

Studies on the Bituminization Process of Radioactive Liquid Waste(I)

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Abstract

Immobilization of the second-cycle radioactive liquid wastes from a Purex process was developed with the blown asphalt(manufactured by Kukdong Shell Oil Company Ltd) to eliminate the possibility that the radioactive materials will be redispersed into the environment.

Attempts to incorporate these wastes directly into the asphalt matrices without any pretreatment were not successful, as it was observed that the sulphuric acid in the waste oxidised the asphalt. Hence, the waste was treated with caustic soda and made alkaline prior to bituminization, so that it was found that this pretreatment made the waste compatible to the asphalt matrices.

The pure blown asphalt samples irradiated with doses of 4.0×10^7 rad showed no evidence of volume increase.

The suitable temperature for incorporation of the alkaline wastes into blown asphalt was 180-200°C. The products containing 50 wt% salts represented the following good properties viz., volume reduction (about 1.4), homogeneity, leachability etc.

During the period of 131 days ^{137}Cs from products containing 40wt% salts was leached at rates ranging from 2.70×10^{-4} to $8.27 \times 10^{-4} \text{g/cm}^2\text{-day}$ but the rate for ^{90}Sr was lower by one to two orders of magnitude by distilled water. The leaching rates for ^{137}Cs and ^{90}Sr by sea water were slightly lower than by distilled water. Both of the leaching rates decreased with increasing pH.

요 약

알카리로 처리한 국산 blown asphalt 를 사용해서 방사성 폐액을 180-200°C 범위 내에서 고화처리한 것이 산처리 한것보다 좋은 결과를 얻었으며, 방사선 조사선량이 $4.0 \times 10^7 \text{rad}$ 까지도 안정된 고화체로 존재하고 있다. 한편 40 wt%의 고형분이 함유되어 있는 ^{137}Cs -asphalt 고화체의 증류수에 의한 ^{137}Cs 의 용출율이 $8.27 \times 10^{-4} \text{g/cm}^2\text{-day}$ 인데 반하여 ^{90}Sr 은 낮았으며, 일반적으로 증류수보다 해수때가 또한 pH가 증가함에 따라 용출율은 낮아진다.

I. Introduction

The radioactive waste increases as the nuclear industry grows apace. Large scale experiments have actively been conducted on the economical treatment of the waste for permanent storage in such a manner that the environment should not be contaminated by the fission products.

It is well known that the cementation process is the simplest and most commonly used method of solidifying radioactive wastes. But, compared with the bituminization process and the vitrification process, the availability of that process is only limited to the disposal of comparatively low-level wastes, and the rate of volume reduction of cemented wastes is low, representing only 0.6. Vitreous materials produced through the solidification of wastes are the most resistant to leaching of the activity by water, thus making it possible to incorporate the high-level radioactive waste into them. But the vitrification process needs the high temperature more than 1000°C and costs greatly.

The use of asphalt has been recently developed as a most promising method for solidifying and insolubilizing the intermediate-level waste generated by nuclear installations. Initial work on the development of bitumen-waste incorporation that has been carried out in various countries results in three different methods: 1) a fixing method for the non-emulsified asphalt-waste that has been developed by Eurochemie, Mol, Belgium,^{1, 2)} 2) a method for temporary emulsion bituminization of radioactive sludges by the Marcoule Nuclear Research Center, France,³⁻⁵⁾ and 3) a method for the emulsified bitumen-waste incorporation by ORNL, USA.⁶⁻⁸⁾ Asphalts

into which the most part of wastes are incorporated are the two types of straight-run distilled asphalt (straight asphalt) and emulsified asphalt. But the first laboratory studies by KAERI mainly used the blown asphalts whose softening point is higher than that of the straight asphalt.

The laboratory studies were concerned the determination of process stoichiometry and process parameters such as operating temperature and stirring rates. The rates were subsequently ascertained at which ⁹⁰Sr and ¹³⁷Cs were leached from the products, and the effects of ⁶⁰Co irradiation on the pure asphalts were observed.

