COMALCO RESEARCH CENTRE

TECHNICAL MEMORANDUM

CRC/TM/16/83

EVALUATION OF TASMANITE OIL SHALE

To: J.C. Nixon
95 Collins St.

From: C.G. Goodes,
B.A. Sadler,
C.R.C., Thomastown

29/3/83

Group Leader Responsible for the Work:

D.J. Milne - Chief Scientist
Extractive Metallurgy

Issue Approved by:

J.A. Eady
Manager
Comalco Research Centre

025:G/TK

EVALUATION OF TASMANITE OIL SHALE

1. OBJECTIVES

To assess the potential of oil shale, and in particular Tasmanite oil shale concentrate as an anode carbon source.

2. INTRODUCTION

Oil shale reserves in Australia are very significant and could be considered as a potential source of anode carbon. It is conceivable that technology similar to that currently being evaluated at C.R.C. could be employed, viz: flash pyrolysis followed by delayed coking of the volatile component. It is necessary, however, to carry out an extensive experimental programme to examine this possibility because there are significant differences in the physical and chemical characteristics of oil shale and coal. Thus coke yields and quality will vary from current experience with coal and are also likely to be quite variable between different oil shales.

This report serves as a preliminary review prior to a larger survey of oil shales as part of the Anode Carbon project. The relevant technology for oil shale processing is briefly reviewed and, as a first stage, some laboratory results for the flash pyrolysis of Tasmanite concentrate are reported. The latter is a low ash oil shale concentrate produced by flotation and originates from Endeavour Resources Limited. In addition to obtaining some specific results for the Tasmanite material, an objective was to obtain some initial assessment of the quality of tar produced from an oil shale and some basic operating parameters for this type of material.

3. TECHNOLOGY OF OIL SHALES

3.1 General

Oil shales contain an organic material known as kerogen which, unlike coal, is insoluble in organic solvents. Kerogen can be released from the shale matrix by pyrolysis; the kerogen degrades to oil and light hydrocarbon gases. Shale oil, with some upgrading, can be used as a crude oil substitute. It may also be suitable as a delayed coker feedstock to produce anode carbon.

3.2 Pyrolysis Technology

Four major above-ground retorting (pyrolysis) technologies have been developed*. These may be categorized according to the mode of heat generation and transfer.

TYPE 1 - Direct heating through retort walls. Heating rates are usually quite slow and the process amounts to a destructive distillation.

TYPE 2 - Direct heating by a flow of gases through the retort; these gases are produced by combustion of residual carbon remaining in the shale after pyrolysis.

TYPE 3 - Heating by gases produced externally to the retort.

TYPE 4 - Contact of hot heat carriers (e.g. sand) with raw shale (these processes involve rapid heating e.g., flash pyrolysis). Examples include the Lurgi-Ruhrgas (L.R.) and Toscoal processes.

Of these four processes Type 4 offers marginally higher tar yields (Table 1) and this technology has been favoured in recent oil shale projects. The CSIRO flash pyrolysis technology currently used for processing coals in the Anode Carbon project falls into the Type 4 category. For the initial investigation of the Tasmanite concentrate the C.R.C. 10gm/hour flash pyrolysis rig was utilized to provide an assessment of tar quality and operating parameters required. In practice, the retort used should reflect a compromise between oil yield and quality, gas quality and preparation costs.

3.3 Retort By-Products

In addition to oil, other products of pyrolysis include gas and spent shale. Gas composition depends to a large extent on processing conditions as well as the nature of the parent shale. Under certain conditions this can be of high fuel value and suitable for combustion.

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* In addition to the four above ground techniques, "in situ retorting" is also being investigated. While this may offer advantages in minimizing waste disposal some major technological barriers still exist.

TABLE 1: COMPARISON OF OIL YIELDS FROM RETORTING

Retorting Class	Oil Yield as % Fischer Assay
Type 1	100%
Type 2	85%
Type 3	100%
Type 4	110%

Spent shale is essentially inorganic material and generally has insufficient carbon to support further separate combustion. The residual carbon remaining in the shale pore structure can, however, be burnt in the retort itself during pyrolysis. This leads to higher overall thermal efficiencies. The problem of spent shale disposal is severe. During pyrolysis the shale matrix expands up to 1.5 times its original volume. After mine-site filling, some spent shale therefore remains and extensive land contouring is frequently necessary. Heavy metal leaching has also been identified as a problem in spent shale disposal.

3.4 Product Yields

Unlike coal, almost all the carbonaceous material present in oil shale can be released during pyrolysis as a volatile portion. This leads to high oil yields on a dry, ash free basis (DAF) although actual yields are low because of the high ash content of the shale. The kerogen is particularly volatile because of its high H/C ratio (1.2-1.6) when compared with coal (0.8-1.0).

Analyses of selected Australian oil shales are shown in Table 2. Commercial yields will depend both on the nature of shale and, as outlined in Table 1, the retorting process selected.

3.5 Oil Composition and Upgrading

The nature of oils from shale depends strongly on both the parent shale and the retorting process. In general they are not suitable as a direct crude oil substitute due to a number of factors, including:

TABLE 2: ASSAY OF AUSTRALIAN OIL SHALES

Product Distribution Weight Percent	Rundle (as mined)	Glen Davis (main seam)	Glen Davis (top seam)
Oil (Fischer)	7	40.3	8.4
H_2O	24	0.5	2.2
Spent Shale	60	53.6	86.9
Gas + Loss	9	5.6	2.5

(i) High aromatic and olefin content.
(ii) High concentrations of S, O and N.
(iii) Low paraffin and naphthene content.
(iv) A hydrogen deficiency.

Further upgrading is therefore required and two refining alternatives can be considered for shale oil. These include:

(i) Hydrotreating/hydrocracking to crude oil quality.

(ii) Delayed or fluid coking followed by hydrotreating of coker oils.

