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in Ceramic Masses

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FROM: Gilbert C. Robinson

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I THE EFFECT OF CONCRETE COMPOSITION ON RETENTION OF RADIOACTIVE WASTE

PART A - PRELIMINARY EXPERIMENTS

INTRODUCTION

The possibility of trapping radioactive waste by using it as the makeup liquid in concrete was suggested briefly in the papers given at Johns Hopkins, June 20, 1957. However, this method was found to be inadequate because the concrete would disintegrate because of high temperatures generated by extremely high-level radioactive materials.

It would seem that the problem of concrete disintegration could be corrected in two ways: First, a temperature-resistant concrete could be prepared by adding certain ceramic substances which would promote sintering of the mass as the hydraulic bond of the ceramic cement is destroyed; second, (for a given weight of material) a lightweight concrete could be prepared which would effectively keep the radioactive particles at greater separation distance than would be possible in heavy concretes.

It was desired to evaluate these ideas by making concretes using portland cement and vermiculite as the solid materials and radioactive waste as the makeup liquor. Although the portland cement and vermiculite will sinter when exposed to elevated temperatures, it was also desired to investigate the possibility of reducing the temperature or increasing the effectiveness of the sinter by adding fluxes such as borax, soda ash, etc.

PROCEDURE

1. Materials

a. Vermiculite

Vermiculite is a mineral that exfoliates upon heating showing expansion up to 30 times its original volume. This expansion produces a lightweight material weighing about seven pounds per cubic foot. The expanded vermiculite is highly absorbent and can pick up three times its weight of liquid and still remain a loose granular material. The chemical composition of a vermiculite is shown in Table I. The chemical composition and physical properties are subject to considerable variation depending on the ore source and the exfoliation procedure.

The vermiculite used in this investigation was provided by the Zonolite Company of Chicago. It came from their Libby, Montana mines and was classed as their size grade No. 4 (essentially minus 6 mesh plus 48 mesh).

TABLE I

THE CHEMICAL COMPOSITION OF VERMICULITE

<u>Theoretical Composition</u>		<u>Actual Composition of South Carolina Vermiculite</u>	
Mg	15.9	SiO ₂	38.7
Si	18.2	MgO	20.0
Fe	3.8	Al ₂ O ₃	17.4
Al	9.2	Fe ₂ O ₃	8.5
O	37.9	K ₂ O	5.2
OH	13.8	CaO	0.8
		Cr ₂ O ₃	0.5
		Mn ₃ O ₄	0.1
		Cl	0.5
		LOI	8.7

TABLE II

THE COMPOSITION OF VERMICULITE CONCRETE TEST MIXTURES

<u>Material</u>	<u>C-1</u>	<u>C-2</u>	<u>C-3</u>	<u>C-4</u>	<u>C-5</u>	<u>C-6</u>	<u>C-7</u>	<u>C-8</u>
Waste Liquor mls	100	100	100	100	100	100	100	84 ml
Vermiculite gms	13.7	13.0	18.0	15.0	17.0	17.0	15.0	10.0
Hi Early Cement gms	30.9	10.0	-----	20.0	20.0	-----	20.0	20.0
Bentonite gms	-----	3.0	-----	-----	-----	-----	-----	-----
5 SC Sodium Silicate gms	-----	-----	6.0	-----	-----	-----	-----	-----
No. 1 Pottery Plaster gms	-----	-----	-----	-----	-----	30.0	-----	-----
Attapulgate HVM gms	-----	-----	-----	-----	-----	-----	-----	10.0

PROCEDURE (continued)

b. Other Materials

The cements used in this investigation were Atlas Hi Early portland cement and U. S. Gypsum No. 1 pottery plaster. The clay used was Attasorb HVM supplied by the Minerals and Chemicals Corporation of America.

2. Mixing Method

The compositions tested are shown in Table II. Different sequences of mixing were tried with Compositions C-1 through C-6. It was found that there was a tendency for the cement to settle out of the mixture and cake on the bottom of the container whenever the mixture or portions of it became fluid. The best procedure was found to be mixing of the cement and vermiculite first and then adding the solution to the dry materials while continually stirring the mixture. This procedure was used in the remaining tests.

Immediately after mixing, the compositions were vibrated into waxed paper cups and six samples were prepared from each composition.