II. Experimental

1. Apparatus

Primarily, the asphalt fixation apparatus (Figs. 1 a and 1 b) consists of an electrically heated, temperature-controlled stainless steel vessel containing a paddle-type stirrer with four blades, a gate drain valve, and the connections for the introduction of asphalt and waste feed solution and for the removal of condensate.

The stirrer was changed into a close fitting paddle-type stirrer with Teflon wipers (Fig. 2) to scrap the heated wall.

2. Waste

A simulated waste prepared as a basis for the aqueous raffinate from the second solvent extraction cycle of fuel reprocessing. The waste is composed of the following:

HNO ₃	3.42 M
H ₂ SO ₄	0.265 M
Fe ₂ (SO ₄) ₃	0.315 M
NaNO ₃	1.52 M
Density	1.32 g/cm ³
Specific activity	0.2 mci/ml

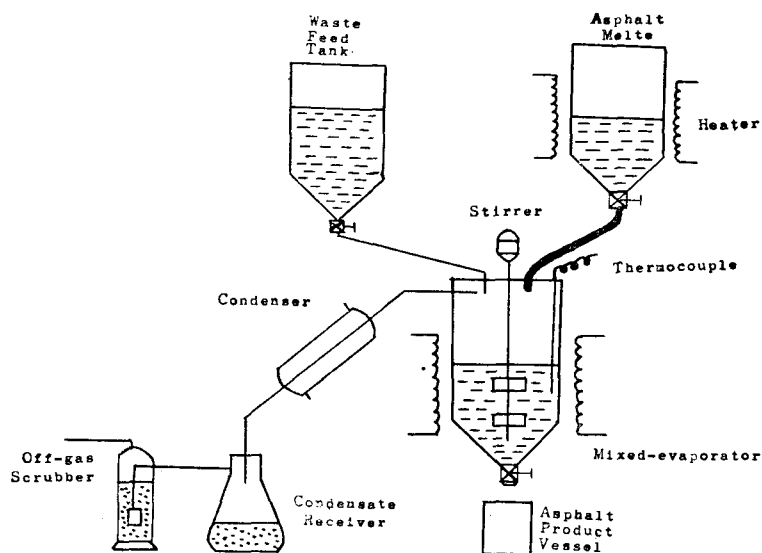


Fig. 1. (a) Flowsheet of the Bituminization Apparatus

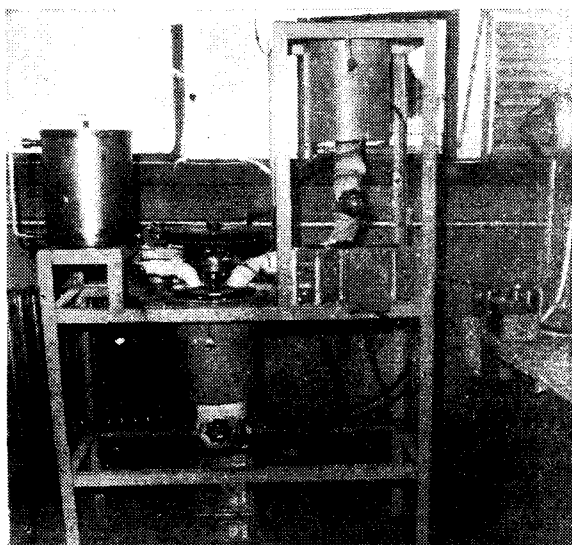


Fig. 1. (b)

Since acids are not compatible with asphalt, this waste was made basic with 50 wt % NaOH solution before their incorporation into asphalt.