The second option could be utilized to produce anode carbon as proposed for flash pyrolysis tars. Shale oils are, however, considerably lighter than coal-derived pyrolysis liquids and coke yields are therefore expected to be less. It is understood that the delayed coking option has been proposed for the Julia Creek deposit in Queensland (see Section 5.1) while the first option is favoured for Rundle.

4. TASMANITE OIL SHALE CONCENTRATE

Tasmanite concentrate differs from most shales in that its ash content has been reduced to relatively low levels (19.3%) by flotation. Beneficiation is usually not possible with most shales. The Tasmanite concentrate is still, however, unsuitable for direct coking because of its ash content. It was, therefore, processed through the C.R.C. flash pyrolysis rig which fits into the Type 4 retort category.

Five runs were completed at two operating temperatures. Product yields are shown in Table 3. Highest tar yields were obtained at 500°C, however, the system was not fully optimized and further improvement of yields would be possible. Although the preliminary series of experiments were not carried out on the same size fractions, the normal trend in flash pyrolysis experiments is for tar yield to increase with decreasing particle size. Thus the high yields at 500°C are considered a real effect and may increase still further at smaller particle sizes. As would be expected almost all of the kerogen was volatilized. Rig operation was smooth; however, it was characterized by almost complete carryover of the residue into the collection system. This is shown by the low levels of residue retained in the bed and is a result of the low density of the material. In comparable runs with bituminous coals char carryover is relatively low.

The proportion of the yield reporting as gas was relatively high although significant "fume" was present. It is possible therefore that some very light naphtha-like material may have been present in this fraction.

TABLE 3: 10gm/hr RESULTS FOR TASMANITE CONCENTRATE

Size Fraction (Microns)	Temperature °C	Tar (DAF) %	Char in Residue (DAF) %	Gas and Uncollected Volatiles % (DAF)	% Residue Retained in Bed
- 106 + 75	600	24.3	5.3	70.4	2.1
- 106 + 75	600	25.2	6.1	68.7	3.6
- 106 + 75	600	24.5	6.5	69.0	1.0
- 150 + 106	500	45.2	2.4	52.4	0.1
- 150 + 106	500	44.1	2.3	53.6	0.0

The current condensing system, while quite adequate for coal tars may not have been sufficient for the oil shale vapours. Thus in full scale operation indications are that very efficient cyclone separators and tar collection systems would be necessary.

Analysis of the oil (Table 4) revealed it to be lighter than flash pyrolysis tar and this was confirmed by the Conradson carbon residue test. A somewhat lower coke yield is therefore predicted for Tasmanite shale oil (Table 5) than from most bituminous coals: however, operation of a delayed coker with this material is quite feasible.

TABLE 4: ANALYSIS OF PYROLYSIS TARS

Feedstock	Oils	Asphaltenes	Toluene Insolubles
Tasmanite (500°C)	81	14	5
Tasmanite (600°C)	65	26	9
Millmerran (600°C)	57	21	22

TABLE 5: COKING YIELDS

Feedstock	Conradson Carbon	Coke Yield
Tasmanite (500°C)	19	20-25*
Tasmanite (600°C)	33	30-40*
Millmerran (600°C)	40	40-50

* Estimated from Conradson residue.

5. DISCUSSION

5.1 Oil Shales - General

Oil shales offer some potential as an anode carbon feedstock. In pyrolysis the shales differ from coal in the following respects:

* After driving off the volatile matter very little carbon remains in the residue. The residue is, therefore, all inorganic material for disposal and there is no carbonaceous char from the process.

* The residue expands during pyrolysis so that the material for disposal is about 1.5 times the volume of the oil shale feed. This may create disposal problems depending on the local circumstances.

* A large amount of mineral matter (50-85%) requires heating during pyrolysis. Ash levels in pyrolysis coals are normally around 10-20% and, therefore, the heat balance in the pyrolysis stage is less favourable for oil shales.

* The product tar, or oil, from oil shale pyrolysis is somewhat lighter than the tar produced by the flash pyrolysis of coals and less hydrogen will be consumed in upgrading to liquid fuels. The product is highly aromatic, as with coal tar, and will require fairly severe conditions for upgrading.

* Although a lighter tar (or oil) will be produced from oil shale, the coking value, at this stage, appears sufficiently high for a delayed coker to be incorporated in the treatment flowsheet. The proposed delayed coker for treatment of Julia Creek shale oil could be designed to produce anode grade coke.

On first examination, there appear to be some significant disadvantages in utilizing oil shale as a source of anode carbon. However, the situation is fairly complex and a meaningful economic assessment cannot be made at this stage. There are no oil shale ventures that are currently considered economical for producing liquid fuels, either in Australia or overseas. The last major venture, the Colony Oil Shale Project (Tosco/Exxon) in the U.S.A. was terminated in 1982. While it does not appear likely that a stand-alone plant, designed for anode carbon as the major product, will be feasible, this possibility should be reviewed in some detail in the near future.

5.2 Tasmanite Concentrate

In the case of Tasmanite concentrate the residual mineral matter is a much lesser quantity than usually found in oil shales and is comparable with ash levels in many bituminous coals currently being evaluated in the Anode Carbon project. Thus there would be few residue disposal problems and the overall energy efficiency would be expected to be quite reasonable. The coking value of the tar produced is fairly high, although less than for most flash pyrolysis tars. However, because of the quite high tar yields (ca 45% DAF at 500°C) an overall high yield of coke would be obtained. The Tasmanite oil shale is unusual in that, unlike other oil shales, a concentrate may be obtained. In this special case a stand-alone anode carbon plant might be feasible, but a more detailed economic assessment is still required.

6. CONCLUSIONS

1. Oil shales, in general, offer some potential as an anode carbon feedstock although they have a number of disadvantages when compared with coal.

2. A more detailed survey is required to determine the economics relevant to the specialized production of anode carbon.

3. Tasmanite concentrate shows good potential for producing a tar suitable for coking to anode carbon in high yields.

CRA

CRA EXPLORATION PTY. LIMITED
(INC. IN N.S.W.)

