

Extraction of Lithium from Geothermal Brines using Thermally Stable Inorganic Ion Exchangers

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KEYWORDS: Lithium Extraction; Inorganic Ion-exchangers; Zirconium Phosphate; Ion Selective; Molecular Sieve; Ionic size.

ABSTRACT

Crystalline acid salts of tetravalent metals such as zirconium and titanium have been known for a long time as inorganic ion-exchangers. Because of their high ion-exchange capacity, their good stability to acid and oxidizing solutions as well as to temperature and ionizing radiations, the potential uses of these materials were subject to intense investigations for separation and concentration of nuclear fission products. Initial materials were amorphous or of low crystallinity but since the mid-sixties acid these ion exchange materials have been obtained as more robust crystalline materials with ion selectivity. Zirconium phosphate has a layered structure, zirconium phosphate of α -type ($\text{Zr}(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$) has layers in which the Zr atoms bond mono hydrogen phosphate groups, with the P-OH groups pointing in the interlayer region, alternatively below and above the main plane. Water molecules are located between the layers in six-sided cavities and form hydrogen bonds with the P-OH groups of the same layer. The interlayer distance of α -zirconium phosphate is 7.56 Å and the presence of protogenic-OH groups is responsible for its cation exchange properties. It has been reported in the literature that $\text{Zr}(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$ can be converted into $\text{Zr}(\text{HPO}_4)_2 \cdot 5\text{H}_2\text{O}$ and other various inter-spacing water molecules and up to β - $\text{Zr}(\text{HPO}_4)_2 \cdot 8\text{H}_2\text{O}$, 100% of the phase with an interlayer distance of 10.4 Å. Thus, by changing the interlayer-spacing, the material can be customized for inclusion and exclusion of specific ions based on hydrated ionic radii. The paper presents a review and ideas to develop an adsorbent/ion exchange material to selectively concentrate Lithium ions from a hot geothermal brine.

INTRODUCTION:

Lithium is the principal component in one of the most promising forms of high-energy-density batteries. Lithium is also a critical component for ceramics, glass, metallurgy, air treatment products, and pharmaceuticals. Lithium is used to make alloys with other metals that are used in various industries. Lithium–aluminum alloys containing 1–3 weight % of lithium is commonly used in aerospace applications. Almost all-electric vehicles are based on lithium-ion batteries and electric vehicles are gaining in popularity and automobile market share. Additionally, electric lithium batteries are also used in grid-scale electric storage from wind and solar energies. All these applications have put a high lithium demand to a point of major national need and put lithium on the list of critical materials necessary for the economy and security of the United States.

Lithium is found in three main types of deposits: saline subsurface waters (continental brines), hydrothermally altered clays (sedimentary deposits), and pegmatites (crystalline hard rock). The primary commercial sources of lithium are hard rock deposits in Australia and China, and brine deposits in Argentina, Chile, and China. Brine deposits account for between 50 and 75 percent of the world’s lithium production. Major brine deposits occur in the US but commercial production of brine lithium occurs predominantly in South America using evaporative ponds. Geothermal fluids are recognized as potentially important brine sources for lithium as part of the US Department of Energy GeoVision study. The estimates are that Salton Sea post-flash geothermal brines to have approximately 200 mg/L; the Imperial Valley, generally have the highest values, exceeding 100 ppm in the produced brine.