3. Procedure

100 g of molten asphalt was poured into

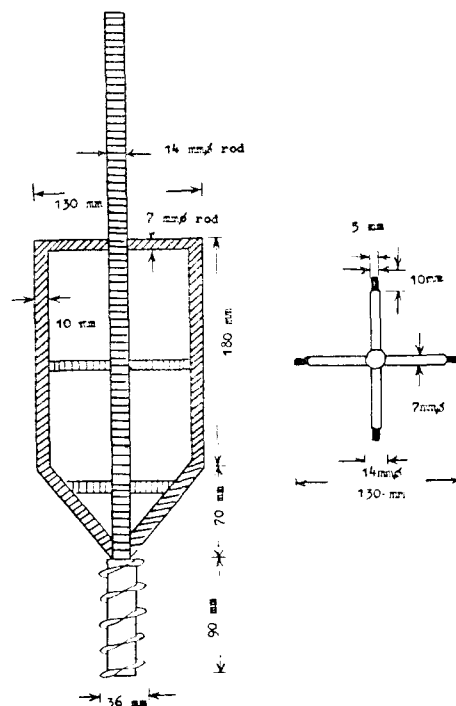


Fig. 2. Paddle-type stirrer close-fitting

the mixer and heated at each of the three different temperatures (160°C, 180°C & 200°C). Then the waste was added into the

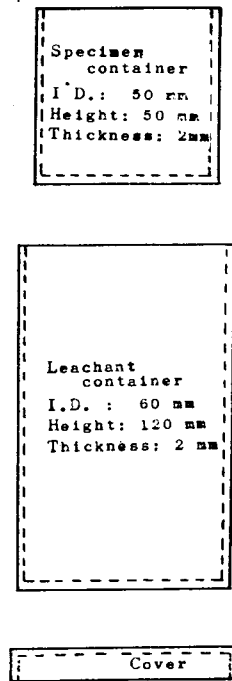


Fig. 3. Cylindrical Containers for Leaching Test

asphalt. The mixture was continuously stirred over a two-hour period whereby the evaporation of water constituents took place. Portions of the asphalt products were finally drained into specimen containers (made of polypropylene, Fig. 3) for leaching tests and into a mould of 60mm ϕ ×15mm for the evaluation of radiation effects.

4. Leaching Test

Portion of the samples was put into each leachant container (made of polyethylene, Fig. 3) and then leachant (distilled water, acid or alkaline water, sea water or rain water) was poured into this container. Each solution was analyzed in respect of fission products (^{90}Sr or ^{137}Cs) with following frequencies and was replaced with fresh leachant.

- i) Daily during the first week
- ii) Once a week for the following five weeks, and
- iii) One a month from the following month

The leaching rate for the fission products was calculated by the following formula¹¹⁾;

$$R_n = \frac{Cn/Co}{(S/G)t_n}$$

where R_n : leaching rate(g/cm²/day)

Cn : concentration in leachant (cpm)

Co : initial concentration in feed waste (cpm)

S : surface area that is exposed to leachants

G : weight of asphalt(g)

t_n : leaching time(days)