LEVEL 4, BELLERIVE QUAY,
CAMBRIDGE ROAD, BELLERIVE, 7018, TASMANIA, AUSTRALIA

P.O. BOX 138
BELLERIVE 7018
TELEGRAMS: CRAEX
TELEX: AA57144
TELEPHONE: 44 3533
AREA CODE: (002)

IN REPLY PLEASE QUOTE

7th April, 1983.

Memorandum To: T.W.DICKSON   CRAE Report 12081

From: I.M.CLEMENTSON

Subject: 1983 TASMANITE OIL SHALE DRILLING - EL 4/74
(ENDEAVOUR JOINT VENTURE)

SUMMARY

Drilling has confirmed the presence of Tasmanite at one locality, and has found typical stratigraphy associated with the Tasmanite at three other localities within the Nook area. The quality of the Tasmanite appears to be lower than that generally intersected in the Railton-Latrobe Tasmanite areas and it is possible that dips are steeper in the Nook area, thereby restricting open-cut potential.

Further investigation would require detailed mapping and relatively close-spaced drilling. This is not warranted unless a commercial end - use for a Tasmanite product can be developed.

INTRODUCTION

Endeavour Resources requested CRAE to assess the potential for shallow Tasmanite oil shale in the Nook area of EL 4/74. A reconnaissance programme consisting of 145 metres of open hole drilling and 2.6 metres of diamond drilling in 5 holes at 4 sites was completed. Tasmanite was located at one site and is believed to exist at depth at the other sites tested.

GEOLOGY

a. General

From an exploration point of view the important features of the Tasmanite horizon are that it is restricted to a single stratigraphic position within the Basal Beds of the Permian of Northern Tasmania and that enclosing sediments above and below the Tasmanite have certain diagnostic features.

Within the Permian succession underlying the Tasmanite horizon are distinctive basal quartz conglomerates and mudstone conglomerates of (?) glacial origin; above the Tasmanite is a thick sequence of mudstones, shales and siltstones with glacial dropstones and occassional thin sandy interbeds. Fossil bryozoa and shell fragments are more abundant above the Tasmanite horizon, particularly in one zone approximately 50-70 metres above the Tasmanite. The stratigraphy is therefore diagnostic enough to indicate whether a drill hole is collared stratigraphically above or below the Tasmanite.

b. <u>Nook Area</u>

The Permian block in the Nook area is bounded by the dolerite of Bonneys Tier to the east and by Precambrian and Lower Palaeozoic sediments to the north, south and west. The Basal Beds which host the Tasmanite are repeated on either side of a north-south fault which bissects this Permian block. The area of interest is that of the Basal Beds west of this fault. Tasmanite outcrops are reported from the area and numerous pits and trenches have been sunk in the search for the Tasmanite. Dip is to the north-east and may be steeper than in the Railton-Latrobe area, the implication of this being that surface Tasmanite could rapidly dip down beyond range of an open-cut mining operation.

DRILLING

The attached plans detail the location of the 1983 drill holes. Four sites were tested with two holes being drilled at one site. These drill sites were chosen because they cover the area of reported Tasmanite occurrences and would therefore serve to confirm its presence and give an indication of the quality. The Basal Beds in this area west of the north-south fault have a greater mapped width, suggesting a lower dip, than the belt of Basal Beds east of the fault, also the lowest part of the succession, including the Tasmanite, may be missing east of the fault.

RD83 NK1 (42 metres), RD83 NK2 (50 metres) and RD83 NK5 (24 metres) intersected sequences of blue grey shales, mudstones and siltstones with glacial dropstones typical of the Basal Beds overlying the Tasmanite. NK1 and NK2 both intersected particularly fossiliferous zones which, in the Railton-Latrobe area, are present 50-70 metres above the Tasmanite. All three holes were stopped as it was considered that they were collared too far above the Tasmanite horizon, they did indicate however that the stratigraphy is similar to the Railton-Latrobe area and that Tasmanite could be anticipated at depth.

RD83 NK3 (15 metres), located close to an old exploration pit, intersected Tasmanite at 14.8 metres. Coring of an adjacent hole, RD83 NK4 (16.6 metres), intersected the Tasmanite between 14.09 - 15.49 metres (1.40 metres). The Tasmanite was of low quality having thin, moderately spore rich zones, seperated by two spore deficient siltstones.

Beneath the lowest spore rich zone, the underlying 0.29 metres of siltstone had a low, but noticeable, spore content. If this is included as part of the overall Tasmanite horizon then the total intersection is 1.69 metres (14.09 - 15.78 metres).

The differences in depth of the Tasmanite intersection between NK3 and NK4, which were collared approximately 1 metre apart, suggests that the Tasmanite dips quite steeply to the north or north-east in this area. This would explain why NK2 proved to be collared well above the Tasmanite horizon yet was not far downdip from these intersections.

I.M.CLEMENTSON

Attach.

Drillhole logs
Location Plan

C.R.A. EXPLORATION PTY. LIMITED

DRILL CORE LOG

SHEET No. 1

TENEMENT NAME Endeavour J.V. Railton Oil Shale No. EL4/74

PLAN – MAP REFERENCE Railton (4442) 1:25000

CO-ORDINATES 5429820 N 443360 E AZIMUTH — DRILLERS Overland COMMENCED 22:3:83 DEPTH 42 metres HOLE No. 2083NK1

RL COLLAR 130 m AMSL INCLINATION -90° DRILL TYPE [illegible] COMPLETED 22:3:83 CASING LEFT Nil DPO No(s)