Direct extraction of lithium from brines include precipitation, well-established sorption technologies such as ion-exchange resins, emerging novel sorbents, such as metal oxides, solvent separation using solvents commonly used for metal extraction, and novel solvents specific to lithium, such as crown ethers. Direct lithium extraction methods may also use electrodialysis, membranes and electrochemical processes to improve lithium extraction. Nanocomposite sorbent comprised of molecular sieve nanoparticles and lithium-imprinted polymeric resins have been developed for the selective recovery of lithium from geothermal brines. Brown (Brown, C. 2019, 2022) described a process for recovery of lithium ions from a lithium bearing brine by contacting with lithium-ion-sieve such as oxides of titanium or niobium. Direct quote from Brown reference “Inorganic ion exchange media, such as ionic sieves, based upon manganese, titanium, or other oxides, have been identified as potentially useful for recovery of lithium from brines where there exist high concentrations of competitive ions, such as calcium, magnesium, sodium, and potassium. These materials can be termed lithium ion sieves (LIS). LIS exhibit a high preference for lithium because the LIS exchange sites are narrower than the ionic radii of Na^+ (0.102 nm), K^+ (0.138 nm), and Ca^{2+} (0.100 nm). The lithium ions are however, small enough (0.074 nm) to enter the exchange sites”. However, the author of this paper has disagreement with Brown paper as these ions in the brine are hydrated and Li^+ has hydrated ionic radii (0.304 nm), which is bigger than Na^+ (0.276 nm) and K^+ (0.232 nm) but smaller than Ca^{2+} (0.313 nm) and Mg^{2+} (0.363 nm). In this for sieves to work, the cavity size will be preferred to be between 0.304 - 0.313 nm).

DISCUSSION:

Ion-exchange is a reversible interchange of ions between ion-exchanger material (usually solid material) and soluble ions in the liquid phase. Ion-exchange processes, except for a few cases, are reversible; the ions can be reversed by suitably changing the concentration of the ions in solution. These processes, in many respects are analogous to adsorption processes, but the two are not the same. One of the main difference between the two processes is that ion-exchange takes place stoichiometrically, by the effective exchange of ions, whereas in surface adsorption the adsorbent takes up dissolved substances without releasing others into the solution. Adsorption can be physical or chemisorption and that may not be completely reversible and may have a limited use in extracting lithium from the geothermal brine. Most synthetic or naturally occurring zeolites can work as molecular sieves and help with the extraction of specific ions from liquid phase, however have a very narrow range of operation with respect to temperature and pH. These materials as crystalline aluminosilicates are manufactured in a thermal process. Synthetic inorganic ion exchangers seem to have overcome some of the shortfalls of the zeolites and organic ion exchangers resins as given below:

1. Synthetic inorganic ion exchangers, typical of which is zirconium phosphate are generally more stable than the original aluminosilicate type zeolites. Unlike zeolites, inorganic ion exchangers can withstand high temperatures, high salinity and radioactivity.
2. These ion exchangers are more resistant to heat and radiations than their organic counterparts. This makes them ideally suited for processing hot brine, especially that may contain naturally occurring radioactive materials (NORMS) as well as processing nuclear fuels or fission products.
3. These materials are generally easy to synthesize with the desired selectivity and therefore help many difficult separations of various ions.

The aforesaid advantages of inorganic ion exchange materials have resulted in a rapid development of many inorganic exchangers with specificity for uptake of certain ions. A large number of insoluble salts such as hydrous oxides, acidic salts of multivalent metals, salts of heteropoly acids, insoluble ferrocyanides have been prepared and studied as ion-exchange materials. Some of the metals studied as ion exchangers are titanium(IV), Zirconium (IV), tin (IV), Cerium (IV), Thorium (IV), Aluminum (III), Chromium 9(II), Iron (III), Vanadium (VI), and Uranium (VI); the anions studied include, silicate, phosphate, antimonate, arsenate, vanadate, and tellurate (Gill, 1972, 1973, 1974). However, there has been a special emphasis on the salts of quadrivalent metals, due to their better chemical stability compared to the salts of trivalent and bivalent metals. These materials, acting mostly as cation-exchangers, are gel-like microcrystalline or amorphous substances with composition and ion-exchange properties largely dependent upon the method of preparation. The mechanism of uptake of ions by these materials arises primarily from the presence of readily exchangeable hydrogen ions, which are associated with the anionic groups present on the ion exchange materials. There are several reviews (Clearfield,1973); (Gill,1974); (Vesely,1972) ;(Schmidt, 2012) that describe almost all the possible combinations of quadrivalent metals with polybasic acids that have been explored for their ion exchange properties. Some of the materials have been obtained as gels with no definite composition and are not very stable towards hydrolysis of their acid groups. However, crystalline