III. Results and Discussion

Detailed properties of some bitumens used

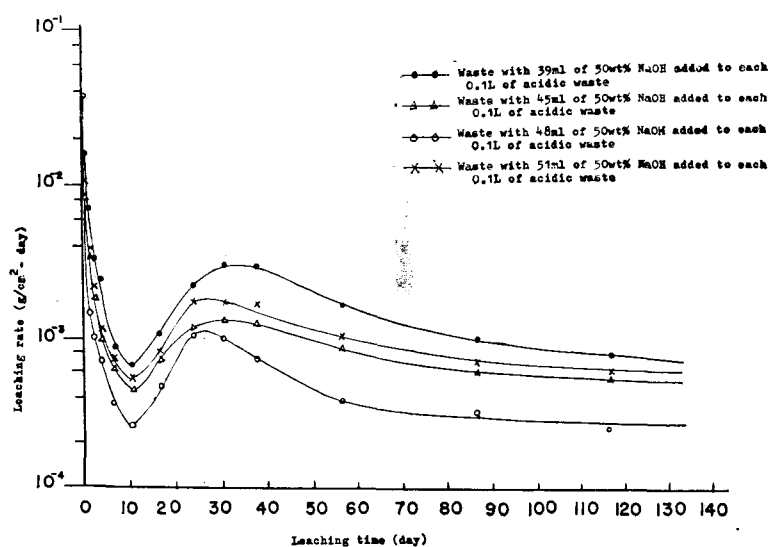
Table 1. Properties of Various Asphalts

	Straight Asphalt				Blown Asphalt	
	M10/20	M20/30	M80/100	SA*	R85/25	BA*
Penetration 25°C	10—25	20—30	80—100	91	20—30	25
Softening Point(°C)	65—75	59—69	46—51	48	80—90	86
Flash Point(°C)	250	250	240	290	240	203
Ductility(cm) 25°C	—	—	100	150	3	3
Solubility in CCl ₄ (wt%)	99	99	99.5	99.9	99	99.1
Density(g/cm ³) 25°C	1.02—1.07	1.02—1.07	1.00—1.05	1.02	1.02—1.05	1.04

*:Produced by KUKDONG SHELL Co., Ltd.

Table 2. Comparison of Specific Activities in the Feed and in the Condensate from Asphalt Products

Product (Waste/Asphalt)	Waste (mci/L)		Condensate(mci/L)		Decontamination Factor	
	^{90}Sr — ^{90}Y	^{137}Cs — ^{137}Ba	^{90}Sr — ^{90}Y	^{137}Cs — ^{137}Ba	^{90}Sr — ^{90}Y	^{137}Cs — ^{137}Ba
20/80—1	79	81	1.07×10^{-4}	1.94×10^{-4}	7.36×10^5	4.17×10^5
20/80—2	198	203	3.26×10^{-4}	7.63×10^{-4}	6.08×10^5	2.66×10^5
20/80—3	315	321	7.54×10^{-4}	1.32×10^{-3}	4.18×10^5	2.43×10^5
20/80—4	1386	1374	3.34×10^{-3}	3.35×10^{-3}	4.15×10^5	4.10×10^5
40/60—1	79	81	3.82×10^{-4}	4.70×10^{-4}	2.07×10^5	1.72×10^5
40/60—2	198	203	5.62×10^{-4}	1.29×10^{-3}	3.52×10^5	2.49×10^5
40/60—3	315	321	6.76×10^{-4}	2.97×10^{-3}	4.81×10^5	1.08×10^5
40/60—4	1386	1374	8.58×10^{-4}	5.44×10^{-3}	1.62×10^5	2.53×10^5
60/40—1	79	81	1.10×10^{-3}	3.66×10^{-3}	7.18×10^4	2.21×10^4
60/40—2	198	203	1.15×10^{-3}	5.94×10^{-3}	1.72×10^5	3.42×10^4
60/40—3	315	321	2.57×10^{-3}	2.02×10^{-3}	1.23×10^5	1.59×10^5
60/40—4	1386	1374	5.23×10^{-3}	9.26×10^{-2}	2.65×10^5	1.48×10^4

Fig. 4. Leaching Rates of ^{137}Cs from Asphalt Waste Products with Distilled Water.

for the waste incorporation process are shown in Table 1 to compare with the asphalt products supplied by Kukdong Shell Co., Ltd. The blown asphalt(BA) has the same characteristics as 85/25, except the flash point, and the straight asphalt(SA) is similar to M80/100. But flash point of BA is higher than that of SA and ductility of BA larger than that of SA. Generally, the specific activity of radionuclides contained in bitum-

en-waste products reveals the limit below 1 Ci/L, because of the decomposition of the bitumen.¹²⁻¹⁴⁾

