

SELEITIVE ION-EXCHANGE OF AN INORGANIC MATERIAL AND APPLICATIONS

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ABSTRACT

The performance of a series of inorganic cation-exchange materials in metathesis reactions, heavy metal removal for waste water treatment, and enrichment of metal ions in a brine has been studied. The material shows different selectivity for ion-exchange with various metal cations, which enables heavy metal removal, ion separation for water treatment and enrichment for metal recovery in aqueous systems. In addition, the material is ideal for production of all kinds of desired salts in aqueous solutions via metathesis reactions (also known as double replacement reactions) which are normally reversible.

I. INTRODUCTION

Ion exchange can be defined as a reversible exchange of ions between a solid (such as zeolites or sulfonic resins) and a liquid (a solution or melting salt) with no substantial change in the structure of the solid skeleton. Ion exchange has been among the key phenomena in the nature and is now a standard unit operation, widely applied in many industrial processes. These applications can be roughly classified into ion separation, substitution, recovery, deionization, catalysis, and chemical synthesis.

There are many, many types of natural ion exchangers, mainly crystalline aluminosilicates, such as clays and zeolites (adding up to over 1000 types).^[1] Sands and soils (with clays, zeolites, and manganese oxides^[2,3] in them) are also ion exchange materials which are so important in the exchange of NH_4^+ , K^+ , Ca^{2+} , Mg^{2+} , etc for plant growth and in maintaining ion equilibrium in the nature. A lot of plant membranes, and chemically treated plant or humus (which have already been used in

treating drinking and industrial water) are also ion exchange materials.

In this work we employed a series of commercial inorganic ion-exchange materials for applications in treatment of brines, heavy metal removal for water treatment, ion separation, and in metathesis chemical reactions. The working capacity, exchange rate, exchange priority or selectivity, and the operational parameters in these processes are studied in detail.

II. EXPERIMENTAL

The materials, with the commercial name of Geolyst series, were products of KL Chemical Technologies, Inc in the form of powders or extrudates (cylindrical 1/8" diameter). The materials have been shown to be of high ion-exchange capacity (> 4 moles of monovalent cations /kg) and ultrafast specific ion-exchange rate (> 8 moles of monovalent cations/kg.s). Elemental analyses of materials and solutions before and after ion-exchange experiments have been done on a Perkin-Elmer 510 E ICP-AES instrument for all elements except

for NH_4^+ , whose analyses are done on a UV-vis spectrometer.

A. Priority Experiments.

Two grams of sodium type of the material (referred to as Na-M) were added to a solution (agitated with a magnetic stirrer) of sodium chloride and chloride of another metal (Li^+ , NH_4^+ , K^+ , Mg^{2+} , Ca^{2+} , Sr^{2+} , and Ba^{2+}), the concentration of the solution (1 liter) being 0.5 M for each of the two metal salts, forming a thin slurry. After agitation for 5 minutes, the slurry was filtered, with the solid washed with deionized distilled water and dissolved with concentrated hydrochloric acid

for ICP or UV-vis analyses. The molar ratio of metal to sodium is defined as the ion-exchange priority index for the metal.

B. Interaction of the materials with a mimic brine solution.

A mimic brine solution was prepared from pure chemicals of the components with the composition after Ref 4, except no boron addition. The composition is shown in Table I. Na type of the material was added cumulatively to the brine and the concentrations at various addition amounts were measured.

Table I. Composition of a Mimic Brine (g/l).

Ion	Cl^-	SO_4^{2-}	Na^+	Mg^{2+}	K^+	Li^+	Ca^{2+}	H_2O
Content (g/l)	192.0	23.3	93.2	12.3	22.0	1.96	0.3	872

C. Removal of heavy metal with powder and extrudate materials.

A solution (1 L and 100 ppm) of heavy metal Ba, Pb, Cd, Hg, alone or in combination was made. For tests with powders, a powder of the material (1 gram) was added to the solution and stirred for 2 minutes. For tests with extruded materials, the solution was pumped to flow through a tube (50 mm in i.d, 600 mm in length) packed with the extrudate material. In both cases, solutions after treatment were collected and analyzed.