DEPTH From (M)	DEPTH To (M)	Core Rec. (M)	Core Size	Graphic Log	CORE DESCRIPTION	SPECIAL FEATURES Weath, Alteration, Fracturing, Veining, Mineralization	Sample No.	From (M)	To (M)	Rec (M)	ASSAY VALUES (Analysed by ...)
0	1.0				Soil: ochre clay soil						
1.0	3.0				CLAYS: brown-ochre	Weathered shales and silts.					
3.0	4.0				CLAYS: greyish brown	Weathered shales and siltstones with relatively fresh, grey shale fragments present.					
4.0	17.0				SHALES & SILTSTONES	Blue-grey, soft shales and subordinate siltstones. Fragments of chert and qz probably represent dropstones. The silts are often lighter grey and are poorly sorted.					
17.0	30.0				SHALES & MUDSTONES	Very uniform blue-grey shales and mudstones with occasional silty horizons and qz or chert dropstones.					
30.0	36.0				SILTSTONES	Dominantly light-mid grey silts and silty mudstones with abundant fossil bryozoan, coral and shell fragments. Occasional thin (20cm) harder, silty sandstone interbeds.					
36.0	39.0				MUDSTONE	Blue-grey very poorly fissile mudstones with occasional dropstones					

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DRILL CORE LOG

SHEET No. 2

TENEMENT NAME Endeavour J.V. No. EL4/74

PLAN – MAP REFERENCE Railton (4442) 1:25000

CO-ORDINATES 443360E 5429520N AZIMUTH – DRILLERS Overland COMMENCED 22:3:83 DEPTH 42.0m HOLE No RD83NK1

RL COLLAR 130m AMSL INCLINATION -90° DRILL TYPE [illegible] COMPLETED 23:3:83 CASING LEFT – DPO No(s)

DEPTH From (M)	DEPTH To (M)	Core Rec. (M)	Core Size	Graphic Log	CORE DESCRIPTION	SPECIAL FEATURES Weath, Alteration, Fracturing, Veining, Mineralization	Sample No.	From (M)	To (M)	Rec (M)	ASSAY VALUES (Analysed by)
39.0	42.0				SILTSTONES	Light-mid grey, fairly hard Sandy in parts. Infrequent dropstones. Fossil fragments common.					
						Hole stopped at 42.0m because the succession is interpreted to be quite a stratigraphic distance above the Tasmanite horizon. The abundance of fossil fragments in dominantly silty horizons may be correlated with similar horizons up to 50m above the Tasmanite (Railton drilling 1981-82)					

SHEET No. 1

C.R.A. EXPLORATION PTY. LIMITED
DRILL CORE LOG

TENEMENT NAME Endeavour S.V. No EL4/74
PLAN – MAP REFERENCE Railton (4442) 1:25000

CO-ORDINATES 5427610N 444250E AZIMUTH – DRILLERS Overland COMMENCED 23:3:82 DEPTH 50 metres HOLE No. RD83NK2
RL COLLAR 165m AMSL INCLINATION -90° DRILL TYPE Warman COMPLETED 23:3:82 CASING LEFT 9m DPO No(s)

DEPTH From (M)	DEPTH To (M)	Core Rec. (M)	Core Size	Graphic Log	CORE DESCRIPTION	SPECIAL FEATURES Weath, Alteration, Fracturing, Veining, Mineralization	Sample No.	From (M)	To (M)	Rec (M)	ASSAY VALUES (Analysed by ....)
0	1.0				Soil						
1.0	9.0				Weathered Argillitic Sediment	: ochre-brown clay and weathered siltstones, shale and mudstone. Soft. Becoming grey with depth					
9.0	23.0				Siltstones	light-mid grey, poorly sorted. Some quartz, chert and sandstone dropstones but not common. Fossil fragments (chiefly bryozoa) quite common.					
23.0	50.0				Mudstones	: blue-grey poorly fissile mudstones with occasion of dropstones and silt interbeds. Very uniform sequence.					
						Hole stopped at 50m in a stratigraphic succession certainly above that of the Tasmanite horizon. Distance to the Tasmanite horizon difficult to estimate; hole stopped as the programme was primarily looking for shallow Tasmanite occurrences.					

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SHEET No. 1

C.R.A. EXPLORATION PTY. LIMITED
DRILL CORE LOG

TENEMENT NAME Endeavour J.V. Railton Oil Shale No. EL41/74

PLAN – MAP REFERENCE Railton (4442) 1:25,000

CO-ORDINATES 444320E 5427490N AZIMUTH – DRILLERS OVERLAND COMMENCED 23:3:83 DEPTH 15.0 m HOLE No. RD83NK3

RL COLLAR 170m AMSL INCLINATION –90° DRILL TYPE Warman COMPLETED 23:3:83 CASING LEFT – DPO No(s)

DEPTH From (M)	DEPTH To (M)	Core Rec. (M)	Core Size	Graphic Log	CORE DESCRIPTION	SPECIAL FEATURES Weath, Alteration, Fracturing, Veining, Mineralization	Sample No.	From (M)	To (M)	Rec (M)	ASSAY VALUES (Analysed by)
0	1.0				SOIL						
.0	3.0				WEATHERED SHALE	: ochre-brown clays.					
.0	14.8				SILTY SHALE	: slightly fissile blue grey shale or mudstone. Silty horizons common. Dropstones (qz, chert) present but not abundant.					
.8	15.0				TASMANITE OIL SHALE	: siltstone with 5% 10% Tasmanites sparse, low grade.					
						Hole stopped to allow coring of the Tasmanite in an adjacent hole (RD83NK4)					

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SHEET No. 1

C.R.A. EXPLORATION PTY. LIMITED
DRILL CORE LOG

TENEMENT NAME Endeavour J.V. Railton Oil Shale No. EL4/74

PLAN – MAP REFERENCE Railton (4442) 1:25000

CO-ORDINATES 444320E 5427490N AZIMUTH – DRILLERS Overland COMMENCED 24.3.83 DEPTH 16.60 metres HOLE No. 2083NK4

RL COLLAR 170m AMSL INCLINATION -90° DRILL TYPE Vacrian COMPLETED 24.3.83 CASING LEFT DPO No(s)

