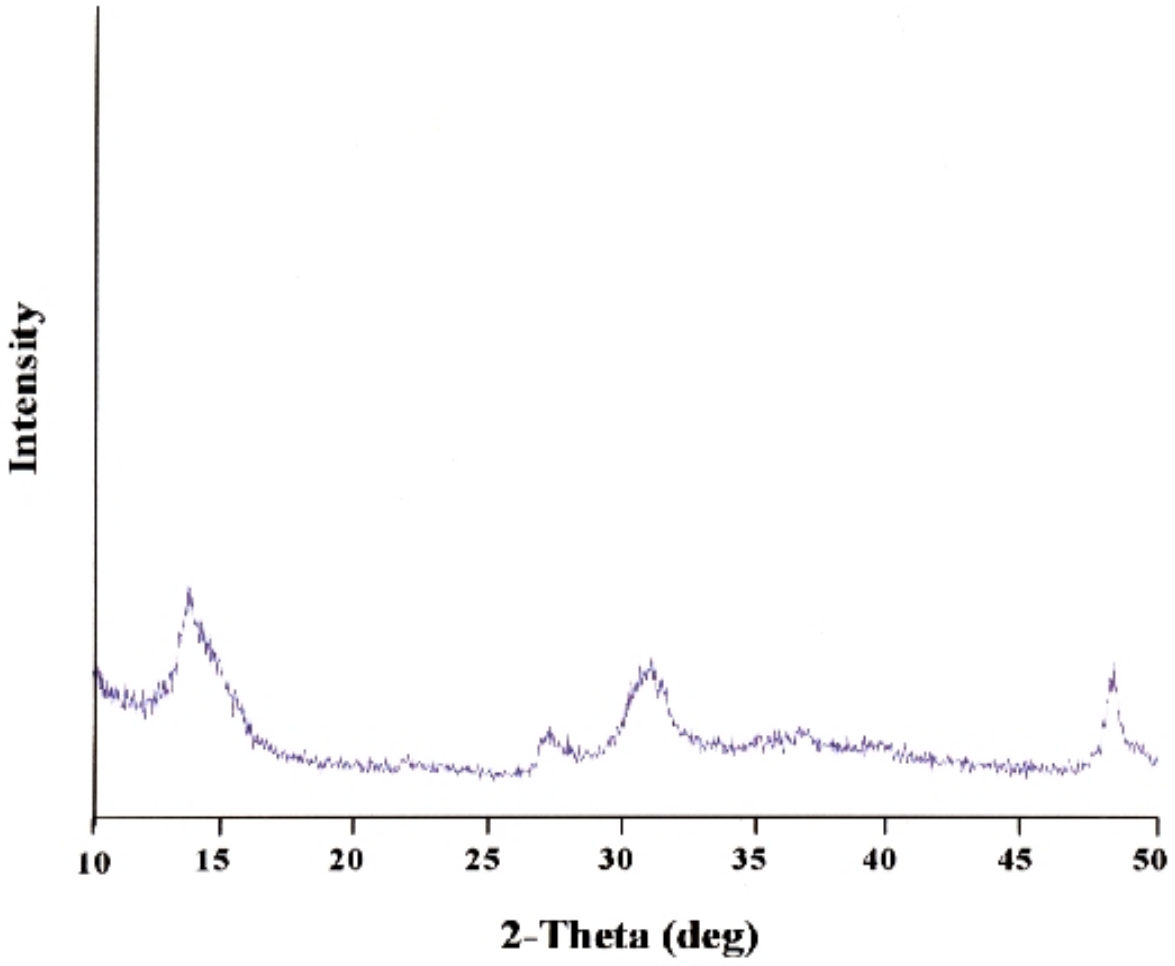
# Pillared Layered Compounds: Synthesis and Application

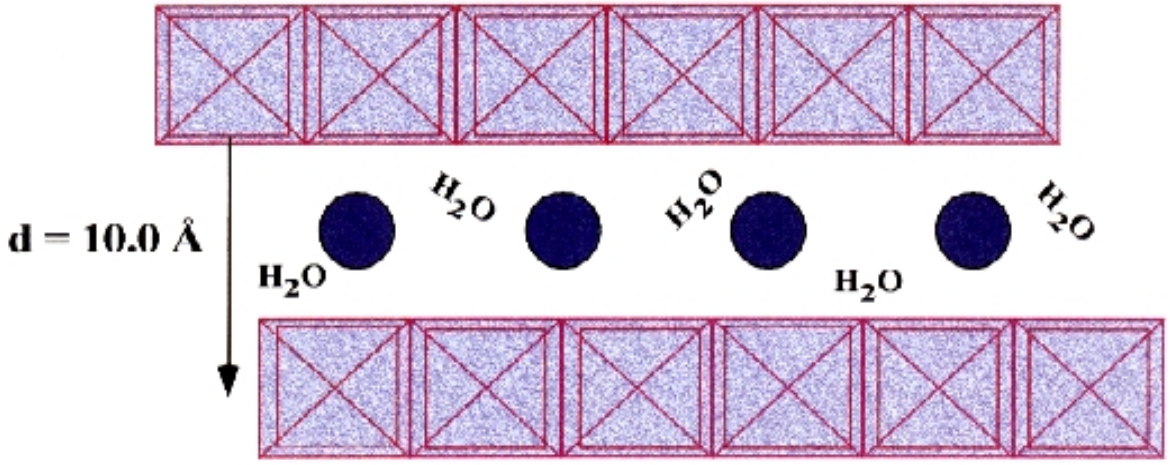


$Cs^+$ ion located in tunnel center bonded to 8 silicate oxygens at a distance equal to sum of ionic radii



# X-ray Powder Pattern and Hypothesized Structure for the Sodium Nonatitanate, $Na_4Ti_9O_{20} \cdot xH_2O$



## Removal of strontium from Seep D groundwater

| Sorbent | Mixing time | | | |
|---|---|---|---|---|
| | 0.25h | | 24 h | |
| | D[a] (mL/g) | % R | D[b] (mL/g) | % R |
| K-Pharm | 414900 | 99.9 | 61000 | 99.7 |
| K-Pharm | 113300 | 99.8 | 49100 | 99.6 |
| RC-5-23A | 149600 | 99.9 | 45800 | 99.6 |
| RC-5-23A | 113400 | 99.7 | 95500 | 99.8 |
| RC-5-27A | 408600 | 99.9 | 99900 | 99.8 |
| RC-5-27A | 224700 | 99.9 | 91100 | 99.8 |
| $Na_4Ti_9O_{20}$ | NM[b] | NM | 127700 | 99.8 |
| $Na_4Ti_9O_{20}$ | NM | NM | 103400 | 99.8 |
| CST | 117800 | 99.8 | 63600 | 99.7 |
| CST | 93600 | 99.8 | 54200 | 99.6 |

[a]supernatant/sorbent ratio = 200
[b]NM = not measured