BITUMINIZATION OF SIMULATED WASTE - SPENT RESINS, EVAPORATOR CONCENTRATES AND ANIMAL ASHES BY EXTRUSION PROCESS

C. E. Grosche Filho, U. Chandra

ABSTRACT

The results of the study of bituminization of simulated radwaste - spent ion-exchange resins, borate - evaporator - concentrates and animal ashes, are presented and discussed.

Distilled and oxidized bitumen were used. Characterization of the crude material and simulated wastes-bitumen mixtures of varying weight composition (30, 40, 50, 60% by weight of dry waste material) was carried out. The asphaltene and parafin contents in the bitumens were also determined.

Some additives and clays were used with an aim to improve the characteristics of solidified wastes.

For leaching studies, granular ion-exchange resins were loaded with Cs - 134 and mixtures of resin-bitumen were prepared. The leaching studies were executed using the IAEA recommendation and the ISO method.

A conventional screw-extrucur, common in plastic industry, was used to determine operational parameters and process difficulties. Mixtures of resin-bitumen and evaporator concentrate-bitumen obtained from differents operational conditions were characterized.

INTRODUCTION

Two distilled bitumens and three oxidized bitumens samples were selected to characterize the locally available commercial bitumens. This choice was made by comparing them with the international bitumens, using the physical properties as selection parameter.

Analysis of the asphaltenes and parafins was carried out for better characterization and interpretation of wastes-bitumen behaviour.

Simulated PWR wastes - spent granular ion-exchange resins, borate-evaporator-concentrates and animal ashes were utilized for the bituminization studies. According to IAEA classification these wastes belong to the category of low-and intermediate-level radioactive wastes ($A \leq 3{,}7 \times 10^{13}$ Bq/m^3).

CHARACTERISTICS OF THE BITUMENS

The characteristics of the distilled and oxidized bitumens selected for the bituminization process are indicated in the table I and II[3].

The physical properties were determined using the standard ASTM tests.

The asphaltene and parafin contents were determined using the method of "Rostler-Sterberg".

Table I

General bitumen properties (average values)

Properties	Bitumen				
	Oxidized			Distilled	
	T 75/25	TB 90	VB 65	T 50/60	V 85/100
Penetration (0.1mm)	25	10	25	54	86
Softening point (°C)	82	84	72	52	46
Flash point (°C)	254	286	234	288	250
Specific density at 25°C (g/cm^3)	1.02	1.02	1.08	1.02	1.04
Burning point (°C)	340	–	–	360	–

Table II

Asphaltene and parafin contents of the bitumen samples

Biturnen	Fractions %	
	Asphaltenes	Parafins
T 50/60	34.3	10.9
T 75/25	31.0	20.1
TB 90	33.3	8.0
V 85/100	37.8	13.1
VB 65	23.2	7.2

Physical properties of the some bitumens utilized in various countries are given in table III[1].

RADWASTES UTILIZED

The simulated wastes considered were:

- Nuclear grade IRN-150 (H^+, OH^-) ion-exchange resins, granular type.
- Evaporador borate-concentrates of the following weight composition:

H_3BO_3	70%
NaOH	12%
Na_2SO_4	12%
Na_2PO_4	2%
NaCl	2%
$Fe_2(SO_4)_3$	2%

- Animal ashes

Table III

Properties of various bitumens

	Distilles			Oxidized	
	Mexphalt 10/20	Mexphalt 40/50	Mexphalt 50/60	R 90/40	R 85/40
Softening point (°C)	65 - 75	59 - 69	50 - 58	85 - 90	80 - 90
Penetration at 25°C (0.1 mm)	10 - 25	20 - 30	50 - 60	35 - 40	35 - 45
Flash point (1°C)	> 250	> 250	> 250	250	240
Density at 25°C (g/cm³)	1.02 - 1.07	1.01 - 1.06	1.01 - 1.05	1.01 - 1.05	1.01 - 1.05

SIMULATED RADWASTE-BITUMEN MIXTURES

The mixtures prepared in the laboratory scale consisted of:

- Resin/bitumen with 30, 40, 50, 60 wt% of the dry waste material;
- Resin/bitumen/additive, with 50 wt% of the dry resin and 2 wt% of the additive by bitumen weight;
- Evaporator borate-concentrates/bitumens with 30, 40, 50, 60 wt% of the dry waste material;

- Evaporator borate-concentrates/bitumens/additive with 40 wt% of the dry concentrate and 2 wt% of the additive by bitumen weight;

- Animal ashes/bitumen with 40, 50, 60, wt% of the ashes in the dry material.

The evaluation of the twin screw extrusion process, was made while using the 40 and 50% by weight mixtures and different operating parameters of the extruder.

The characteristics of the extruder were as following:

- screw (twin, coupled, with no auto-cleaning and without extra gas/vapor outlets).

diameter	·	50 mm
length	·	1000 mm
pitch	·	12 → 8 mm (variable)
depth	·	10 → 2 mm (variable)
rpm	·	0 ~ 60

- Heating,
  three heating zones with temperature range between 0°C - 230°C

- Motor,
  7,5 HP/1750 rpm.

LEACH TESTS

For leaching studies resin -bitumen specimens were prepared. Cesium-134 was used for labelling the resin.

The dimensions of the cylindrical specimens were: diameter 5 cm, height 10 cm - with volume/surface ratio $\simeq$ 1. The resin-bitumen mixtures studied contained 30, 40, 50 and 60 wt% of the dry material. 1.6 ℓ of distilled water was used as leachant.

