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(54) Borosilicate zeolite for nuclear waste disposal.

(57) The application of borosilicate zeolites, such as zeolite beta is described for extraction of hazardous cations, especially radioactive cesium and strontium, from radioactive waste solutions and for isolation of these cation-loaded zeolites in glass at lower and therefore safer temperatures than present practice.

BOROSILICATE ZEOLITE FOR NUCLEAR WASTE DISPOSAL

This invention relates to a process for removing ions from highly alkaline waste liquors. More particularly, this invention relates to a process for removing radioactive cesium and strontium from highly alkaline waste liquors.

Most radioactive waste material is in liquid form and is obtained, for example, by dissolving spent fuel in nitric acid. In the Purex process, for recovering fission values from spent nuclear fuel elements, for example, the fuel element is dissolved in nitric acid for subsequent separation of uranium and plutonium from the fission products, whereby the fission products are retained in nitric acid solution which is a waste liquor. This waste liquor is then neutralized by the addition of excess sodium hydroxide, sufficient excess of sodium hydroxide being added to render the waste liquor highly alkaline. The neutralization of the waste liquor causes most of the fission products to be precipitated out of solution, leaving a supernatant liquid containing radioactive cesium and trace amounts of other fission products such as strontium. Many of the fission products present in the waste liquid have a short half-life and, therefore, present no problem as to safe disposal thereof. Cesium 137, however, is an entirely different matter because it has a half life of 30 years which means its radiation is strong enough to be hazardous but its radiation decays too slowly to reach complete decomposition by decay within a reasonable period of time. Thus, it is one of the most predominant and most dangerous fission products in the waste liquor.

Radioisotopic elements in liquid waste are ultimately safely disposed of by burial in the ground, in the ocean, or in geological formations of suitable composition. The concentration of radioisotopic elements in liquid waste, especially low-level waste, is too low to permit the economic disposal of the entire liquid by direct burial. Therefore, the liquid waste must undergo preliminary treatments so as to concentrate the radioactive waste's values in the liquid. Various methods have been suggested to effect this result, examples being: evaporation of the liquids; fixation of radioisotopic elements by solids; precipitation of radioisotopic elements from the waste liquids; and calcination of the waste liquids. Some of these pretreatments of waste liquids, especially waste liquids containing a low level of radioisotopic elements, are not economically feasible when carried out on a large scale. Thus, for example, concentration of waste by evaporation is not practical for handling large volumes of low-level radioactive waste.

One of the most practical approaches to the disposal of the waste liquids is the fixation of the radioactive elements on a solid, as by adsorption or ion-exchange, in which radioactive ions in the waste are exchanged with non-radioactive ions in a solid ion-exchanger. The liquid, free from radioactive ions, can be safely released to its normal environmental liquid waste disposal sites or waters.

Commonly used ion exchangers include organic resins such as styrene-divinyl benzene polmers containing sulfonic, phosphonic, carboxylic, phenolic, thiol, amino, or chelating groups for ion exchange. Commercially available resinous ion exchangers include Ionac C-240 and A-540 (Ionac Chemical Corp.); Amberlite IRC-120, IRC-938, and Amberlyst A-21 (Rohm & Haas); Dowex 50, Retardion (Dow Chemical); and Duolite C-10, A-101 (Diamond Shamrock Co.). The resinous ionic exchangers, however, after continued use and exposure to the heat and radiation from the radioisotopes will deteriorate and thus lose the ability to hold the radioactive ions. Moreover, the selectivity of resinous ion exchangers for removing the more hazardous radioactive isotopes such as cesium 137 or strontium 90 is also impaired upon continued use.

Inorganic ion exchangers are also known and include sulfonated coal, mineral loughlimite, talc, kaolin, bentonite, vermiculite, amorphous silica-alumina, and crystalline aluminosilicates including such zeolites as NaA, chabasite, NaX, NaY, etc. The inorganic ion exchangers have greater stability under the conditions of heat and radioactivity encountered during waste treatment as compared to the resinous ion exchange materials. The zeolitic ion exchangers also have improved selectivity for cesium and strontium radioactive isotopes, thus, enabling a more efficient removal of these radioactive ions as is achieved with amorphous clay ion exchangers.