3. Firing

The samples were allowed to air dry for 24 hr and then were placed in porcelain crucibles and fired in electric muffle furnaces to various temperatures as shown in Table III. The furnaces were started at room temperature and brought up to the soaking temperature as fast as the furnace would permit. The samples were maintained at the final temperature for two hours.

4. Radioactivity Measurements

The radioactivity of the fired samples was determined by powdering the samples in their crucibles and then adding water to the crucible. The suspension of fine particles in water was poured into small aluminum dishes. The suspension was allowed to settle 30 sec before pouring into the aluminum dish, thus, eliminating the larger particle sizes from the sample; however, this was not completely effective since some of the coarse particles of vermiculite would float even though the samples were fired up through 800°C and these were transferred to the dish. Thus, the surface appearance of the samples varied considerably.

The radioactivity was determined on an end window G. M. beta counter, 64 Scaler. It was necessary to use four sheets of aluminum shielding above the solid-suspension specimens to reduce the count to a readable level.

Approximately half of each fired specimen was transferred to a leaching bottle containing 10 ml. of tap water to each gram of specimen. A one ml. sample of the leach liquor was transferred to an aluminum dish after seven days of leaching. The dish was dried at 104°C and then its radioactivity determined on the G. M. counter.

TABLE III
THE EFFECT OF EXPOSURE TO ELEVATED TEMPERATURES
ON THE RETENTION OF ACTIVITY IN COMPOSITIONS C-7 AND C-8

Temperature °C	C-7		C-8	
	Wt. of Sample gms.	Radioactivity c/min/gm	Wt. of Sample gm	Radioactivity c/min/gm
Room		228,000*		167,000*
160	0.4231	86,048	0.1218	95,147
560	0.2835	140,268	0.0695	98,287
860	0.2846	166,047	0.0629	100,877
1020	0.1647	152,141	-----	-----
1125	0.0793	189,634	0.0401	107,830
1190	0.0916	159,356	0.0265	154,377

*Calculated from the amount of waste liquor used in the concrete.

RESULTS OF INVESTIGATION

1. Procedure for Making Concrete

Compositions C-1 through C-6 were made to determine a satisfactory procedure for forming concrete and to investigate three different types of cementing agents.

Composition C-1 with the dry cement and dry vermiculite were mixed together and 100 ml. of Hope solution was added to the mixture. This composition evolved considerable heat after addition of the Hope solution and formed a solid cake within two minutes of the addition of the waste liquor.

The mixing sequence was changed for Composition C-2 and the Hope solution was added to the vermiculite as the first step and then cement and bentonite were sprinkled over the dampened vermiculite. This composition showed no indication of setting within 12 hr of the time of mixing. The lack of set may have been caused by both the small proportion of cement to vermiculite and by the mixing sequence. There was a tendency for the cement to segregate in this mixing sequence rather than uniformly coating the vermiculite grains. Whenever there was a very wet mix, the liquid washed the cement away from the vermiculite and then the cement set on the bottom of the mixing container. This mixing sequence might be desirable with lower ratios of vermiculite to liquid and with machine mixing. This should be investigated.

Composition C-3 used type SC powdered sodium silicate as the binder. The same mixing sequence was used as in Composition C-2. However, the vermiculite to liquid ratio was increased to 18.0 gms to 100 ml. (C-2 used 13.0 gms to 100 ml.). It is interesting that the vermiculite was still granular and free from a surface liquid when 100 mls. of simulated waste liquor was added. This would indicate an absorption capacity of about 1000 per cent. The addition of the sodium silicate did not produce a set in this mixture. It is suggested that other brands of sodium silicate should be tried.

Composition C-4 used the same mixing sequence as C-1. However, a lower ratio of cement to vermiculite was used. This composition gave an excellent set. A still lower ratio was used in C-5 and this composition also gave a good set.

Composition C-7 was the same as C-4. Composition C-7 was prepared for radioactivity measurement.

It was also desired to determine if attapulgite additions would increase the effectiveness of the concrete in trapping waste material. Composition C-8 contained attapulgite Attasorb HVM.

2. Radioactivity in Solid Specimens

The radioactivity contained in the solid specimens is shown in Table III. There was a large variation in the weight of the specimens and this variation along with variations in the surface texture of the specimens probably caused the

variation in the measured activities. There was no indication of a loss in beta activity with increasing firing temperature; however, a new test should be made which would eliminate the errors of this test procedure.