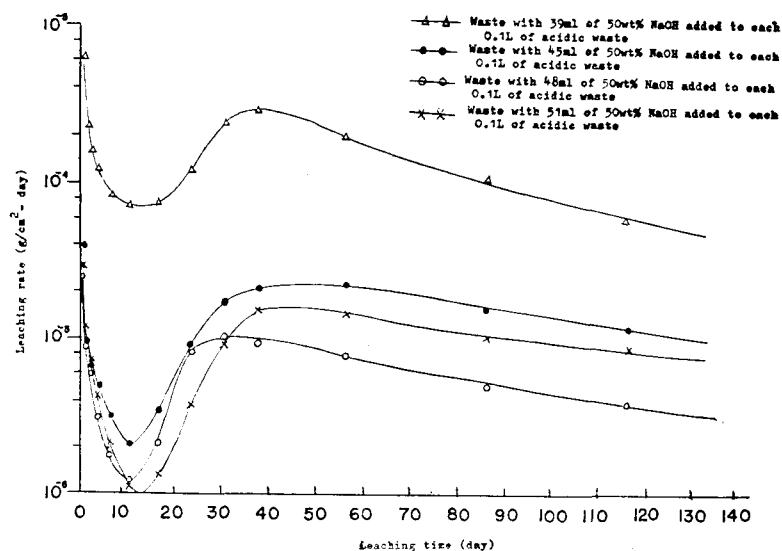
Compared with SA, the softening point of BA is higher than 40°C. The effect of irradiated doses of 4.0×10^7 rad on pure asphalt (BA) that has been recorded until now is negligible, but by Voorde,⁵⁾ irradiation samples of Mexphalt 80/100 with doses not exceeding 10^7 rad resulted in only minor

Table 3. Comparison of the Constituents for Incorporation of the Waste into Blown Asphalt

	Density (g/cm ³)	Constituent (wts%)			Weight Ratio				Volume Ratio			
		Salt	Water	Asphalt	Waste	Asphalt	Conden- sate	Product	Waste	Asphalt	Conden- sate	Product
Waste	1.34	37.1	62.9	0								
Conden- sate	1.00	0	100	0								
Product												
20/80	1.12	20	0	80	0.539	0.8	0.339	1	0.451	0.862	0.380	1
40/60	1.27	40	0	60	1.078	0.6	0.678	1	1.022	0.733	0.861	1
60/40	1.48	60	0	40	1.617	0.4	1.017	1	1.788	0.569	1.508	1
80/20	1.67	80	0	20	2.156	0.2	1.356	1	2.697	0.321	2.265	1

Waste; Acid Waste (100ml) + 50% NaOH (48ml)

*: Constituent Ratio to (Asphalt-Waste) Product

Fig. 5. Leaching Rates of ⁹⁰Sr from Asphalt Waste Products with Distilled Water.

alteration of its properties. There is a possibility, however, that the specific activity of more than 1Ci/L is retained in the asphalt product (BA). A Study on the radiation stability is now being carried out in detail.

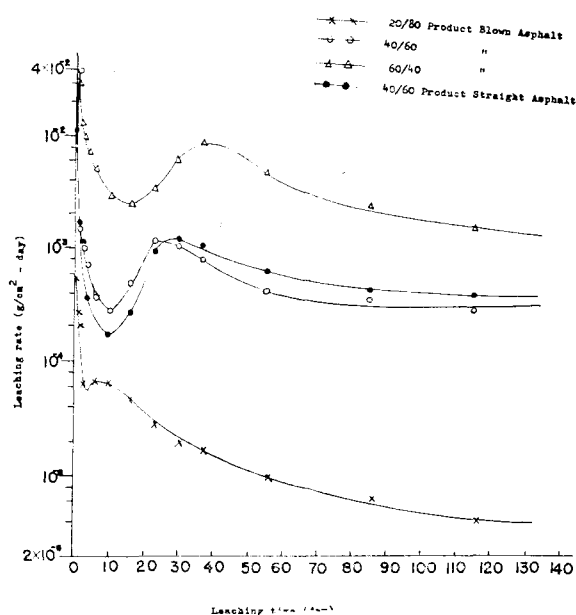
As the direct incorporation of acidic waste into the melting asphalt hardened the asphalt, it was difficult to mix the waste with the asphalt because of its oxidation by the sulphuric acid in the waste. On the other hand, when the waste was treated with 50% solution of sodium hydroxide and became

alkaline prior to bituminization, it was easy to incorporate the waste into the asphalt. Hence, it was found that this pretreatment made the waste compatible to the asphalt matrices.