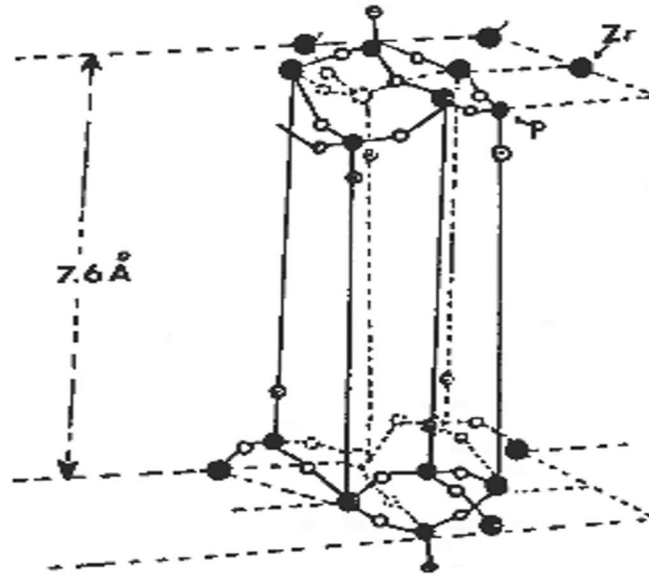
materials have been found to have definite composition and quite stable towards hydrolysis. Their well-defined composition and tunable structural feature allow minute tailoring of their specific properties for different applications such as water softening, water remediation, catalyst, molecular sieving and selective adsorption in medical applications such as kidney dialysis. Besides zirconium phosphate, other well studied crystalline materials such zirconium arsenate $Zr(HASO_4)_2 \cdot H_2O$, titanium phosphate $Ti(HPO_4)_2 \cdot H_2O$ and Titanium arsenate $Ti(ASO_4)_2 \cdot H_2O$ all have layered structures. Cerium(IV) phosphate and thorium phosphate are also crystalline materials with a fibrous structure, which may be useful for the development of ion exchange membranes. Oxides of Ti, Zr, and V have been used for removing pollutants from water and air. Zirconium phosphate is the most studied material and has found many industrial applications (Amphlett, 1964).

Zirconium phosphate: Amorphous insoluble acid salts of tetravalent metals are not very stable towards hydrolysis of their acid groups and therefore their composition is often not well defined, however, crystalline salts are considerably more stable than amorphous salts. Crystalline zirconium phosphate can either be prepared directly by slow decomposition of zirconium fluoro complexes in the presence of phosphoric acid or by digesting and refluxing amorphous zirconium phosphate in concentrated phosphoric acid. In the latter method materials with different degrees of crystallinity can be obtained by varying concentration of phosphoric acid and reflux time (Gill, 1979). Alberti, et.al. synthesized new organic-inorganic ion exchanger (Albert, 1979) by slowly decomposing zirconium fluoro complexes in the presence of trimethyl phosphonoacetate.

Crystalline zirconium phosphate has a layered structure (Clearfield, 1969) and in many respects similar to that zeolitic clay minerals. Each layer consists of zirconium atoms lying very nearly in a plane and bridged through phosphate groups located above and below this plane. The crystalline structure of zirconium phosphate is built up by bonding together these sandwiches either by long hydrogen bonds or Vander Waal forces. In this arrangement, each phosphorus atom in the lower sandwich lies along a perpendicular line drawn from zirconium atom of the upper sandwich. This arrangement as shown in Figure 1, creates zeolite-type cavities that interconnected by windows whose maximum opening in acid form is 2.64 \AA (0.264nm). The interlayer distance and size of the opening to the cavities will depend upon such bond distances as Zr-Zr, Zr-O, Ti-Ti and Ti-O, etc. When zirconium is replaced in Zr phosphate with a smaller tetravalent metal such as titanium, smaller cavities are expected as Ti-O distance is shorter than Zr-O as well Ti-Ti distance in the plane of metal atoms should be shorter than Zr-Zr distance and indeed it has been found to be the case from X-ray diffraction. Similarly, the substitution of zirconium atoms in zirconium phosphate with larger tetravalent metals is expected to provide an ion exchanger with slightly larger cavities. However, substitution of Zr with Ce(IV) or Th (IV) resulted in fibrous structure instead of layered structure, Similar trends are observed when phosphate group in zirconium phosphate is substituted with different size polybasic acid group such as arsenate; Zr-Zr distance in the arsenate should be longer than the phosphate containing material. This makes the cavities larger for zirconium arsenate than zirconium phosphate; zirconium arsenate is able to uptake while it is not possible by zirconium phosphate and it is the result of larger cavity size of zirconium arsenate.

