

1

3,196,106

METHOD FOR PURIFYING RADIOACTIVE WASTE LIQUID

Walter L. Haden, Jr., Metuchen, and Frank J. Dzierzanowski, Somerset, N.J., assignors to Minerals & Chemicals Philipp Corporation, Menlo Park, N.J., a corporation of Maryland

No Drawing. Filed Oct. 4, 1961, Ser. No. 142,763
8 Claims. (Cl. 210—24)

This invention relates to a method for eliminating radioactive isotopic material from radioactive waste liquids and relates especially to the elimination of radiocesium from such liquids by adsorption.

The handling and disposal of radioactive wastes is a constant problem in nuclear energy operations. As the utilization of nuclear energy increases, the safe and economical disposal of radioactive waste becomes more pressing.

Most radioactive waste material is in liquid form and it is obtained for example, by dissolving spent fuel in nitric acid. Many of the fission products present in the waste liquid have a short half-life and, therefore, their safe disposal presents no problem. The difficulty comes about as a presence in the waste liquid of radiocesium (Cs^{137}) and radiostrontium.

Radioisotopic elements in radioactive wastes are ultimately safely disposed of by burial in the ground, ocean or other 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 treatment so as to concentrate the radioactive values in the liquid. Various methods have been suggested to effect this result, as examples of which may be mentioned evaporation of the liquid, fixation of radioisotopic element by solids, precipitation of radioisotopic elements from the waste liquid, and calcination of the waste liquid. Some of these pretreatments of radioactive waste liquids, especially low level liquid wastes, are not economically feasible when carried out on large scale. Thus, for example, concentration of wastes by evaporation is not practical for handling large volumes of low level wastes.

One of the most practical approaches to the disposal of liquid radioactive waste liquids is the fixation of radioactive elements in the liquid waste on a solid, as by adsorption or ion-exchange, so that the liquid can be safely released to normal environmental liquid waste disposal sites or waters.

To accomplish this result it has been suggested to contact the waste liquid with certain naturally occurring minerals which are capable of selectively adsorbing radioactive elements. Montmorillonite, illite, clinoptilolite and orionite have been recommended for fixing radiocesium. All of these minerals are crystalline silicates. Montmorillonite and like illite are clay minerals; clinoptilolite and erionite, which are most promising, are naturally occurring zeolites.

However, naturally occurring materials generally have definite limitations as adsorbents unless they can be economically processed to assure uniform purity and, there-

2

fore, consistent performance. Thus mineral composition varies in many instances because of the presence of impurities which frequently cannot be removed easily during processing. Some minerals cannot be put into the desired physical form and still maintain sufficient stability. Many minerals, such as naturally occurring zeolites, are not found in extensive deposits in the form of a material of relatively uniform pure composition. Therefore, naturally occurring minerals such as zeolites have very limited application to the purification of large volumes of liquid fuel wastes.

Accordingly, an object of this invention is the provision of a method for adsorbing radiocesium from liquid fuel wastes with a synthetically produced zeolite which may be readily prepared in the desired purity from abundant raw material.

A more particular object of this invention is the provision of an economical method for selectively adsorbing radiocesium from low level liquid radioactive wastes which contain also an appreciable concentration of other ions, especially sodium ion.

Further objects and advantages will be apparent from a description of this invention which follows.

After extensive experimentation with the adsorptive properties of scores of silicates, including various naturally occurring and synthetic silicates, we have discovered that a particular type of synthetic zeolitic silicate which may be readily prepared from abundant raw material in the desired purity possesses exceptional adsorptive selectivity for radiocesium ions.

Briefly stated, in accordance with this invention, aqueous waste liquids containing radiocesium ions in solution such as, for example, liquids obtained by leaching spent uranium nuclear fuel with acid solutions, are directly contacted with particles of the synthetic crystalline lithium aluminum silicate hydrate of the approximate formula $\text{Li}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 4\text{H}_2\text{O}$ for a time sufficient for the synthetic zeolite to adsorb substantially completely all of the radiocesium in the waste liquid. The cesium-depleted waste liquid may be discharged to waste or, in some instances, it may be further processed for removal of other radioactive elements before disposal. The zeolite with sorbed radiocesium can be sealed in a suitable container which is then buried in a suitable geological formation.

This process appears to be especially applicable to the purification of low level waste liquids, especially substantially neutral liquids containing an excess of sodium ions over radiocesium ions, since these liquids do not lend themselves to economical treatment and disposal procedures which are feasible with waste liquids having a high concentration of radioactive elements.