In order to solidify, or fix, radio-nuclides contained in the waste liquids, particularly aqueous waste solutions from the first extraction cycle of the reprocessing process for irradiated nuclear fuel or breeder materials, it has long been the custom, among other methods of solidification, to melt the radioactive ion-loaded ion-exchanger in glass or ceramic materials. Solidification in borosilicate glass has been considered to be particularly suitable for highly radioactive wastes and for transporting the solidified products to a permanent storage location intended for such purpose, as well as for storing the waste in metal containers in such permanent storage locations.

The most acceptable and widely practiced way of disposal at the present time comprises removing radioactive nucleides from liquid or gaseous wastes by adsorption or ion exchange with a naturally-occurring or synthetic zeolite, mixing the radwaste-loaded zeolite with glass particles, and firing the mixture at 1050°C to form leach-resistant and corrosion-resistant glass which can be stored in geologically stable sites.

U.S. Patent 3,017, 242 describes clinoptilolite, a sodium-aluminium silicate type of zeolite, which has preferential affinity for radioactive cesium-137 when contacted by a radioactive waste solution.

U.S. Patent 3,167,504 describes a solid synthetic amorphous hydrous zeolite which is effective for removing radiocesium from radioactive liquors. The synthetic crystalline silicate has the approximate empirical formula Na_2O $(1\text{-}2)Al_2O_3$ $(4\text{-}14)$ SiO_2.

U.S. Patent 3,262,885 describes a process for consolidating fission-products-containing zeolites by mixing the zeolite with lithium flouride, silica and boron oxide, heating the mixture at about 800°C and cooling to room temperature.

U.S. Patent 3,380,916 teaches the removal of radioactive cesium and strontium from highly alkaline waste liquor by ion exchange with a zeolite which is sodium, potassium, calcium, cadmium, strontium, copper, zinc, cobalt, iron, silver, or nickel aluminosilicate.

U. S. Patent 4,087,375 describes the capture of corrosive radionucleides, including Cs(137) and Sr(89-90) by ion exchange or mechanical adsorption with the mordenite form of zeolite, sintering of the zeolite to a ceramic form, and thereby sealing and fixing the nuclides in sintered mordenite.

U. S. Patent 4,097,401 relates to a borosilicate glass which is particularly suitable as the solidification matrix for highly radioactive wastes by denitrating and calcining the radioactive waste solution, melting the calcined waste product together with a borosilicate frit containing nucleation agents at a temperature of 1050-1200°c, maintaining the melted frit for 3-5 hours, and subsequently cooling and then heating the frit to permit nucleation to occur.

The crystalline zeolites used for ion exchange of radioactive solutions are preferably partially in the hydrogen form. The original cations associated therewith may be replaced by a wide variety of other cations according to techniques well known in the art. For catalytic usages, typical replacing cations include hydrogen, ammonium, and metal cations, including mixtures of the same, particular preference being given to cations of metals such as rare earth metals, manganese, and calcium, as well as metals of Group II of the Periodic Table. For treatment of radioactive waste solutions, all dissolved cations are acceptable to, and are received within, the zeolite structure.

Typical ion-exchange techniques involve contacting the zeolite with a solution of a salt of the desired replacing cation or cations. Although a wide variety of salts can be employed, particular preference is giving to chlorides, nitrates, and sulfates. In radioactive waste solutions, nitrates are the predominant and indeed almost the sole anion.

Ordinary zeolites or aluminosilicates, although very effective in adsorbing radioactive nucleides from liquid or gaseous wastes, contain substantial amounts of aluminum. The high aluminum content increases the melting point and viscosity of the glass mix used to contain the radioactive-containing zeolite, thus making the disposal process extremely difficult and uneconomical to operate.