DEPTH From (M)	DEPTH To(M)	Core Rec. (M)	Core Size	Graphic Log	CORE DESCRIPTION	SPECIAL FEATURES Weath, Alteration, Fracturing, Veining, Mineralization	Sample No.	From (M)	To (M)	Rec (M)	ASSAY VALUES (Analysed by)
0	1.0				SOIL						
1.0	3.0				WEATHERED SHALES	: ochre-brown clays					
3.0	14.0				SILTY SHALE	: bluegrey shale +dropstones					
14.00	14.09	.09	NQ		SHALE	: bluegrey shale with dropstone clasts to 40% of total. Clasts are chert, shale (black) and quartz, subangular and up to 1cm. Interstitial pyrite is abundant					
14.09	14.18	.09	NQ		TASMANITE	low - moderate grade Tasmanite oil shale with approx. 10% clasts up to 1cm (qz, qzite, chert, black shale) Upper contact sharp but contorted, lower contact gradational by decrease in spore content.					
14.18	14.45	.27	NQ		SILTY MUDSTONE	: midgrey, silty mudstone with a very small %age of Tasmanite spores. Small (up to ½cm) clasts (5%) increase in size (2cm) and frequency (70%) towards lower contact which is sharp but irregular					
14.45	14.90	.45	NQ		TASMANITE	: moderate grade. Few dropstone clasts, those present being small (2mm) Foliation at 75°					

SHEET No. 2

C.R.A. EXPLORATION PTY. LIMITED

DRILL CORE LOG

TENEMENT NAME ENDEAVOUR J.V. RAILTON OIL SHALE No. EL4/74

PLAN – MAP REFERENCE RAILTON (4442) 1:25000

CO-ORDINATES 5427490N 444320E AZIMUTH – DRILLERS OVERLAND COMMENCED 24:3:83 DEPTH 16.60 metres HOLE No. RD83NK4

RL COLLAR 170 m AMSL INCLINATION –90° DRILL TYPE [illegible] COMPLETED 24:3:83 CASING LEFT – DPO No(s)

DEPTH From (M)	DEPTH To(M)	Core Rec. (M)	Core Size	Graphic Log	CORE DESCRIPTION	SPECIAL FEATURES Weath, Alteration, Fracturing, Veining, Mineralization	Sample No.	From (M)	To (M)	Rec (M)	ASSAY VALUES (Analysed by)
14.90	15.30	0.40	NQ		MUDSTONE	: poorly fissile, blue grey. Infrequent clasts, subangular to subrounded, up to 1cm, generally qz, black shale, chert. Traces of Tasmanite spores. Lower contact sharp at 70°					
5.30	15.49	0.19	NQ		TASMANITE	: moderate grade. up to 8% clasts (to 1/2cm), dominantly subangular grey chert and black shales. Lower contact gradational.					
5.49	15.78	0.29	NQ		SILTSTONE	: micaceous, mid grey, fairly massive. Tasmanite spores present to ± 5% and some dropstone clasts up to 1/2cm. Lower contact sharp at 75°					
15.78	16.60 (EOH)	0.82	NQ		MUDSTONE CONGLOMERATE	: blue grey massive to poorly fissile mudstone matrix supporting ± 30% clasts up to 6cm (range 1mm–6cm). Slight increase in clast size downwards.					

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DRILL CORE LOG

SHEET No. 1

TENEMENT NAME Endeavour J.V. Railton Oil Shale No. EL4/74

PLAN – MAP REFERENCE Railton (4442) 1:25000

CO-ORDINATES 443720 E 5428490 N AZIMUTH – DRILLERS Overland COMMENCED 24·3·83 DEPTH 24 metres HOLE No RD83NKS

RL COLLAR 140 m AMSL INCLINATION –90° DRILL TYPE Warman COMPLETED 24·3·83 CASING LEFT – DPO No(s)

DEPTH From (M)	DEPTH To(M)	Core Rec. (M)	Core Size	Graphic Log	CORE DESCRIPTION	SPECIAL FEATURES Weath, Alteration, Fracturing, Veining, Mineralization	Sample No.	From (M)	To (M)	Rec (M)	ASSAY VALUES (Analysed by ......)
0	1.0				SOIL						
1.0	3.0				WEATHERED SHALES	: buff-ochre brown clays on shale/silt.					
3.0	24.0				SILTY SHALE	: blue grey silty shale and mudstones with few dropstones, occasional sandy interbeds					
						Hole stopped somewhere stratigraphically above the Tasmanite horizon.					