Our results are surprising and unexpected since, to the best of our knowledge, only silicates having an appreciably higher SiO_2 to Al_2O_3 mol ratio than our lithium aluminum silicates have appeared promising as adsorbents for radiocesium.

More specifically, the hydrated lithium aluminum silicate adsorbents we use in carrying out this invention have a mol ratio of Li_2O to Al_2O_3 of about 1:1, a mol ratio of SiO_2 to Al_2O_3 of about 2:1 and about 4 mols H_2O per mol Al_2O_3 . Depending on the method of preparation,

3

the zeolite may be one which has the X-ray powder diffraction pattern reported on ASTM Card 5-0181, i.e.:

"d" Spacing, A.	Relative line intensity, I/I ₀
6.42	100
5.21	50
4.20	100
4.06	20
3.27	20
3.15	100
3.03	100
2.490	80
2.392	40
3.326	60
2.243	20
2.173	50
2.042	40
1.952	50
1.868	20
1.754	60
1.725	50
1.556	40
1.524	50
1.474	60
1.445	20
1.405	50
1.371	20
1.348	20
1.327	20
1.300	20
1.270	40
1.244	20

The zeolite may be the hydrated lithium aluminum silicate which has the following interplanar spacings alone or in addition to those in the above-mentioned ASTM card.

"d" Spacing, A.	Relative line intensity, I/I ₀
7.02	100
4.79	30
3.93	14
3.67	11
3.28	19
3.09	97
2.97	42
2.82	61
2.47	19

Suitable lithium aluminum silicate hydrates can be produced by reaction of metakaolin ($\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) with a quantity of dilute aqueous solution of LiOH (e.g. solutions of about 1% to 10% concentration) in amount sufficient to provide at least 1 mol of Li_2O per mol of metakaolin.

To obtain metakaolin of suitable quality, kaolin is dehydrated by calcination at a temperature within the range of from about 800° F. to about 1600° F., and preferably 1200° F. to 1500° F. for a time sufficient to remove substantially completely the water of crystallization from the clay. Calcination should not be severe enough to cause the clay to undergo the characteristic kaolin clay exotherm.

By "kaolin clay" is meant a naturally occurring clay containing at least one of the following as the chief mineral constituent: kaolinite, halloysite, anauxite, dickite and nacrite. The aforementioned minerals are hydrous aluminosilicates whose composition may be represented by the formula:



where X is usually 2, or 4 in the case of certain halloysites. The weight ratio of SiO_2 to Al_2O_3 indicated by this formula is 1.177 to 1. Kaolin clays are frequently

4

associated with foreign materials such as quartz; and the removal of such impurities from the starting clay is recommended.

Using 2 mols of LiOH per mol of metakaolin, it has been found that reaction requires about 20 hours for completion at a reaction temperature of 100° F. Only about 2 to 3 hours is required at a reaction temperature of 215° F. The reaction mixture may be held at reaction temperature for longer periods than required to complete reaction. Completion of reaction is determined by periodically analyzing the LiOH content of the aqueous phase of the reaction medium and ascertaining the point at which LiOH concentration of the reaction medium remains essentially constant.

The zeolite employed in the adsorptive contact process of this invention may be in the form of the precipitated powder or the powder may be pelleted by means known to those skilled in the art to form granular particles of the desired form and shape.

Our adsorptive contact process can be carried out at ambient temperature. Contact of waste liquid containing radiocesium with the adsorbent zeolite may be for a time within the range of about ½ hour to 96 hours. Total pickup of radiocesium with our zeolite is rapid as compared with pickup of prior art radiocesium adsorbents and, generally speaking, contact periods of more than about 12 hours may not effect a significant improvement in radiocesium adsorption.

Following are examples which are illustrative of the practice and utility of this invention.

Synthetic hydrated lithium aluminum silicates within the scope of this invention were tested for cesium adsorption in the presence of interfering ions and compared to several natural materials (clinoptilolite, illite, grunite and erionite) that have shown promise as adsorbents for Cs^{137} . Also evaluated, for purposes of comparison, were other alkali and alkaline earth aluminum silicate hydrates having about the same $\text{SiO}_2/\text{Al}_2\text{O}_3$ mol ratio as our lithium aluminum silicate hydrates. The composition of the test waste aqueous solution was made up to simulate an actual low level radioactive waste liquid.