RESULTS

The laboratory scale results of the resins, evaporator-concentrates and animal ashes are shown in tables IV, V and VI.

The operational conditions of the extruder tests are indicated in table VII and some characteristics of the bituminized products are shown in table VIII. The results of the leaching studies are shown in table IX.

DISCUSSION

The data in the tables I to IX demonstrate the compatibility of the bitumens used by us in comparison to the bitumens used in other countries. The characteristics of the bitumen, however, depend on the origin of the petroleum and processing in the refineries.

The bitumens studied showed easy workability in the temperature range between 150°C and 180°C. In this aspect distilled bitumen demonstrated better workability as compared to the oxidized bitumen.

Table IV

Physical properties of resin/bitumen mixtures in laboratory specimens

Granular resin (%)	Flash point (°C)	Softening point (°C)	Penetration at 25°C (0.1mm)	Bitumen
30	228	88	13	
40	228	88	12	
50	220	93	11	T 75/25
60	197	108	9	
70	120	113/119	(*)	
30	234	61	32	
40	234	66	29	
50	222	67	20	T 50/60
60	208	85	7	
70	116	90/117	(*)	
30	238	52	53	
40	232	54	43	
50	230	59	29	V 85/100
60	230	69	17	
70	136	115/130	(*)	
30	232	76	17	
40	232	79	12	
50	216	89	10	VB 65
60	182	126	5	
70	136	128/131	(*)	

(*) Values not determined

Table V

Physical properties of borate – concentrates/bitumen mixtures in laboratory specimens.

Borates concentrates (*)	Flash point (°C)	Saftening point (°C)	Penetration at 25°C (0.1 mm)	Bitumen
30	238	91	(*)	
40	258	88	(*)	T 50/60
50	210	105	13	
60	273	90	(*)	
30	202	95	20	
40	174	102	(*)	T 75/25
50	288	102	(*)	
30	218	122	(*)	
40	208	116	(*)	T 90
50	218	107	(*)	
30	215	56	44	
40	215	77	(*)	V 85/100
50	227	91	(*)	
30	178	80	21	
40	200	84	12	VB 65
50	186	86	(*)	

(*) Values not determined

Table VI

Physical properties of ashes/bitumen mixtures in laboratory specimens

Ashes (%)	Flash point (°C)	Softening point (°C)	Penetration at 25°C (0.1 mm)	Bitumen
40	263	95	15	
50	287	105	8	T 50/60
60	211	129	7	
40	218	97	17	
50	230	115	14	T 75/25
60	225	142	10	
50	264	116	6	TB 90
60	252	137	6	

Table VII

Operational conditions in the extruder for bituminization

Waste	Sample test (n°)	Water content (wt%)		Speed (rpm)	Temperature (°C)			
					Heating zone			Product
		Waste	Product		1	2	3	
Resin	1	40	–	–	–	–	–	–
	2	70	25	20	150	150	190	110
	3	0	0	20	150	150	180	160
	4	78	22	30	250	150	150	140
	5	80	1.7	48	200	200	150	125
	6	78	2.6	54	180	180	180	125
	7	78	3	54	180	180	180	115
Borate - concentrates	1	17	–	–	–	–	–	–
	2	0	0	20	150	150	190	165
	3	0	0	60	170	170	230	195
	4	64	7	60	170	170	230	–
	5	69	1.4	20	150	200	200	125
	6	75	2.2	48	200	200	180	120
	7	63	0	54	180	200	200	125
	8	70	5	54	180	180	180	110
	9	61	8	54	180	180	180	120
	10	60	4	54	180	180	180	110

Table VIII

Physical characteristics of some resin and borate concentrates bituminized by extruder process

Waste	Sample test (nº)	Physical characteristic		
		Flash point (°C)	Softening point (°C)	Penetration at 25°C (0.1 mm)
Resin	2	302	72	16
	3	302	77	46
	4	286	64	30
	6	300	62	48
Borate Concentrates	3	285	70	57
	6	280	60	33

Table IX

Results of leach test (250 days)

Bitumen type		(Cumulative fraction leached). (volume/surface) (cm) . 10 ⁻¹
Distilled	T 50/60	1.5 – 5.5
	V 85/100	2.2 – 6.0
Oxidized	T 75/25	1.2 – 6
	VB 65	1.5 – 5.5

Characterization of the bitumen waste mixture by penetration test is not an adequate procedure. More than 50% by weight resin-bitumen mixture demonstrate an uneven surface thus invalidating the penetration test.

Due to the anionic resin (amine) content in the resin-bitumen products the flash point decreased with the increase of the resin quantities. The borate-concentrate bituminized products, however did not show any such behaviour of the flash point.

The results of the 250 days leaching tests performed in distilled water, showed no significant difference among the various bitumen types. The range of the diffusion coefficients are between $10^{-14} \cdot 10^{-12}$ cm^2/sec. The long-term studies are necessary for understanding the leaching behaviour of the bituminized resin.

The extruder showed better product performance in the temperature range between 150-180°C and 50-60 rpm range. Plugging in the extruder was observed with the evaporator-concentrates because of the geometrical characteristics of the screw and limit of the maximum attainable rpm. In the extrusion of resin-bitumen no such difficulty was observed. It was possible to obtain homogeneous products with small residual water contents. With extra gas/vapor outlets, the final products could be obtained without trapped moisture.

CONCLUSION

The preliminary experiments executed in the laboratory and with a conventional industrial extruder demonstrate that bituminization by extrusion is a satisfactory process for immobilization of granular ion-exchange resins, evaporator borate-concentrates and animal ashes. The process results in waste forms with good characteristics.

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