3. Radioactivity in Leach Liquor

The beta count for the leach liquors is shown in Table IV. It can be seen that the count decreases for both compositions with increasing firing temperature. Composition C-8 is considerably better than Composition C-7. A count of only 10 was obtained with C-8 after firing at 1190°C, whereas C-7 gave a count of 640 per min. per ml. It is not known whether or not the lower counts in C-8 came from the use of attapulgite or from the use of a greater ratio of liquid to solids.

Firing temperatures above 1100°C seem advisable for these compositions. A firing temperature of 1190°C gave a reduction in activity of 16,700 to one.

TABLE IV

RADIOACTIVITY IN ONE ML. OF
LEACH LIQUOR AFTER SEVEN DAYS

Temperature °C	C-7 Radioactivity c/min/ml	C-8 Radioactivity c/min/ml
160	3727	2031
560	1360	392
860	1052	262
1020	835	175
1125	975	38
1190	640	10

PART B - ADDITIONAL EXPERIMENTS

INTRODUCTION

Previous tests indicated that vermiculite-concrete could successfully contain radioactive waste against water leaching if the concrete were fired to 1200°C. The tests also indicated that a vermiculite-concrete containing attapulgite gave a lower count lixivium. However, it was not clear whether this resulted from the presence of the attapulgite or from the use of a higher solids to waste ratio.

It was desired to determine the effect of attapulgite additions to vermiculite-concrete, the effect of varying quantities of cement, and the effect of limestone additions.

PROCEDURE

The compositions tested are shown in Tables V, VI, and VII. All the dry ingredients were first mixed together and then the Hope solution was added rapidly to the dry batch. The mixing was accomplished in paper cups and the concrete was allowed to set in the cups. Twelve hours after mixing the compositions were divided into two portions and each portion was transferred to a porcelain crucible. One portion of each composition was dried at 104°C for 24 hr. The other portion was fired to 1100°C. The furnace temperature was elevated to 900°C in 2-1/2 hr and maintained at 900°C for four hours. The furnace temperature was then elevated to 1000°C and maintained at this temperature for four hours. Finally, the temperature was raised to 1100°C and held for two hours.

After firing, the samples were prepared for leaching by transferring the samples to a leaching bottle and adding 10 ml. of tap water for each gram of concrete specimen. A one ml. sample of the leach liquor was transferred to an aluminum dish after seven days of leaching. The dish was dried at 104°C and then its radioactivity determined on the G. M. counter.

TABLE V

THE EFFECT OF VARYING AMOUNTS OF CEMENT ON THE EFFECTIVENESS OF VERMICULITE-CONCRETE (1) IN TRAPPING RADIOACTIVE WASTE

Sample No.	Vermiculite gms	Composition Cement - gms	Waste Liquor ml.	Beta Count of Lixivium after seven days -	
				104°C	c/min/ml. 1100°C
10	15	20	100	3054	590
11	15	40	100	2139	572
12	15	60	100	1843	500

(1) For description of materials see Part A.

TABLE VI

THE EFFECT OF REPLACEMENT OF CEMENT AND VERMICULITE BY ATTASORB HVM OR LIMESTONE ON THE EFFECTIVENESS OF VERMICULITE-CONCRETE IN TRAPPING RADIOACTIVE WASTE

Sample No.	Vermiculite	Cement	Composition		Limestone	Beta Count of Lixivium after 7 days c/min/ml	
			Attasorb	Waste Liquor		104°C	1100°C
11	15	40	---	100	---	2139	572
13	15	30	10	100	---	2202	88
14	15	20	20	100	---	1766	52
17	--	40	20	100	---	1183	107
18	15	20	--	100	20	2363	1204

TABLE VII

THE EFFECT OF QUANTITY OF VERMICULITE ON THE EFFECTIVENESS OF VERMICULITE-CONCRETE IN TRAPPING RADIOACTIVE WASTE

Sample No.	Composition			Beta Count of Lixivium after 7 days c/min/ml	
	Vermiculite gm	Cement gm	Waste Liquor ml	104°C	1100°C
11	15	40	100	2139	572
15	20	40	100	1877	625
16	25	40	100	1877	441

RESULTS OF INVESTIGATION

1. Effect of Quantity of Cement

Compositions 10, 11, and 12 differed only in the amount of cement used as shown in Table V. There was some reduction in the beta count of the lixivium with increasing amounts of cement; however, the reduction was very small compared to the large increases in cement. It would seem that there is no advantage to be obtained in increasing the cement above that quantity needed to produce a firm set.