Even though the Department of Energy has adopted base exchanging of radioactive waste liquids with zeolites, the subsequent drying of the radwaste loaded zeolites and mixing thereof with glass, and the firing of the mixture to form leach-resistant and corrosion-resistant glass, there remain several troublesome problems. One of these problems is the volatilization of radioactive cesium and strontium during the melting operation. One such study entitled "Volatilization From Borosilicate Glass Melts of Simulated Savannah River Plant SOP Waste", is reported in Chemical Abstracts, Vol. 91, 1979, page 198, 286. Moreover, as stated above, high temperature requirements for melting the glass matrix renders disposal uneconomical. Lowering the melting temperature of the mix is consequently badly needed.

Accordingly, the present invention provides a process for removing radioactive ions from waste water comprising: contacting said radioactive ion-containing-waste water with a zeolite which contains boron within the crystal framework thereof for a contact time sufficient for said zeolite to adsorb said radioactive ions, admixing said radioactive ion-containing zeolite with a soft glass powder to form a uniform mixture; and sintering said mixture to form a glass like melt.

The boron-containing zeolite is surprisingly effective for removing both strontium and cesium from radioactive waste liquors and due to the replacement of aluminum in the zeolite framework the radwaste-loaded zeolite can be consolidated with glass at lower temperatures than has been previously feasible.

The important fundamental properties of zeolites which determine their performance in nuclear waste treatment are: (1) structural stability under high temperature and intense radioactivity; (2) composition that is compatible with the subsequent glass making step; and (3) high selectivity for the ions of strontium and cesium. Thus, while it is known that high-silicate borosilicates have structures which are thermally more stable than low SiO_2/Al_2O_3 aluminosilicates, and that boron in a glass mix tends to lower the melting point of the mix and is compatible therewith, the use of boron-containing zeolite adsorbents has not been suggested for removing radioactive nuclides from waste liquors. It has been found that the substitution of boron for framework aluminum does not effect selectivities of the zeolite for individual ions and thus the boron sites exhibit ion exchange capacity equivalent to that of the aluminum sites.

The figure is a comparison of various ion exchange isotherms for aluminosilicate zeolite beta and borosilicate zeolite beta.

The process of this invention for treating waste water containing radio cesium and radio strontium in solution, comprises the following steps:

A. contacting the waste water with a borosilicate zeolite for a contact time sufficient for the zeolite to adsorb the radio cesium and the radio strontium;

B. separating the radio nuclide-containing zeolite from the water;

C. dehydrating the radio nuclide-containing zeolite;

D. admixing the radio nuclide-containing zeolite with a soft glass powder to form a uniform mixture;

E. sintering the mixture to form a glass-like melt; and

F. cooling the melt to ambient temperature.

In this process, the melt begins to soften at about 850°C and is completely vitrified at about 950°C. Preferably, the contacting step of the process is conducted by:

A. providing the zeolite in particulate form and arranging it in a column having a selected length; and

B. passing the waste water as a stream through the column for a selected flow time that is sufficient for adsorbing the radio cesium and the radio strontium from the water.

The borosilicate zeolites useful in the present invention can be any zeolite which can be formed with boron atoms in the zeolite crystal framework. Thus, useful zeolites can be true borosilicates with only impurity levels of aluminum present in the zeolite framework or boron-containing aluminosilicate zeolites in which a portion of the framework aluminum atoms are replaced by boron atoms. Generally, the useful zeolites will contain sufficient boron such that the firing temperature of the radwaste-loaded zeolite and glass mixture can be lowered from the typical 1050°C.