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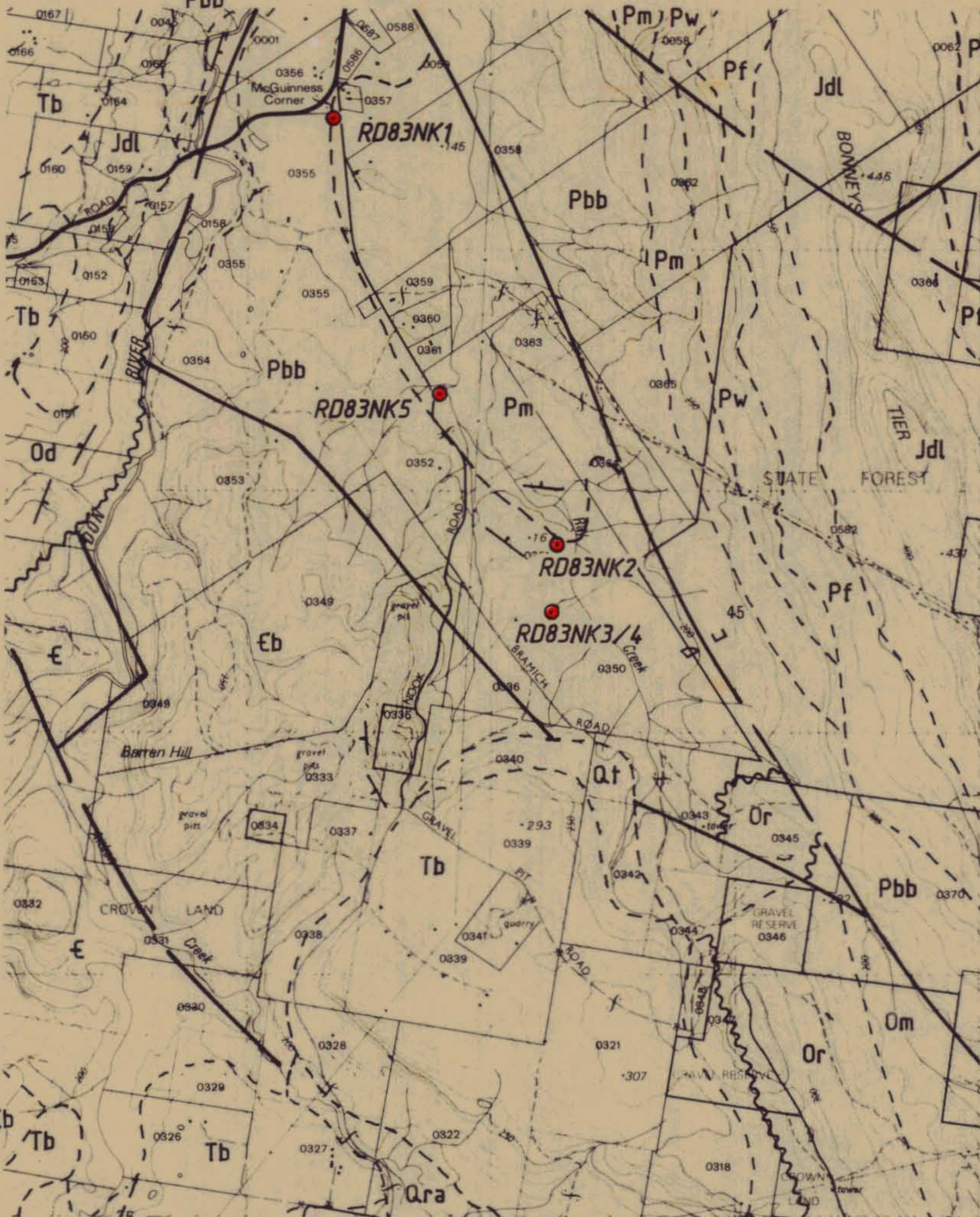

LEGEND

● RD83NK2 1983 Drill Hole & Number

QUATERNARY

Qra Recent Alluvium

Qt Basalt Talus

PERMIAN

Pf Ferntree Group

Pw Woodbridge Group

Pm Mersey Coal Measures

Pbb Basalt Beds

ORDOVICIAN

Om Moina Sandstone

Or Roland Conglomerate

Od Dial Conglomerate

CAMBRIAN

Ɛb Bott Conglomerate

Ɛ Unassigned

IGNEOUS ROCKS

Tb Tertiary Basalt

Jdl Jurassic Dolerite

5 cm

CRA EXPLORATION PTY. LIMITED

E.L. 4/74
DRILL HOLE LOCATION PLAN
AND GEOLOGY
NOOK TASMANITE

REF. SK55 - 3	
SCALE 1 : 25000	DRAWN. R. T.
AUTHOR. I. M. C.	REPORT Nº. 12081
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Proposals For Further Investigation Of Tasmanite Shale As A Source Of Bituminous Binder For Paving Purposes.

E.J. DICKINSON

Assessment of Previous Work.

1. Previous investigations have centred around the examination of products from a concentrate of the mineral encapsulated kerogen which was produced by froth flotation of the comminuted shale in 1939 (Hunt, 1975).

2. Heat treatment of the concentrate in a stirred horizontal retort at temperatures of about 400°C produced a thermoplastic bituminous material containing about 50% by mass of a bitumen. In all about 3400 l were manufactured and about half of this was used for spray sealing road trials.

3. No information is available on the long time performance of the trial seals but initial performance was satisfactory.

4. A laboratory examination of the bituminous product as a paving binder (Dickinson, 1976) indicated satisfactory flow properties but a high content of volatile oils. In pavement service the loss of these constituents by evaporation would lead to premature hardening of the bitumen and poor long term performance. This has been the case for paving binders made from tars produced by the carbonization of coal in coke ovens.

5. Examination of the kerogen (demineralized concentrate - CSIRO, 1978) indicated that it is mainly aliphatic hydrocarbon in character (atomic C/H ratio of 0.63). When heated to 390 - 400°C it is partly or wholly decomposed to give a bitumen which, in the case of the 1939 product, had an atomic C/H ratio of o.76 and consisted of about 6% of very volatile oils and a residue with a Ring and Ball softening point of about 70°C. This hard residue still contained about 10% of oils volatile at 100°C (Dickinson, 1976).

This suggests that the 1939 thermal decomposition

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product was a blend of undecomposed kerogen and relatively low molecular weight oils.

Future Laboratory Studies.

6. The control of the thermal decomposition of the encapsulated kerogen and the nature of the products (particularly their volatility) needs to be further examined. This should preferably be done on a low ash concentrate (Amdel, 1981).

7. Good control of digestion temperature might be achieved by micro-wave heating of the concentrate and this should be done on a 1 - 2 kg scale so that separation of the product by distillation (to give sufficient material for paving binder evaluation) can be done. Decomposition temperatures in the range 375 to 400°C should be examined. Temperatures higher than 250°C should be avoided in the distillation process and a second stage distillation under reduced pressure would be needed.

8. If such an investigation indicated a lack of relatively non-volatile plasticising oils in the decomposition product, any hard residue (mainly undecomposed kerogen ?) might be useful for blending with the soft vacuum distillation residues of the currently used M.E. crude petroleums to produce high quality paving binders.

Venues for Future Laboratory Work.

9. Enquiries to CSIRO have indicated that there is no experience in Australia on micro-wave heating to temperatures up to 400°C.