It is interesting that unfired concrete demonstrated some capacity to retain radioactivity. It is suggested that this should receive further study and attempts should be made to reduce the porosity of the concrete. Some methods that might be tried could be incorporation or coating concrete with sodium silicate or addition or formation of gelatinous compounds such as iron hydroxide with the cement. Increased amounts of Attasorb should be tried. (See Part A).

The results of this investigation showed some better retention than a similar composition, C-7, of a previous investigation. Composition 16 showed a count of 590 at 1100°C as compared with 975 for composition C-7 fired at 1125°C. It is believed that part of the improvement resulted from more skillful mixing in this series of compositions.

2. Effect of Replacement of Cement and Vermiculite by Attasorb HVM or Limestone

Compositions 11, 13, and 14 demonstrate the effectiveness of replacing cement with Attasorb HVM. Increasing the Attasorb at the expense of the cement seemed to have no significant effect on the retention of activity in the 104°C samples. However, it had a very pronounced effect on the 1100°C samples. Composition 11 with no Attasorb gave a count of 572 c/min/ml. while Composition 13 with 18% Attasorb reduced the count to 88 and Composition 14 with 36% Attasorb gave a count of 52.

These results indicate that much of the reduction in count of Composition C-8 of the previous report was caused by the presence of Attasorb rather than the increased solid to liquid ratio of Composition C-8 compared to C-7.

There is no direct comparison with Composition C-8 of the preceding report and the compositions of this report. The nearest similarity is Composition-13. Composition-13 contained 55 gms solids to 100 ml. of liquid while Composition C-8 contained 40 gms of solids to 84 ml. of liquid. Composition-13 fired to 1100°C gave a beta count of 88 c/min/ml. Composition C-8 fired to 1020° gave a count of 175 c/min/ml., whereas at 1125°C it gave a count of 38 c/min/ml. Interpolation between these two temperatures would give a very similar count for Composition-13 and C-8. This illustrates that firing temperature is much more critical than is composition. It would seem that a desirable firing temperature for these mixtures would be 1200°C.

The desirable limit of replacing cement with Attasorb was not established. It is suggested that quite a range of compositions would work satisfactorily and that the composition could be selected to give the lowest raw material cost within this range.

The cement alone and without modification is a poor trap for waste material; instead, its function is to mold and set more effective materials into units of desired dimensions rather than having loose granular or gelatinous masses. It also serves to eliminate a drying period for clay-like masses since the cement will develop a hydraulic set very rapidly. The Attasorb and vermiculite act as the major radioactivity traps.

Composition-17 was a cement Attasorb mixture without vermiculite. This composition provided the most effective material after firing at 1040°C, although it still fell far short of being effective enough. The results on firing to 1100°C indicate that a mixture of Attasorb and vermiculite is more effective than Attasorb alone. Thus Composition-13 with 55 gms of solids to 100 ml. of liquor gave a lower count than the all Attasorb composition with 60 gms of solids to 100 ml. of liquor.

Composition-18 of Table VI shows the effect of replacing Attasorb with limestone in a vermiculite-concrete. It can be seen that this composition gave extremely poor results.

Additional tests are desirable to obtain more conclusive information. Thus, a composition containing 30 gms cement and 25 gms of Attasorb and a second containing 20 gms of cement and 35 gms of Attasorb should be highly informative.

3. The Effect of Quantity of Vermiculite

Compositions-11, 15, and 16 of Table VII show the effect of increasing amounts of vermiculite on retained radioactivity. It can be seen that there is no increase in trapped activity as the vermiculite is increased above 15 gms to 100 ml. when fired to 1100°C. There may be an advantage of increasing the amount of vermiculite with hotter waste liquid, since the increased bulk of the vermiculite will give less concentration of radioactivity per unit volume.

It is suggested that further studies of the influence of quantity of vermiculite be made using fixed amounts of Attasorb and cement with varying amounts of vermiculite.