Zeolites which contain a relatively high aluminum content such as to provide a silica/alumina mole ratio of at least 5 can have incorporated in the zeolite framework a boron content sufficient to lower the melting temperature of the glass matrix or at least lower the viscosity of the mix. Thus, in acoordance with this invention such high aluminum content zeolites will contain sufficient boron to provide a silica/boria ratio of at most about 1000. Preferably, the zeolite ion exchanger will have a silica to alumina ratio of 12 to 1000 and contain sufficient boron to provide a silica/boria ratio of 10 to 500. More preferably, the zeolite ion exchanger will be free of alumina providing a silica/alumina ratio of at least 200. To provide sufficient ion exchange sites for such aluminum-free zeolites, the boron content should be such to provide a silica/boria ratio of no greater than 1000. Preferably, such aluminum-free zeolites will have a framework silica/boria ratio of 5 to 500.

As will be more fully explained below it has been found that the boron framework sites of the zeolite are just as capable of ion exchange as the aluminum sites such that there is no loss in effectiveness in regards to the ion exchange capacity and ion-exchange selectivity of the borosilicate for the radioactive cesium and strontium ions. Thus, aluminum-free zeolites which contain framework boron are effecrive ion exchangers and additionally substantially lower the temperatures required for fixing the radwaste loaded zeolite into the glass matrix for disposal.

The formation of borosilicates or boron containing zeolites wherein at least a portion of the aluminum framework atoms of the zeolite are replaced with boron is known and described in the patent literature. For example, U.S. Paten No. 3,328,119 discloses a synthetic crystalline aluminosilicate zeolite containing boria as an intricate part of the crystal framework in general and, more specifically, discloses boria-substituted synthetic zeolite A, synthetic faujasite and synthetic mordenite. U.S. Patent Nos. 4,268,429; 4,269,813; and 4,285,919; issued to Klotz disclose the formation of borosilicate zeolites.

The medium and large pore zeolites are preferred in this invention. Such zeolites include ZSM-5, ZSM-11, ZSM-12, ZSM-23, ZSM-35, ZSM-38, ZSM-48, and zeolite beta. Aluminosilicate zeolite beta is disclosed in U.S. Patent No. Re 28,341.

In general, the borosilicate zeolites useful in the present invention can be prepared from reaction mixtures containing a source of cations, such as, for example, organic nitrogen-containing cations, an alkali or alkaline earth metal ion source, a source of silicon, such as an oxide of silicon, a source of aluminum such as an oxide of aluminum, water and a source of boron, such as, for example, an oxide of boron. The reaction mixtures will have compositions, in terms of mole ratios of oxides, within the following ranges:

	Broad	Preferred
OH^-/SiO_2	0.005 - 0.8	0.01 - 0.6
H_2O/OH^-	30 - 1,000	50 - 500
SiO_2/Al_2O_3	5 - 50,000	12 - 20,000
SiO_2/B_2O_3	5 - 1,000	10 - 500
R/R+M	0.01 - 0.99	0.2 - 0.9

wherein R represents organic cations and M represents alkali or alkaline earth metal ions.

Reaction conditions consist of heating the foregoing reaction mixtures to a temperature of 80°C to 200°C for 24 hours to 90 days. A more preferred temperature range is 100°C to 180°C for 24 hours to 21 days.

The digestion of the gel particles is carried out until crystals of the desired boroaluminosilicate form. The crystalline product is separated from the reaction medium, as by cooling the whole to room temperature, filtering and water washing at conditions including a pH above 7.