Preparation of synthetic crystalline lithium aluminum silicate hydrates and other alkali or alkaline earth aluminum silicate hydrates

(a) 150 gm. of commercial metakaolin (Pigment 33) having an L.O.I. of 0.62% was slurried in 1500 ml. of distilled water. The slurry was heated to about 100° F. in an agitated flask connected to a reflux condenser. To this slurry there was added with agitation a solution of 55.4 grams of lithium hydroxide monohydrate in 300 ml. of distilled water. The $\text{Li}_2\text{O}:\text{Al}_2\text{O}_3$ mol ratio of the composition was 1.0:1.0 and the $\text{SiO}_2:\text{Al}_2\text{O}_3$ mol ratio was 2.1:1.0. The LiOH concentration was 1.53%. The mixture was maintained at 100° F. to 102° F. with agitation for about 24 hours. The slurry was then filtered, the insoluble precipitate washed with 5 liters of distilled water and dried at 220° F. for about ½ hour and pulverized.

An X-ray diffraction pattern of the dried product, equilibrated at 70% R.H., was obtained by standard procedures using K-alpha radiation, an X-ray diffractometer using a scintillation counter and a strip chart pen recorder. The relative intensity of the peaks and the inter-planar spacings ("d" values) were calculated from the peak heights recorded on the chart in conventional manner. The product was found to possess the "d" values and corresponding line intensities of the material reported in the table. Also present was the lithium aluminum silicate hydrate having the diffraction pattern reported in ASTM Card 5-0181.

The analysis of this product, identified as Sample No. 1,

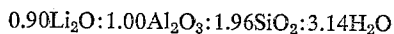
was as follows (where all oxide are reported on a volatile free basis):

	Wt. percent
Li ₂ O -----	10.58
Al ₂ O ₃ -----	40.24
SiO ₂ -----	46.32
TiO ₂ -----	1.36
Fe ₂ O ₃ -----	0.24
F.M. ¹ -----	0.99
L.O.I. ² -----	18.54

¹ Free moisture, determined by heating sample to essentially constant weight at about 220° F.

² Loss on ignition, determined by heating sample to essentially constant weight at about 1800° F.

This analysis indicated the formation of a hydrated lithium aluminum silicate of the following composition:



(b) Another hydrated lithium aluminum silicate was prepared by repeating the procedure described above, except for carrying out reaction at about 215° F., rather than at about 100° F., as in (a), and shortening reaction time to 2 hours to account for the more rapid reaction between the metakaolin and LiOH solution at the elevated temperature.

There was obtained a hydrated lithium silicate (Sample No. 2) analyzing (all oxides reported on a volatile free basis):

	Wt. percent
Li ₂ O -----	10.31
Al ₂ O ₃ -----	40.35
SiO ₂ -----	46.51
TiO ₂ -----	1.40
Fe ₂ O ₃ -----	0.20
F.M. -----	2.06
L.O.I. -----	16.42

An X-ray diffraction pattern of an equilibrated sample of the product indicated that the only crystalline material present was the zeolite identified in ASTM Card 5-0181.

(c) NaOH was substituted for LiOH in part (a) above with the production of a sodium aluminum silicate hydrate identified as Sample No. 3.

(d) NaOH was substituted for LiOH in part (b) above with the production of a sodium aluminum silicate hydrate identified as Sample No. 4.

(e) Samples of a crystalline potassium aluminum silicate hydrate (Sample No. 5) and a crystalline barium aluminum silicate hydrate (Sample No. 6) were prepared from kaolin clay and alkali under conditions of high pressure and high temperature.

Testing adsorbents for cesium adsorption

The method used for testing cesium adsorption was patterned after that used at the Health Physics Division, Oak Ridge National Laboratory, United States Atomic Energy Commission, and was as follows:

A stock solution was made up to simulate radioactive waste liquid by incorporating 6.3 mg. of purified CsCl in 1 liter of 0.6 N NaNO₃ (reagent grade). To this stock was added approximately 2.5 microcuries of radio-cesium. The radiocesium was in the form of a dilute aqueous solution of the chloride salt containing 45 microcuries of radiocesium in 8 ml. of 1 N HCl and was made up by dilution of Cs¹³⁷Cl in the 1 N HCl.