As shown in Table 2, the condensated from asphalt products during water evaporating the solution was ranged from 10⁻⁴ to 10⁻³ mCi/L, and the activities of the condensate were increased as, because of entrained ⁹⁰Sr or ¹³⁷Cs, those in the feed increased. The decontamination factors are presented

Table 4. Leaching of ^{137}Cs as a Function of pH and with Sea-water

Leachant Solution	Leach Rate ($\text{g}/\text{cm}^2\cdot\text{day}$)			
	1 d	20 d	71 d	101 d
pH 1.2	2.57×10^{-1}	2.82×10^{-2}	1.87×10^{-2}	1.63×10^{-2}
pH 4.7	8.95×10^{-2}	3.13×10^{-2}	9.05×10^{-3}	7.44×10^{-3}
pH 8.4	3.16×10^{-3}	4.76×10^{-4}	3.01×10^{-4}	3.46×10^{-4}
pH 12.1	2.87×10^{-3}	3.13×10^{-4}	2.12×10^{-4}	2.09×10^{-4}
Sea-water	6.45×10^{-3}	4.68×10^{-4}	2.82×10^{-4}	2.21×10^{-4}

Fig. 6. Leaching Rates of ^{137}Cs from Asphalt Waste Products With Distilled Water.

in Table 2 (which are obtained from 1.5×10^4 to 7.4×10^5). The factors of ^{90}Sr were slightly higher than those of ^{137}Cs , and then all these factors show some dependence on the fission product contents of the waste.

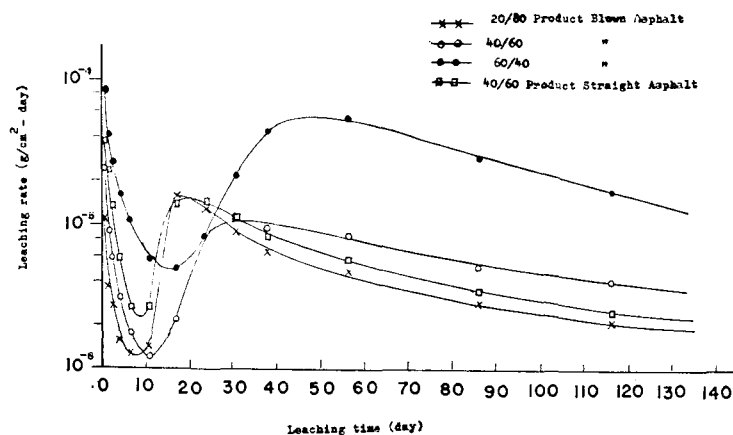
Table 3 shows the weight and volume relationships obtained between waste, blown asphalt, condensate, and asphalt product for the waste with added caustic soda. The amount of salt from the waste contained in the asphalt products ranges from 20 to 80 wt% with an increase of 20wt% in each step. The weight or volume of each constituent was normalized to represent a unit

weight or volume to be used in making a unit asphalt product. The densities of various products are also included in this normalization. The products which contain 40 wt% of salt are greater than the unit of column 5 under the volume ratio of this Table, and these products represent the reduction of waste volume to be stored.

The products that contained 20 wt% salt from the waste were homogeneous and had a free flow movement of flow at 200°C . The mixture that contained 80wt% salt showed neither a complete homogeneity nor a free movement of flow, but there was no

Table 5. Leaching of ^{90}Sr as a Function of pH and with Sea-water

Leachant Solution	Leach Rate ($\text{g}/\text{cm}^2 \cdot \text{day}$)			
	1 d	20 d	71 d	101 d
pH 1.2	1.54×10^{-3}	2.21×10^{-4}	1.21×10^{-4}	1.08×10^{-4}
pH 4.7	7.05×10^{-4}	6.35×10^{-5}	3.10×10^{-5}	2.55×10^{-5}
pH 8.4	2.04×10^{-5}	4.41×10^{-6}	6.27×10^{-7}	4.66×10^{-7}
pH 12.1	1.83×10^{-5}	2.28×10^{-6}	4.21×10^{-7}	3.79×10^{-7}
Sea-water	3.79×10^{-5}	2.50×10^{-6}	3.38×10^{-6}	9.67×10^{-7}