The above reaction mixture compositons can be prepared utilizing materials which supply the appropriate oxides. Such compositons may include sodium silicate, silica hydrosol, silica gel, silicic acid, sodium hydroxide, a source of aluminum, a source of boron and an appropriate organic compound. The source of aluminum way be an added aluminum-containing compound or silica-containing materials or alkali metal-containing materials containing aluminum. The organic compounds contain an element of Group VA, such as nitrogen or phosphorus. The organic compound selected may direct synthesis toward one or another zeolite structure for the boroaluminosilicate material prepared. For example, primary organic amines containing from 2 to about 10 carbon atoms or organic ammonium compounds such as tetraalkylammonium compounds in which the alkyl contains from 2 to 5 carbon atoms will direct the formation of boroaluminosilicate having the structure of zeolite ZSM-5 from the above reaction mixture under appropriate conditions. The quaternary compounds of tetrabutylammonium chloride or hydroxide may be used to direct synthesis under appropriate conditions of boroaluminosilicate have the structure of ZSM-5/ZSM-11 intermediate or ZSM-11. Tetraethylammonium cation sources may be used to direct synthesis of boroaluminosilicate having the structure of ZSM-12 under appropriate conditions. A boroaluminosilicate having the structure of ZSM-23 may be directed from the reaction mixture to using pyrrolidine as the organic compound. Ethylenediamine as well as pyrrolidine will direct a ZSM-35 structure and 2-(hydroxyalkyl)trialkylammonium compounds such as 2-(hydroxyethyl)trimethylammonium chloride will direct a ZSM-38 structure. If the reaction mixture contains a molar ratio of C_2-C_{12} alkylamine/tetramethylammonium compound within the range of from 1/1 to 10/1, a boroaluminosilicate having the structure of ZSM-48 may be formed under appropriate conditions.

In particular, when a boroaluminosilicate having the structure of zeolite ZSM-5 is desired, for example, the reaction mixture from which it is to be crystallized will have a composition, in terms of mole ratios of oxides, within the following ranges:

	Broad	Preferred
OH^-/SiO_2	0.005-0.30	0.01-0.2
H_2O/OH^-	40-1,000	50-500
SiO_2/Al_2O_3	5-50,000	12-20,000
SiO_2/B_2O_3	5-1,000	10-500
R/R+M	0.05-0.99	0.2-0.9

wherein R and M are as above defined.

Reaction conditions here include a temperature of 80°C to 200°C, preferably 100°C to 180°C, for 40 hours to 30 days, preferably from 60 hours to 15 days.

When a boroaluminosilicate having the structure of zeolite ZSM-11 is desired, for example, the reaction mixture from which it is to be crystallized will have a composition, in terms of mole ratios of oxides, within the following ranges:

	Broad	Preferred
OH^-/SiO_2	0.005-0.30	0.01-0.2
H_2O/OH^-	40-1000	50-500
SiO_2/Al_2O_3	5-50,000	12-20,000
SiO_2/B_2O_3	5-1,000	10-500
R/R+M	0.05-0.99	0.2-0.9

wherein R and M are as above defined.

Crystallization temperatures and times are as indicated above for preparation of boroaluminosilicate ZSM-5.

When, for example, a boroaluminosilicate having the structure of zeolite Beta is desired, the reaction mixture from which it is to be crystallized will have a composition, in terms of mole ratios of oxides, within the following ranges:

	Broad	Preferred
OH^-/SiO_2	0.1-0.8	0.1-0.2
H_2O/OH^-	60-300	70-90
SiO_2/Al_2O_3	5-3000	10-500
SiO_2/B_2O_3	5-300	20-200
R/R+M	0.01-0.95	0.2-0.7

wherein R and M are as above defined.

Reaction conditions here include a temperature of 85°C to 175°C, preferably from 130°C to 150°C, for 24 hours to 50 days, preferably from 24 hours to 21 days.

When a boroaluminosilicate having the structure of zeolite ZSM-35 is desired, the reaction mixture from which it is to be crystallized will have a composition, in terms of mole ratios of oxides, within the following ranges:

	Broad	Preferred
OH^-/SiO_2	0.005-0.30	0.05-0.25
H_2O/OH^-	40-1,000	50-500
SiO_2/Al_2O_3	5-50,000	12-20,000
SiO_2/B_2O_3	5-1,000	10-500
R/R+M	0.05-0.99	0.2-0.9

wherein R and M are as above defined.

Reaction conditions here include a temperature of 85°C to 200°C, preferably from 130°C to 175°C, for 24 hours to 90 days, preferably from 24 hours to 21 days.