II THE EFFECT OF FIRING TEMPERATURES ON THE VOLATILIZATION OF RADIOISOTOPES FROM CLAY MASSES

INTRODUCTION

It was desired to determine if a selective loss in beta or gamma radiation occurred on heating ceramic mixtures containing radioactive wastes.

METHOD OF INVESTIGATION

The ceramic mixtures used in this investigation contained 60% vermiculite, 20% kaolin and 20% pyrophyllite. This mixture was pre-fired at 1980°F and produced a lightweight, porous brick. Small pieces of the porous brick were saturated with Hope solution tagged with mixed fission products at 79,600 beta counts per minute per ml. After saturating with liquid the samples were dried on a hot plate and then re-saturated with the Hope solution. This was repeated to give four cycles of soaking in the liquid. After the final soaking, the sample was air dried and then pulverized in a small crucible. Water was added to the crucible and a suspension of the powdered ceramic in water was obtained. The suspension was allowed to settle 30 sec to permit settling of any coarse particles present and then part of the suspension was poured into each of five vitreous silica dishes. Care was taken to pour similar quantities in each dish. The dishes had been weighed prior to adding the sample in order that the weight of sample could be determined.

Dish A was allowed to air dry for 24 hr and then its radioactivity was determined with an end window G. M. beta counter and 64 Scaler. Four aluminum shields were placed between the counter and the specimen.

The same dish, A, was then heated successively to 104°, 340°, 560°, 860°, and 1000°C with a beta count taken after each firing. The final temperature was maintained for 1-1/2 hr at each temperature. Finally, dish A was returned to the kiln and allowed to remain at 1000°C for 24 hr.

Dishes one through four were subjected to different heat treatments. Their radioactivity was determined on the Ceramic Laboratory beta counter. The samples were also submitted to Dr. S. A. Reynolds for determination of gamma counts and a confirmation of the beta count since the activity of the samples was considerably above the recommended level for the Ceramic Laboratory counter.

RESULTS OF INVESTIGATION

The results on the firing of a single dish to several temperatures are shown in Table VIII. The test procedure of this investigation gave a much smaller variation in the activity at different temperatures. The data in Table VIII indicate that there may be a slight loss in activity between room temperature and a temperature of 104°C. There is no further loss in beta activity up through a firing temperature of 1000°C maintained for 24 hr.

The results also show that there is a large loss in weight upon firing this material. A loss of 18.2% of the initial weight was recorded at 104°C followed by a loss of 43.8% of initial weight at 340°C.

There was a slight additional loss up to 1000°C. Because there is no loss in total activity upon heating the specimen, the loss in weight of the specimens results in a concentration of the activity into a smaller mass. This is shown

TABLE VIII

THE RETENTION OF RADIOACTIVITY AT ELEVATED
TEMPERATURES BY A CERAMIC COMPOSITION

Dish No.	Temperature °C	Weight gms.	Weight Loss %	Beta Count per gm (room temp.)	Beta Count per gm (fired)
A	Room	0.4213		121,000	121,000
A	104	0.3446	18.2	111,000	136,000
A	340	0.2359	43.8	109,500	195,000
A	560	0.2291	45.6	110,500	201,000
A	860	0.2264	46.2	112,000	208,000
A	1000	0.2239	46.8	114,000	214,000
A	1000 - 24 hr	0.2245	46.6	109,000	204,000

* Based on room temperature weight

in the column giving beta counts per fired gram. It can be seen that firing almost doubles the activity per gram of material remaining after firing.

Table IX shows the results of gamma counts on the series of dishes. A single dish was not used, since it would have involved a round trip to X-10 after each firing. A check made on the activity of all the dishes in the dry condition showed similar counts for all the dishes.

It can be seen in a comparison of the Ceramic Laboratory beta counts and the beta counts determined by Reynolds that the Ceramic Laboratory counter gave less than half the correct counts. This confirms the instructions that the Ceramic Laboratory machine is inadequate for counting this level of activity.

Table IX also shows that there is a gradual increase in total beta activity with temperature. This would be expected as the shielding water is expelled between room temperature and 104°C. However, no explanation is offered for the increases above 104°C.