D. Application of the material in metathesis reactions.

200 kg of the Na-M powder was agitated with 500 kg water to form a slurry, which was then converted to a cake in a centrifuge. A solution of KMnO_4 (12% wt, 45 °C) was transported through the cake and collected, converting to a solution of sodium permanganate. After the reaction, water (100 L) was used to clean the cake, followed by a solution of sodium chloride (20 % wt.) passing through the cake to regenerate the material into sodium type.

III. Results and Discussion.

A. Priority of Ion-Exchange for Group I and II Elements.

In this series of experiments, the amounts of cations in the aqueous phase are far more than those in the solid phase. So the ion-exchange should not substantially change the concentrations in the solution. The concentrations of cations are therefore regarded as constant. The molar ratio of certain metal ion (other than sodium) to sodium is defined as the priority index (against sodium) with Na-type of the exchange media. The results are listed in Table II.

Among the elements tested, Ba^{2+} and Sr^{2+} showed the highest priority, followed by Ca^{2+} , Li^+ , and Mg^{2+} . This priority is proximately in accordance with the strength in interaction between the cation and the negative skeleton of the exchange media. Divalent cations are generally of higher priority to monovalent cations. This sequence in priority might suggest a selective ion-exchange with multi-cation systems.

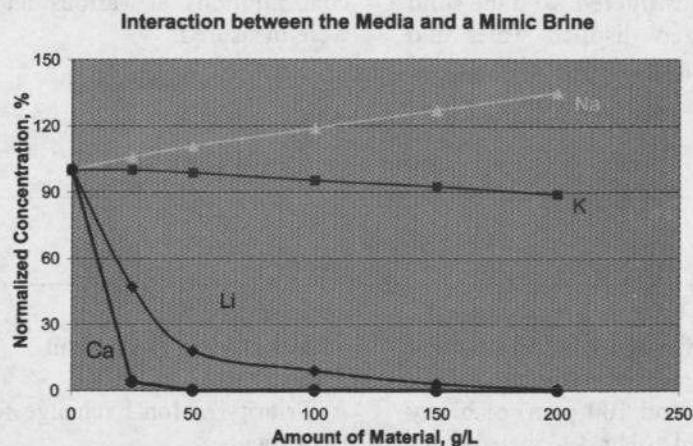
Table II Ion-Exchange Priority Index Against Sodium.

Cation	Li^+	K^+	NH_4^+	Mg^{2+}	Ca^{2+}	Sr^{2+}	Ba^{2+}
Priority Index	38	6.9	4.4	20	72	110	> 200

B. Interaction of Ion-Exchange Media with a Mimic Salt Lake Brine.

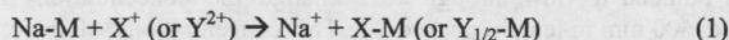
The variation of normalized relative concentration of all the cations with the cumulative amount of ion-exchange material added is shown in Fig. 1. With the addition of ion-exchange media, the concentration of calcium decreased sharply, almost total disappearing when 50 grams of material was added. The amount of Li also decreased during this period, with a reduction of over

80%. The concentration of Mg also decreased substantially with the addition of the ion-exchange media, but with a slower rate as compared to Ca and Li. The amount of K decreased slowly during this process. On the contrary, the concentration of sodium increased as the amount of the ion-exchange material was added and the amount of the material increased. At a certain amount, Ca^{2+} and Li^+ can be separated out of the brine.



What happened in the process are ion-exchanges between sodium in the

material and various cations in the mimic brine solution, as shown in Equation 1,



where X is Li, K and Y are divalent cations of Mg, or Ca. As is discussed in the priority index section, the ion-exchange of different cation is selective, with Ca and Li prior to Mg and K. The speed of decreasing the normalized relative concentrations of the cations is exactly the same as predicted by the index as shown in Table II, with the replacement of Na in the material by the cations in the brine, releasing Na^+ into the solution.