When a boroaluminosilicate having the structure of zeolite ZSM-12 is desired, for example, the reaction mixture from which it is to be crystallized will have a composition, in terms of mole ratios of oxides, within the following ranges:

	Broad	Preferred
OH^-SiO_2	0.2-0.8	0.4-0.6
H_2O/OH^-	30-200	50-90
SiO_2/Al_2O_3	8-200	20-90
SiO_2/B_2O_3	5-300	30-160
R/R+M	0.01-0.95	0.4-0.7

wherein R and M are as above defined.

Crystallization temperatures and times are as listed above for preparation of boroaluminosilicate ZSM-11.

Another way to direct synthesis of the present boroaluminosilicate molecular sieve having a particular crystal structure is to provide seed crystals of the desired structure, e.g. boroaluminosilicate zeolite of ZSM-5 structure, in the reaction mixture initially. This may be facilitated by providing at least about 0.01 percent, preferably at least 0.1 percent and still more preferably at least 1 percent seed crystals of the desired boroaluminosilicate (based on total reaction mixture weight).

Example 1

This example compares the ion exchange capacity of borosilicate zeolite beta with aluminosilicate zeolite beta. The borosilicate zeolite beta samples were converted to the sodium form by conventional nitrogen precalcination followed by sodium back exchange. Inasmuch as it has been shown that the boron in borosilicate zeolite beta is quite labile in solutions of pH lower than 7, all exchange solutions in this example were kept at a pH higher than 9 by the addition of sodium hydroxide. The properties of borosilicate zeolite beta and aluminosilicate zeolite beta are shown in Table I below.

TABLE I

TABLE I

	Borosilicate	Aluminosilicate
Chemical Composition		
SiO_2	91.80	92.29
Al_2O_3	0.71	4.10
B_2O_3	3.10	-
Na	2.01	1.86
N	0.053	0.03
$SiO_2/(Al+B)_2O_3$	29.7	38.2

The borosilicate zeolite beta was ion exchanged with various alkali metal ions and strontium.

The chemical compositon analysis and cation balance of the exchanged zeolite beta indicate that the boron, indeed, is incorporated within the framework and has ion exchange capacity. Furthermore, the selectivities of the various alkali metal and alkali earth metal cations for either the borosilicate or aluminosilicate zeolite beta are indistinguishable. This can be seen from Figure 1, where the solid lines are ion exchange isotherms for the aluminosilicate zeolite beta and data points are those for the boron containing sample. The equivalent fractions Z_M, S_M can be defined more explicitly as follows:

$$Z_M = \frac{\text{equivalents of M in zeolite}}{\text{gram-atoms of Al or B in zeolite}}$$

$$S_M = \frac{\text{normality of M in solution}}{\text{total normality of cations in solution}}$$

Example 2

The borosilicate zeolite beta of Example 1 was compared with sodium exchanged zeolite X and zeolite A for strontium and cesium ion exchange capacity. The temperature of ion exchange was 25°C with a pH of the exchange solution kept higher than 9. The results are shown in Table 2.

TABLE II

			Separation Factor (1)	
			Alpha Sr/Na	Alpha Cs/Na
	SiO_2/B_2O_3	SiO_2/Al_2O_3	Sr(25°C)*	CS(25°C)
Borosilicate Beta	30	200	6	13
NaX	No boron	2-5	9*	0.8*
NaA	No boron	2-0	5*	0.5*
NaZSM-5	No boron	70	0.2*	20*

*Estimated from isotherms in literature. For example, Journal of Physical Chemistry Vol. 70, 1158 (1966) and Vol 72, 4086 (1968).

(1) Relative ion exchange selectivity of zeolites for various cations has been obtained and expressed as the separation factor, alpha A/B, which is defined as:

$$\text{Alpha}\ \frac{A}{B} = \frac{Z_A\ S_B}{Z_B\ S_A}$$

Where alpha A/B is the separation factor of ion A over ion B and Z_A, Z_B, S_A and S_B are ionic fractions of A and B in the zeolite and solution phase, respectively. The alpha X/Na of the zeolite is for a variety of cations obtained with an equi-molar equilibrating solution ($S_X = S_{Na} = 0.5$) at 25°C.