Figure 1:

Layered structure of crystalline Zirconium Phosphate ion Exchanger



Both hydrogen atoms with different pK values can be exchanged with other cations for total ion exchange capacity of 6.64 mequiv per grams of zirconium phosphate. Counter ions with hydrated ionic diameter greater than 2.64 Å will find it difficult to exchange with H⁺ due to steric hindrance. However, if sufficient energy for ion exchange is supplied to either expand the interspacing of the layers or dehydrate the exchanging ion prior to exchange large ions such as hydrated Li⁺, Cs⁺, Mg²⁺ and even tetravalent ions can enter inside the crystal cavities. Size of the hydrated ion is in order Li⁺>Na⁺>K⁺>Rb⁺≥Cs⁺, which is just reverse of ionic size Reason.

The windows connecting the cavities can be enlarged by replacing the protons with other counterions or water molecules as water of hydration.



2.64 Å

7.6 Å

11.8 Å

When Na⁺ is replaced by H⁺ in monosodium form of zirconium phosphate, the monohydrate dihydrogen phosphate is not formed, but instead a polyhydrated form with 5-7 molecules of water is obtained with an interlayer distance of 10.4 Å



11.8 Å

10.4 Å

Thus, by changing the counter ion and water of hydration in zirconium phosphate ion exchange material one can easily change the interspacing interlayer distance to include or exclude ions for separation. This is a unique property of this material to custom tailor the inclusion and exclusion of the ions for the purpose of separation of ions of interest. Selected ion form of zirconium phosphate with different distances can be obtained depending on hydration, size and composition of the counter ions (Table 1).

Table 1:

Interlayer Distances of some of the many phases of crystalline Zirconium Phosphate

Phase Composition	Interlayer Distance (Å)
HH	2.64
HH.H ₂ O	7.56
HH.nH ₂ O (n=5-7)	10.4
Li Li.H ₂ O	7.9
NaNa.H ₂ O	8.40
Na Na.3H ₂ O	9.90
K K H ₂ O	8.90
K K.3H ₂ O	10.80
Rb Rb.H ₂ O	8.90
Cs Cs.H ₂ O	9.50
H Li.4H ₂ O	10.10
H Na.5H ₂ O	11.80

In this table HH.H₂O is zirconium phosphate monohydrate in acid form; KK represents both protons on zirconium phosphate have been exchanged for potassium ions.

This can provide a very specific ion-exchange material serving as ionic-sieves. This technique has been even extended to incorporate large organic molecules such as alkanols and glycols while the original interlayer structure of zirconium phosphate is preserved. The organic-inorganic ion exchanger such as Zr(HOOCCH₂PO₃)₂ retains the layered structure of zirconium phosphate. In this case, since the portion of the carboxylic group can be exchanged by other cations, the compound behaves as an inorganic-organic ion exchanger with carboxylic groups fixed to the insoluble crystalline inorganic matrix. While layered structured inorganic ion exchangers provides molecular sieves, the fibrous structured inorganic ion exchangers are useful in the preparation of ion-exchanger papers, thin layers suitable for chromatographic separation, and as support and binder free inorganic ion-exchange membranes.

CONCLUSIONS:

Crystalline inorganic ion exchangers, which are more stable than their organic counterparts at high temperature and around radio-active materials (NORMS) provide a fit for extracting Li^+ from the hot brine. The paper has provided a large amount of scientific information for the selection of the suitable material based on the specificity requirements. It is possible to include and exclude ions for separation based on the openings to the cavities by selecting the chemical composition of the ion-exchange material. Both quadrivalent metals as well as polybasic acid to prepare the crystalline form of the inorganic ion exchanger influence the molecular sieving. Proper selection of the counter ions on the io-exchange material by replacing one or both protons can further narrow down the selection of the openings to the cavities for the uptake and exchange lithium ions from the hot brine.

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