The selective adsorption, or more accurately, ion-exchange of different cations in brine to the material suggests that the material can be used for low-energy consumption separation of the species as compared with distillation and re-crystallization.

C. Heavy Metal Removal.

The highest priority index of Ba suggests the highest tendency of heavy metals into the

ion-exchange media. The results of static treatment of heavy metal-containing solutions supported this prediction. After treatment for two minutes with a powder material (liquid to solid ratio of 1000:1), the heavy metals were removed by over 99% from the solution for all the four cations of Ba, Pd, Cd, and Hg. Similarly, in a flow system with extrudates, the levels of heavy metals were all below 0.5 ppm at a residence time of 5 minutes. These results indicate that the material is good for heavy metal removal in polluted aqua systems due to the highest tendency of the metal species into the ion-exchange media.

D. Applications in Metathesis Reaction.

The breakthrough curve for conversion of KMnO_4 into NaMnO_4 in our study is shown in Fig. 2. in the initial stage when a solution of KMnO_4 transported through the cake of Na-M (with about 28% moisture in the cake), water in the cake is gradually

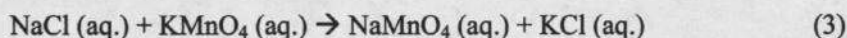
replaced by the solution, purple solutions of NaMnO_4 is observed at a volume of about 20 L. The concentration of NaMnO_4 rapidly becomes very steady, 10.7%. No potassium is detected in the solution. In this system the



In the process when Na^+ in the cake almost depletes, K^+ can be detected in the solution of NaMnO_4 . This is the breakthrough point for the process, after which the concentration of Na rapidly decreases to zero. The cake becomes K-M. After washed with water, K-M is regenerated

solution pass through the cake like a piston flow, therefore the ion-exchange between Na and K is steadily and completely occurs in the cake, as is shown in Equation 2,

into Na-K via transporting a solution of NaCl through the cake, forming a solution of KCl. The overall reaction, or net reaction, is therefore an aqueous metathesis as shown in Eq. 3 via the ion-exchange media which remains unchanged in the process.



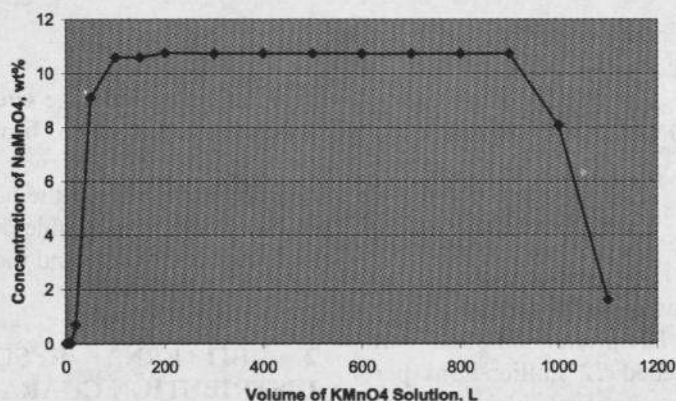
With the participation of the ion-exchange media which remained unchanged an commonly reversible unable-to-achieve reaction can occur readily. Relatively lower value reactants can be efficiently converted into more valuable products.

reactions with other soluble salts can similarly occur via the ion-exchange process.

IV. Conclusions.

Other permanganates, such as LiMnO_4 , $\text{Mg}(\text{MnO}_4)_2$, and $\text{Ca}(\text{MnO}_4)_2$ have also been produced in the same manner. Metathesis

Fig. 2 Breakthrough Curve in Metathesis of KMnO_4 and NaCl



Ion-exchange of the studied inorganic material is selective. In general, divalent cations are of priority to monovalent cations while heavier cations are prior to light ones, with the exception of lithium, which is even prior to magnesium with the material. This selective ion-exchange property makes it suitable for separation and enrichment of cations, removal of heavy metals in aqueous systems, and metathesis reactions among soluble salts which might be reversible in absence of the ion-exchange media.

V. References.

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