Example 3

A borosilicate beta was used for ion exchanging strontium ion. When saturated with strontium ion, the zeolite was dried and one part thereof was mixed with four parts of type 0220 soft glass powder from Owens Corning Illinois Company to form a uniform mixture. This mixture was then heated in an electric furnace. The mixture started to soften at about 850°C and completely vitrified into a glass-like melt at about 950°C, a temperature that is considerably lower than 1050°C which is the melting temperature of a mix of the same glass powder and aluminosilicate.

The glass melt was cooled to room temperature. Fifty parts of water were then added to one part of the glass solids. The aqueous mixture was heated at 100°C for 24 hours. The glass solids, after cooling and after leaching in water, were analyzed. The strontium contents in the glass solids before and after the water-leaching step were found to be exactly the same, indicating that the strontium ion containing Beta was fixed and formed an integral part of the leach-resisting glass compound.

Claims

1. A process for removing radioactive ions from waste water comprising: contacting the radioactive ion-containing-waste water with a zeolite which contains boron within the crystal framework thereof for a contact time sufficient for the zeolite to adsorb the radioactive ions, admixing the radioactive ion-containing zeolite with a soft glass powder to form a uniform mixture; and sintering the mixture to form a glass like melt.

2. The process of claim 1 wherein the zeolite contains sufficient boron whereby the mixture begins to soften at a temperature no greater than about 850°C and is completely vitrified at about 950°C.

3. The process of claim 1 or 2 wherein the contacting is conducted by providing the zeolite in particulate form and arranged in a column having a selected length; and passing the waste water as a stream through the column for a selected flow time that is sufficient for adsorbing the radioactive ions from the water.

4. The process of any of claims 1 to 3 wherein the radioactive ions include radiostrontium and radiocesium.

5. The process of any of claims 1 to 4 wherein the zeolite contains a silica/alumina mole ratio of at least 5 and a framework boron content to provide a silica/boria mole ratio of at most 1000.

6. The process of claim 5 wherein the zeolite has a silica to alumina mole ratio of 12 to 1000 and contains sufficient boron to provide silica/boria ratio of 10 to 500.