In testing the adsorptive capacity of solid adsorbents for radiocesium adsorption, a 1.6 gram portion of a sample of powdered adsorbent was added to 40 ml. of the stock solution in a 50 ml. glass-stoppered volumetric flask. The adsorbent and stock solution were shaken for 30 to 100 minutes and then allowed to stand overnight in the stoppered flask. The next morning a 1 ml. portion of the supernatant solution was withdrawn and was counted three times to determine the Cs¹³⁷ content. Each sample was again shaken for approximately one hour and allowed to stand for two days. A 1 ml. portion of supernatant was removed from each sample and another count was made.

The plateau for the scaler and Model 163 Scaling Unit was determined with three different standards (Cs¹³⁷ rod, Cs¹³⁷ disc and U glass) in place in the detector, a DS5-5 Scintillation Detector, a well-type instrument with a TI-activated NaI crystal. The working voltage was found to be 1200-1250 volts. The detector was shielded with a lead case especially designed for it. The scaling unit was used at integral counting for the plateau determination, but for the sorption studies differential counting was employed, the discriminator giving a good background of only 8.5 counts per minute.

No detectable adsorption of cesium by the glass-stoppered volumetric flask was found. The largest error in the results appears to be the standard statistical error due to the magnitude of the counts recorded in the radioactivity determinations.

The results of the cesium adsorption determination and other data on the adsorbent samples are shown in the accompanying table. Surface area measurements were determined by the nitrogen adsorption method described by S. Brunauer, P. H. Emmett and E. Teller in their article entitled "Adsorption of Gases in Multi-Molecular Layers," on page 309 of J.A.C.S., vol. 66, April 1944. Base exchange capacities of the samples was analytically determined by the ammonium acetate exchange method. The composition of reference minerals was checked by standard X-ray powder diffraction procedure.

Cesium adsorption of natural and synthetic silicates

Sample No.	Adsorbent Sample Identification	Surface Area m ² /gm.	Base Exchange Capacity meq./100 gm.	Cesium Adsorption, ^a Percent	
				Sample Standing Overnight	Sample Standing 48 Hours
1	Synthetic lithium aluminum silicate tetrahydrates from kaolin clay:				
2	Li ₂ O · Al ₂ O ₃ · 2SiO ₂ · 4H ₂ O (reacted at 100° F.)	31	332	94.1	95.6
	Li ₂ O · Al ₂ O ₃ · 2SiO ₂ · 4H ₂ O (reacted at 215° F.)	45	133	97.6	97.4
	Other aluminum silicate hydrates from kaolin clay:				
3	Na ₂ O · Al ₂ O ₃ · 2SiO ₂ · 4.6H ₂ O	10.5	662		21.1
4	Na ₂ O · Al ₂ O ₃ · 2SiO ₂ · 4.5H ₂ O			48.9	49.4
5	K ₂ O · Al ₂ O ₃ · 2SiO ₂ · nH ₂ O			56.9	70.7
6	BaO · Al ₂ O ₃ · 2SiO ₂ · nH ₂ O			52.3	72.4
	Natural silicate minerals:				
7	Clinoptilolite	30	217	83.8	93.4
8	Illite ¹			70.5	78.9
9	Grundite ²			70.1	68.3

¹ American Petroleum Institute Research Project, Reference Clay Mineral No. 35.

² A type of illite obtained from Oak Ridge National Laboratory.

³ All values subject to a rather uniform absolute error of about 4 units in each percent adsorption value due to magnitude of counts recorded.

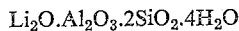
7

The data show that at least about 94% ($\pm 4\%$) of the radiocesium was adsorbed by overnight contact with Samples No. 1 and 2—lithium aluminum silicate hydrates. These samples were at least as effective during the short contact time as a 48 hour contact time with Sample No. 8, clinoptilolite, the most effective of the minerals reported in the screening, and were significantly more effective than the illites.

Also shown by the data was that substitution of other alkalis or an alkaline earth element for lithium in the lithium aluminum silicate hydrate resulted in products which were extremely poor cesium adsorbents as compared with the lithium aluminum silicate hydrates.

We claim:

1. A method for purifying an aqueous radioactive waste liquid having dissolved therein a low level of radiocesium in the form of a salt of a mineral acid and also having dissolved therein a substantially larger amount of a mineral acid salt of another metal which is nonradioactive, said method comprising contacting said liquid with a solid synthetic crystalline lithium aluminum silicate hydrate of the approximate formula



whereby radiocesium in said liquid is selectively adsorbed by said lithium aluminum silicate hydrate, and separating the liquid thus contacted from said lithium aluminum silicate hydrate with adsorbed radiocesium.