Fig. 7. Leaching Rates of ^{90}Sr from Asphalt Waste Products with Distilled Water.

such phenomena in case of the mixtures, though homogeneous, that contained 40 and 60wt% of salt. The incorporation of the waste into the asphalt in order to produce the mixtures that contain 60 and 80 wt% salt was very difficult and this was because of the increasing of the softening point and the viscosity of the asphalt that was attributable to the increasing of salt.

To evaluate the safety required for permanent disposal, the leaching rates of ^{137}Cs or ^{90}Sr that were obtained with leachant solutions are represented in Figs. 4, 5, 6 and 7, and Tables 4 and 5. These figures and tables show that much quantities of radionuclides

were initially leached and, after 30 or 40 days, the leaching rates were comparatively steady. And each curve in these figures has one trough. It is considered that, as soon as the leachant has penetrated to the surface of salts, the salts are dissolve and, under the resulting osmotic pressure, are drawn in more leachant which displace the asphalt. The more the amount of salt in the products is, the higher the leaching rate of ^{137}Cs or ^{90}Sr . The fraction of ^{137}Cs or ^{90}Sr leached from the product incorporated with the waste which 48ml of 50 wt% NaOH solution was added to each 0.1 liter of the acidic waste was lower than those obtained from

products with other wastes (Fig. 4 and 5). And as shown in Table 4 and 5, the leaching rates are decreased against the increasing of pH of leachant solution. These phenomena may be due to the effect of adhesion energy of asphalt by leachant solution.

As illustrated in Fig. 6, the leaching rates of ^{137}Cs from each product (20/80, 40/60, 60/40) that had been measured during four months were 3.89×10^{-6} , 2.70×10^{-4} and 1.36×10^{-3} g/cm²-day, respectively.

The leaching rate of ^{137}Cs from the product 40/60 made of the straight asphalt was 3.62×10^{-4} g/cm²-day (Fig. 4), and this value is similar to the leaching rate of ^{137}Cs from the product 40/60 made of the blown asphalt.

Fig. 7 shows the leaching rate of ^{90}Sr from each product with the leaching time. The leaching rates of ^{90}Sr were very lower than those of ^{137}Cs . Compared with the leaching rate of ^{137}Cs from the product 40/60, that of ^{90}Sr from the product was lower by 66 times than ^{137}Cs . The effect of leaching rates of ^{90}Sr with an increase of salt contained in the product has a same tendency as that of ^{137}Cs . The rates of ^{90}Sr from each product that had been measured during four months were 2.14×10^{-6} , 4.06×10^{-6} and 1.66×10^{-5} g/cm²-day, respectively. The leaching rate of ^{90}Sr from the product made of the blown asphalt was higher by about the two times than that made of the straight asphalt.

IV. Conclusion

The tests of asphalt-waste products with fission product have shown that the waste can be satisfactorily incorporated into asphalt to yield a product containing 50 wt% solids. The condensates obtained from the waste during fixation were decontaminated from beta and/or gamma emitters. Essentially

the radioactivity in the condensates was the result of entrainment.

No evidence of volume increase was shown in pure blown asphalt by an exposure of 4.0×10^7 rads. At present, a study on the radiation stability of asphalt-waste products is being demonstrated in detail.

The leaching rate of ^{90}Sr from the product 40/60 was less than 10^{-5} g/cm²-day. The leaching rate for ^{137}Cs , about 10^{-4} g/cm²-day, was sufficiently low that long-term storage of asphalt-waste product in drums is expected to be satisfactory.

Further studies should be needed to demonstrate reduction of the leaching rate of ^{137}Cs by means of mineral additives to sorb cesium and then they will improve cesium retention since cesium is the principal soluble fission product.

Acknowledgement

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