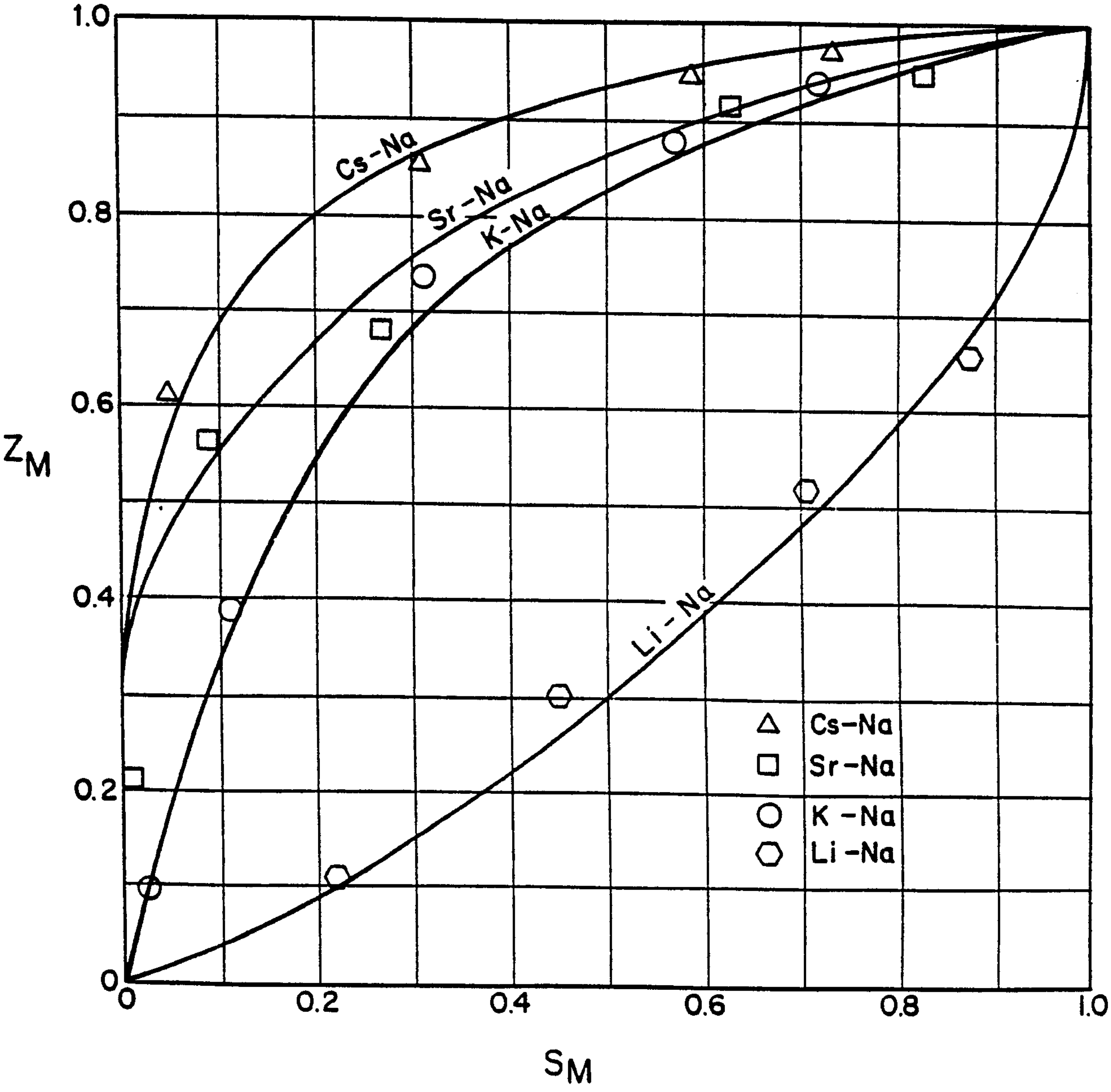
7. The process of any of claims 1 to 6 wherein the zeolite is a borosilicate with a silica/alumina mole ratio of at least 200 and a silica/boria ratio of no greater than 1000.

8. The process of claim 7 wherein the borosilicate zeolite has a framework silica/boria mole ratio of 5 to 500.

9. The process of any of claims 1 to 8 wherein the zeolite is a large pore zeolite.

10. The process of any of claims 1 to 9 wherein the zeolite is zeolite beta.

11. The process of any of claims 1 to 10 wherein the waste water is alkaline.


1.0
0.8
0.6
0.4
0.2
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Z_M
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0.2
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S_M
Cs-Na
Sr-Na
K-Na
Li-Na
△ Cs-Na
□ Sr-Na
○ K-Na
⬡ Li-Na

European Patent Office

EUROPEAN SEARCH REPORT

Application number

EP 85 30 6341

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
A	FR-A-2 440 778 (MACEDO) * Claims 1,2,4,8 * ---	1,4	G 21 F 9/12 G 21 F 9/16
A	FR-A-2 291 583 (ATOMENERGI) * Claims 1,3; example 1 * ---	1-4	
A,D	FR-A-2 310 616 (TOHOKU CHEMICAL) * Claims 1,3,5 * ---	1-4	
A	GB-A-2 025 685 (NUKEM) ---		
A	EP-A-0 049 936 (EURATOM) -----		

TECHNICAL FIELDS SEARCHED (Int. Cl.4)
G 21 F B 01 J

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	11-12-1985	NICOLAS H.J.F.

CATEGORY OF CITED DOCUMENTS

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