Div. of Building Research (Highett/Vic.) has studied the drying of clays and plasters using this technique and Dr. Alfredson (Div. of Materials Science, Lucas Heights) reports that 'in situ' pyrolysis of torbanite shale by the method is being studied in the U.S.A. He advises consulting Dr. R.Cane (Hon. Research Associate, Dept. of Chemistry, University of Tasmania) on the matter. Indus-

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trial uses of micro-wave heating being developed in the U.S.A. include 'in situ' recycling of bituminous paving materials (see enclosed news item).

10. On the assumption that a laboratory can be found to study the thermal decomposition process as outlined above, with or without the use of micro-wave heating, the Australian Road Research Board could evaluate the products. The distillation residues and any high boiling (plasticising) oils obtained would be blended (or the distillation residues would be blended with soft petroleum bitumens) to produce paving grade binders and these would be evaluated using methods developed to assess paving grade bitumens.

Road Trials of Promising Products.

11. If the quality and projected manufacturing costs of a product indicate that road trials (spray seals) should be laid, semi scale plant to produce at least 5000 l (1000 gallons) of paving binder would be needed. It is assumed that any such trials would be planned and conducted by the P.W.D. Tasmania in cooperation with the A.R.R.B.

E.J. DICKINSON

Feb. 1983.

13, Consort Ave.,
Vermont Sth./Vic.,3133
Tel.: Melbourne 232-2896.

5th February, 1983.

Mr. T.W. Dickson
CRA Exploration Pty. Ltd.
Level 4, Bellerive Quay
Cambridge Road,
Bellerive 7018/ Tasmania

Dear Mr. Dickson,

PAVING BINDER FROM TASMANITE SHALE

Thank you for your letter of January 27th and the research reports on the Tasmanite Shale.

My report on proposals for further investigation of the Shale as a source of bituminous binder for paving purposes is enclosed.

I have been unable to find any laboratory in Australia which has experience of microwave heating to temperatures of the order of 400°C - the method proposed for further investigation of the thermal decomposition of the kerogen. Dr. Cane of the Chemistry Dept., University of Tasmania, may, however, be able to advise you about expertise on this subject in the U.S.A.

A copy of the ARRB restricted report (AIR 213-3) on my investigation of the digested concentrate manufactured in 1939 is enclosed for your personal information.

I am also enclosing my invoice for services rendered and will return the research reports to you under separate cover by parcel post.

Yours sincerely,

E.J. Dickinson

Encls.

ARRB INTERNAL REPORT AIR 213-3

DIGESTED TASMANITE SHALE CONCENTRATE AS A SUBSTITUTE FOR PAVING BITUMEN

by

E.J. Dickinson
Principal Research Scientist

July 1976
Australian Road Research Board
500 Burwood Highway
Vermont
Victoria

Project No. 213 - Bitumen Replacement from Brown Coal.

SUMMARY

A sample of digested Tasmanite Shale concentrate manufactured in 1935 has been examined as a possible substitute for paving bitumen. The material is a dispersion of fine mineral matter in a soft bitumen and was used for road sealing trials in Tasmania when it was produced.

The bituminous part of the concentrate (approximately 50 per cent by weight and 70 per cent by volume) has an elemental composition similar to some of the bitumens derived from petroleum and shows superior flow and deformation properties. The presence of a considerable amount of volatile material in the bituminous fraction after reduction to paving grade consistency prevented on accurate assessment of its resistance to hardening by oxidation by test procedures used for paving bitumens of petroleum origin. This casts some doubt on the durability of the material in pavement surfacings.

Further laboratory investigation is needed to assess durability and further road trials should be laid with the material.

INTRODUCTION

1. A deposit of oil bearing shale, estimated to be from 10 to 12 million tonnes, is located in the Mersey River basin area of Northern Tasmania. Unlike most of the other oil bearing shales which have been discovered, the kerogen (oil) in this 'Tasmanite' shale is present in numerous small discs distributed in a matrix of quartz sand or silt and clayey material. The discs are believed to have been formed from spores. The kerogen content of the shale ranges from 20 per cent to 25 per cent by weight.

2. In the early 1930's, the Tasmanian State Department of Mines initiated an investigation into the potential of this shale as a source of liquid fuel and/or paving bitumen (Department of Mines 1932) and over 10 tonnes of a bituminous product was produced from a small pilot plant.

The comminuted rock was subjected to a flotation process to obtain a concentrate of the kerogen and this concentrate, containing more than 50 per cent by weight of organic material, was heated in a stirred retort. The heat treatment breaks down the disc structure to give a soft bitumen in which finely divided mineral matter is dispersed. A sample of the product - called 'Digested Tasmanite Shale Concentrate' (DTSC) - was obtained from the Public Works Department of Tasmania, and is the subject of this investigation.

POTENTIAL OF DEPOSIT AS A SOURCE OF PAVING BITUMEN

3. If 12 million tonnes of shale are available and the yield of concentrate is one-seventh of this then, for a concentrate containing 50 per cent by weight of bitumen, the deposit would yield about 1 million tonnes of bituminous binder. At current consumption rates, this would supply Australian needs for a paving binder for two years and Tasmanian needs for about 75 years.

DEVELOPMENT OF A MANUFACTURING PROCESS

4. The initial investigation was not on a sufficient scale to accurately evaluate the energy balance of the process. Gas and oil are produced as by-products from the digestion but the indications were that these were insufficient for drying the wet concentrate and heating the digestor. A semi-continuous plant to process 60 tonnes of shale/day was set up in 1939, and some preliminary runs were done before the project was abandoned (Department of Mines 1940).

ROAD TRIALS WITH DTSC

5. The Tasmanian Public Works Department laid at least two spray sealing trials with DTSC in 1936. One on a highway near Launceston (22 mm aggregate and the concentrate sprayed at 1.8 l/m^2) and one on a street in Latrobe. Both sites have been reconstructed within the last 25 years and there is no traceable record of the performance of the trial seals. There were, however, no reports of poor performance.