It can be seen in Table IX that 39.7% of the gamma activity is lost between 104°C and 990°C. The loss appears to be approximately proportional to weight loss. It might be interesting to check this ratio in the temperature range

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14

TABLE IX

THE RETENTION OF RADIOACTIVITY AT ELEVATED TEMPERATURES

Dish No.	Temp. °C	Weight		Weight Loss %	Cer. Lab. c/min/gm (room temp.)	Beta Count Reynolds c/min/gm (room temp.)	Reynolds c/min/gm (fired)	Gamma Count	
		Wet gms	Dry gms					c/min/gm (room temp.)	c/min/gm (fired)
1	Room	0.2442	0.2593	---	95,340	209,412	195,333	155,913	146,834
3	104	0.2958	0.2812	4.9	-----	221,264	232,752	153,222	161,177
4	835	0.2337	0.1039	55.5	-----	231,878	521,560	96,304	216,612
2	990	0.2174	0.0886	59.3	-----	244,296	599,435	91,270	223,950
3	Room				95,390				
4	Room				94,860				
2	Room				99,210				

between room and 600°C. Although a loss is shown in total gamma activity, the gamma activity per gram of fired material increases with temperature.

Fired ceramic pieces of the composition used in this experiment are capable of holding 599,435 beta counts and 223,950 gamma counts per gram of fired material when saturated with liquor showing a beta count of 79,600 per ml. It should be noted that the count for the liquor was determined on the Ceramic Laboratory machine and is thus subject to considerable error, since this level of counting is considerably higher than that recommended for the counter. A count of 160,000 might be closer to the actual count.

Additional tests, made on these samples, showed that the loss in gamma activity was caused almost entirely by the volatilization of ruthenium.

Table X shows the relative gamma intensities from spectrometer data of cerium and ruthenium isotope tracers retained by these samples.

TABLE X

THE VARIATION IN RELATIVE GAMMA
INTENSITIES WITH TEMPERATURE IN
A CERAMIC BODY

Sample *	Temperature °C	Relative Intensity Per gm of Sample on a Room Dry Basis	
		0.14 MEV(Ce-141-144)	0.50 MEV(Ru-103)
1	Room	1.0	1.0
2	104	0.98	0.95
3	835	0.84	0.22
4	990	0.90	0.06

* Sample 1, 2, 3, and 4 contain same material fired to different temperatures.

III THE ENTRAPMENT OF RADIOACTIVE WASTE IN POROUS CERAMIC BODIES

INTRODUCTION

It was desired to determine how effectively porous ceramic bodies can tie up radioactive waste. Two procedures were utilized; one in which the porous body was used as a wick (one end kept dry) and the other in which the entire piece was immersed in the waste solution, dried and re-immersed for a total of four cycles.

METHOD OF INVESTIGATION

A porous brick was made from a mixture of 60% vermiculite, 20% kaolin and 20% pyrophyllite. The brick was fired at 1980°F and then suitable specimens were cut from the brick. The material had a bulk density of 42 lb per cubic ft and a crushing strength of 800 psi.

A wick shape specimen measuring 7/8 in x 1/2 in x 5 1/2 in. was cut from the brick. This wick was then sealed into a 100 ml. graduate with Permoplast clay. The graduate was filled to the 100 ml. mark with Hope solution prior to placement of the wick. The wick was so placed that it remained above the 100 ml. mark and it was necessary to tilt the assembly for the liquid to contact the wick. The assembly was tilted sufficiently for the liquid to contact the wick on its lower side all the way up to the place where the wick contacts the plastic clay seal. The liquid remaining after specified time intervals was determined by returning the graduated cylinder to its vertical position and recording the liquid level in the graduate.

In the initial period of the test the wick protruding from the graduate was left exposed to room temperature. An attempt was made to speed up evaporation from the exposed portion of the wick by blowing warm air from a hair dryer across it and by applying a low flame from a gas burner to it.

Small specimens measuring approximately 1 in. x 1 in. x 3/4 in. were cut from the vermiculite brick and soaked in Hope solution tagged at 79,600 counts per min per ml. After soaking, the samples were dried and then re-soaked in the liquor. This was continued to give a total of four soakings. Previous work indicated that the specimens would pick up 43% of their dry weight as added solid salts. Tests on the samples of this experiment indicated that the samples picked up 200,000 counts per gm on a room dry basis or 500,000 counts per gm on a fired basis. The activity of the Hope solution was determined on a Ceramic Laboratory counter and this counter was found to be in error. The actual count of the initial tagging solution was possibly 160,000 counts per ml.