2. The method of claim 1 in which said silicate is one which possesses the following identifying X-ray diffraction characteristics:

"d" Spacing, A.	Relative line intensity, I/I ₀
7.02	100
4.79	30
3.93	14
3.67	11
3.28	19
3.09	97
2.97	42
2.82	61
2.47	19

3. The method of claim 1 in which said silicate is one which possesses the following identifying X-ray diffraction characteristics:

"d" Spacing, A.	Relative line intensity, I/I ₀
6.42	100
5.21	50
4.29	100
4.06	20
3.27	20
3.15	100
3.03	100
2.490	80
2.392	40
3.326	60
2.243	20
2.173	50
2.042	40
1.952	50
1.868	20
1.754	60
1.725	50
1.556	40
1.524	50
1.474	60
1.445	20
1.405	50
1.371	20
1.348	20
1.327	20
1.300	20
1.270	40
1.244	20

4. A process for separating radiocesium from an aqueous radioactive waste liquid having dissolved therein a microquantity of radiocesium in the form of a salt of a

8

mineral acid and also having dissolved therein a macroquantity of a salt of another metal which is nonradioactive, which comprises contacting said liquid at ambient temperature with a solid synthetic crystalline lithium aluminum silicate hydrate of the approximate formula $\text{Li}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 4\text{H}_2\text{O}$, whereby radiocesium in said liquid is selectively adsorbed by said lithium aluminum silicate hydrate, and separating the liquid thus contacted from said lithium aluminum silicate hydrate with adsorbed radiocesium.

5. A process for separating radiocesium from a low level aqueous liquid obtained by leaching spent uranium nuclear fuel with acid solution and having dissolved therein a microquantity of a salt of radiocesium and also having dissolved therein a macroquantity of a sodium salt, said process comprising contacting said liquid at ambient temperature with a solid synthetic crystalline lithium aluminum silicate hydrate of the approximate formula $\text{Li}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 4\text{H}_2\text{O}$, whereby radiocesium in said liquid is selectively adsorbed by said lithium aluminum silicate hydrate, and separating the liquid thus contacted from said lithium aluminum silicate hydrate with adsorbed radiocesium.

6. The method of claim 5 in which said silicate is one which possesses the following identifying X-ray diffraction characteristics:

"d" Spacing, A.	Relative line intensity, I/I ₀
7.02	100
4.79	30
3.93	14
3.67	11
3.28	19
3.09	97
2.97	42
2.82	61
2.47	19

7. The method of claim 5 in which said silicate is one which possesses the following identifying X-ray diffraction characteristics:

"d" Spacing, A.	Relative line intensity, I/I ₀
6.42	100
5.21	50
4.29	100
4.06	20
3.27	20
3.15	100
3.03	100
2.490	80
2.392	40
3.326	60
2.243	20
2.173	50
2.042	40
1.952	50
1.868	20
1.754	60
1.725	50
1.556	40
1.524	50
1.474	60
1.445	20
1.405	50
1.371	20
1.348	20
1.327	20
1.300	20
1.270	40
1.244	20

8. The method of claim 5 wherein said liquid is substantially neutral.

References Cited by the Examiner

UNITED STATES PATENTS

2,616,847	11/52	Ginell	210—24
2,962,355	11/60	Breck et al.	252—455 X
3,017,242	1/62	Ames	23—25

(Other references on following page)

OTHER REFERENCES

"The Hydrothermal Chemistry of Silicates, Part I. Synthetic Lithium Aluminosilicates," Barrer et al., J. Chem. Soc., 1951, pp. 1267-1278.

Molecular Sieves Adsorb I-131 from Air, Wahlgren et al., Nucleonics 15, No. 9, pp. 156-60, 1957.

Zeolitic Extraction of Cesium from Aqueous Solutions, Ames, U.S. Atomic Energy Comm., HW-62607, 25 pages,

1959, cited in Chem. Abstracts, vol. 54, 1960, 24077b.

Removal of Cs¹³⁷ and Sr⁹⁰ from Aqueous Solution by Ion Exchange on Vermiculite, Sammon et al., Atomic Energy Research Estab. (Gt. Brit.) R-3274, 14 pp., 1960, cited in Chem. Abstracts, vol. 54, 1960, 23873i.

MORRIS O. WOLK, *Primary Examiner*.

EARL M. BERGERT, *Examiner*.