After soaking, the samples were fired to selected temperatures and then leached by water using a ratio of 1 ml. of water to 1 gm of fired sinter. After leaching

for seven days, 1 ml. sample of the lixivium was dried on an aluminum tray and a beta count made with the Ceramic Laboratory end window G. M. counter.

RESULTS OF INVESTIGATION

1. Wick Test

The results of the wick test are shown in Table XI. It can be seen that the wick was capable of drawing the Hope solution up from its container and the wick saturated itself in 20 min. The rate of evaporation from the exposed end was undetectable at room condition. The hair dryer did not produce a measurable rate of evaporation.

The gas burner caused some evaporation and additional pickup of liquid. However, "strong" heating rates drove the liquid back into the graduate. Turning off the burner would give a net gain in the amount of liquid picked up by the wick. Full pickup could be obtained only by intermittent heating and cooling.

It was concluded that the wick system was not as good as the soaking and drying cycle system for liquids of low volatility like the Hope solution.

2. Soak and Dry Test

Previous tests indicated that repeated cycles of immersion of porous brick into Hope solution followed by drying would permit pickups of at least 3 ml. Hope solution or 0.5 gm of dry salts per 1 gm of brick. Thus, 1 cubic ft of porous brick could contain 20 lb of dry salts or 14.4 gal of waste liquor (1.91 cu. ft of waste liquor). During firing, it would be possible to flux the porous brick and shrink it to a volume of 1/2 cubic ft. Thus, on a fired basis 1 cubic ft would contain 3.8 cubic ft of waste liquor or 40 lb of dry waste salt.

Table XII shows the results of leaching tests made on the saturated and dry specimens. Firing temperatures of at least 1000°C seem to be necessary. Such temperatures reduced the lixivium count to below 400 beta counts per ml. This represents approximately a 400 to one reduction in activity from the base solution. It is believed that this figure could be improved by spraying a coating of clay or glaze on the brick prior to the final firing, since there was some tendency for the salts to concentrate on the surface of the specimens.

IV EFFECTS OF FUSED COATINGS ON RETENTION OF RADIOISOTOPES BY POROUS CERAMIC MASSES

INTRODUCTION

In the investigations on retention of radioactivity by porous bricks, it was noted that rather high leach test results were being obtained. It was further

TABLE XI

THE RATE OF SATURATION BY A CERAMIC WICK

Elapsed Time Min	Quantity of Liquid Absorbed ml	Remarks
0	---	Room air circulation
5	15	
10	18	
15	21	
20	24	Soaked to top of wick
25	24	
40	24	Hair dryer on
45	24	
55	24	
60	24	Gas burner on
75	25	
85	26	
90	28	
95	30	
115	31	

TABLE XII

THE RETENTION OF RADIOACTIVITY AGAINST
WATER LEACHING BY POROUS CERAMIC BRICK

Sample	Temperature °C	Total Beta Counts per ml/min
C-9	500	964
C-9	800	1545
C-9	1090	383
C-9	1150	258

noted that there seemed to be a concentration of dried salts at the surface of the pieces. It, therefore, seemed expedient to put some protective coating on the piece after the waste solution had been soaked up. Various materials were utilized as coatings with the best results being obtained from a lead-oxide and attapulgite glaze.

METHOD OF INVESTIGATION

The ceramic mass utilized in this investigation contained 60% vermiculite, 20% kaolin and 20% pyrophyllite. This mixture had been pre-fired to 1980°F and produced a lightweight porous brick. Small pieces were then cut from this brick and dipped in the tagged waste solution. These were dried and the procedure repeated four times. It was found after some experimentation that it was necessary to fume the waste-soaked pieces prior to coating with the glaze. The pieces were put on a wire hanger and dipped in the glaze suspension for a predetermined time and then fired. After firing, the pieces were examined for any unhealed cracks and if none were present, the piece was put in leach water. One ml. samples were taken of the leach water after one week, one month, and six months and counted with a beta counter.

RESULTS OF INVESTIGATION

Several materials were used as the glaze material; borax, lead-oxide, attapulgite, and several compositions of lead-oxide and attapulgite. The most successful composition was one consisting of 10 weight per cent of attapulgite and 90 weight per cent of lead-oxide. Enough water was added to form a suspension with low viscosity. Dipping time was approximately 3 sec, after which the piece was dried for two hour at 104°C. The piece was then transferred to a furnace pre-heated to 700°C with firing time of three to seven minutes. This glaze gave an impervious coating that had a low enough viscosity at fusion to heal most of the drying and shrinkage cracks. Many of the other glaze materials used did not have this property and as a result were not acceptable.

Results of a number of tests of a number of pieces soaked in waste solution that had been tagged with mixed fission products and glazed with various materials may be seen in Table XIII.

V SUMMARY OF WASTE DISPOSAL EXPERIMENTS MADE IN JULY AND AUGUST 1957

INTRODUCTION

A series of experiments were made to obtain information that would permit a better evaluation of the proposed systems of waste disposal. These experiments have developed two effective compositions and two methods of procedure for disposing of wastes. The experiments also produced information on the retention

TABLE XIII

EFFECT OF FUSED COATINGS ON
RETENTION IN POROUS BRICKS

Glaze Material	Beta count of leach water or lixivium		Comments
	c/m/ml 1 week	c/m/ml 1 month	
Attapulgate	17	-----)	Very difficult to apply to piece. Difficult to heal drying and shrinkage cracks.
Borax	0	-----)	
Lead-Oxide	0	-----)	
Lead-Oxide 10% attapulgate	16	17	Easily applied.
Lead-Oxide 25% attapulgate	120	120	Excess clay caused heavy shrinkage.
Standard piece No glaze	383	350	

of gamma and beta activity in ceramic mixtures when fired to various temperatures.

EFFECTIVE COMPOSITIONS

The investigations developed two compositions that appeared to be very effective in containing radioactive materials against water leaching.

The first composition was a pre-fired vermiculite-clay unit containing 60% vermiculite, 20% kaolin and 20% pyrophyllite. It is believed that this composition is not critical but that the vermiculite could vary from 20% to 100% and that the remainder of the mixture could be any clay material. This composition produced a porous, lightweight unit which was capable of picking up 3.2 ml. of Hope solution per gm of material using four soaking cycles. After saturation, the brick with Hope solution, the unit was coated with a thin suspension of lead-oxide and clay and then fired. The fired sample contained in excess of 500,000 counts per min per gm of fired weight and the lixivium from these units showed low beta counts after seven days of leaching.

The second composition was a vermiculite concrete containing 10 gm of vermiculite, 10 gm Attasorb HVM, 20 gm portland cement and 84 ml. of Hope solution. This unit when fired to 1190°C produced a lixivium with a beta count of 10 c/min/ml. after 10 days.

METHODS OF PROCEDURE

The investigations indicated the possibility of disposing of wastes in ceramic masses by two different procedures. The first procedure would involve the use of pre-formed porous ceramic slugs. These slugs would then be placed in contact with the waste liquid and allowed to soak up the liquid. After soaking, the units would be sprayed with a glaze and then allowed to heat up to a temperature no lower than 800°C.

It is suggested that the pre-formed slug would facilitate a hot cell test on this method of waste disposal. The slugs could be dipped in waste liquid and then transferred to an inexpensive kiln. They could be fired and then transferred to a leaching vessel.

The second procedure would involve the making of high-temperature concrete. The pre-mixed cement and aggregate would be fed into a ribbon type mixer along with a stream of the waste liquor and the concrete would be discharged continuously into either molds or prepared pits. The concrete should be allowed to heat up to 1200°C and if furnacing is required, the discharge from the mixer could be fed through a moving belt kiln or a rotary kiln.

It is suggested that the second procedure would facilitate shipment of waste or disposing of liquid waste in laboratories. Converting liquid waste into concrete should reduce the danger of spillage during shipment. Also, it might be more convenient in laboratories to dump waste material into containers containing vermiculite and concrete. This would reduce the danger of spilling during removal operations.

VI RETENTION OF ACTIVITY IN CERAMIC SUBSTANCES AT INCREASING TEMPERATURES

Experiments were made to determine if loss in activity occurs during firing as a result of volatilization of radioactive constituents. It was found that there was no loss in beta activity up through a firing temperature of 1000°C. Furthermore, soaking at 1000°C for 24 hr did not cause a significant loss in beta activity.

It was found that there was a pronounced loss in gamma activity between 104°C and 835°C. It was determined that this loss was the result of volatilization of ruthenium. There did not appear to be a significant loss in cerium.

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