ARRB LABORATORY EXAMINATION OF DTSC

ISOLATION OF THE BITUMINOUS PART OF THE CONCENTRATE

6. The concentrate was dispersed in benzene (volume ratio solvent/concentrate of 5 to 1) and the dispersion allowed to settle overnight. After separation of most of the solution by decantation, the residue was treated again with 5 volumes of benzene and the settlement and decantation procedure repeated. The two benzene extracts were then combined and most of the benzene removed from them by distillation at atmospheric pressure, in an atmosphere of carbon dioxide. The benzene remaining was removed by distillation in a thin film evaporator at 100°C also in an atmosphere of carbon dioxide. A small sample of the concentrate was exhaustively extracted with benzene and then attempts were made to extract further soluble organic material with acetone, carbon disulphide and carbon tetrachloride.

None of these solvents extracted more material.

7. The extract was 49.3 per cent by weight of the concentrate.

PROPERTIES OF THE BENZENE EXTRACT

8. The extract was a light brown bitumen with an apparent viscosity of 4.19 log PaS at 25°C and a shear rate of 1 x $10^{-2}S^{-1}$. Its ash content was 1.3 per cent by weight.

9. The atomic carbon/hydrogen ratios and nitrogen, sulphur and oxygen contents of the extract are compared with those of vacuum distillate residues from two Middle East crude petroleums (Haley 1972) and a paving bitumen of 'torbanite' shale oil origin which was used in South Africa (Dickinson 1960) in Table I.

The South African bitumen was the distillation residue of the product formed by thermal cracking of the oil obtained from destructive distillation of a 'torbanite' shale.

The DTSC has a much lower atomic carbon/hydrogen ratio than the Torbanite bitumen and, in this respect, is similar to the petroleum residues. Both materials of 'shale' origin have a lower sulphur content than the petroleum residues.

PROPERTIES OF A 'REDUCED' BENZENE EXTRACT OF DTSC

10. The viscosity of the benzene extract would be considered rather low for normal paving purposes so it was treated in a thin film evaporator at 135°C under an atmosphere of carbon dioxide for two hours. Volatile material amounting to 3.3 per cent by weight of the extract was lost and the apparent viscosity at 25°C and a shear rate of 1 x $10^{-2}S^{-1}$ increased to 5.63 log PaS.

11. The deformation and flow properties of the material under sinusoidal loading (Dickinson 1974) are compared with those of two Middle East Petroleum vacuum distillation residues and a Middle East bitumen of paving grade produced by blowing the Kuwait residue in Table II.

The reduced DTSC has a significantly lower T_s than the paving grade bitumen and a significantly higher value of β.

12. When subjected to the standard Rolling Film Oven Test (RFOT) (Dickinson 1973) treatment (75 minutes in the oven at 163°C) there was a loss in weight of 2.3 per cent and the ductility at 15°C of the residue was only 104 mm. This low ductility would be expected from the high β value of the reduced DTSC and, for a blown bitumen, could be associated with colloidal instability. In this case, however, there was no evidence of breakdown in internal structure.

13. After RFOT treatment, the residue was tested by the ARRB method for assessing the durability of 85/100 pen paving bitumens by exposure to air as a thin film at 100°C (Dickinson 1973).

Considerable loss in weight and hardening took place in this treatment and apparent viscosities were measured on the sliding plate viscometer at 60°C instead of 45°C. The results for increase in apparent viscosity and loss in weight of the films were as follows:-

	% loss in weight	Apparent viscosity at 60°C (log PaS) shear rate in parenthesis.
Before treatment	0	3.85 ($5 \times 10^{-3} s^{-1}$)
2 days treatment	10	7.00 ($5 \times 10^{-3} s^{-1}$)
5 days treatment	7	8.43 ($1.8 \times 10^{-4} s^{-1}$)

DISCUSSION OF RESULTS AND POSSIBLE USE

14. The laboratory investigation of the DTSC has indicated that the bituminous part of it has superior deformation and flow properties to the currently used paving bitumens of petroleum origin. It does, however, contain a large amount of relatively volatile oils and, possibly, has poor resistance to hardening by

oxidation. Further laboratory work is needed on the assessment of its durability probably by examination of a vacuum reduced extract fluxed to paving grade consistency with a heavy oil of petroleum origin.

15. Although spray sealing road trials were laid in 1936 there is no record of their subsequent performance so further trials are needed to establish long term behaviour in a pavement surfacing.

16. No major problems would be anticipated in the handling of the material either for spray sealing or hot process plant mix. For successful use in either context, the material would have to have a consistent composition (amount and particle size range of mineral matter and viscosity of the bituminous constituent). The mineral matter would almost certainly increase the rate of wear of pumps but this was overcome in the case of fluxed Trinidad Lake Asphalt by the use of special equipment.

TABLE I ELEMENTAL COMPOSITION OF DIFFERENT BITUMINOUS MATERIALS

	Atomic carbon/ hydrogen ratio	Sulphur content % wt.	Nitrogen content % wt.	Oxygen content % wt.
Benzene extract of DTSC	0.76	1.0	1.7	1.7
Kuwait petroleum short residue	0.68	4.2	1.5	1.3
Light Arabian petroleum short residue	0.71	4.3	1.6	1.0
'180 pen' bitumen of shale origin (South Africa)	0.89	0.8	1.6	1.5

TABLE II

DEFORMATION AND FLOW PROPERTIES OF DIFFERENT BITUMINOUS MATERIALS

	Apparent Viscosity at 25°C and a shear rate of $1 \times 10^{-2} S^{-1}$ (log PaS)	Limiting Viscosity at 25°C (log PaS)	Shear Susceptibility Parameter (β)	Temperature Susceptibility Parameter T_s(°C)
Reduced DTSC	5.63	6.34	3.08	31
Distillation residue from Light Arabian Crude	3.61	4.21	1.43	31
Distillation residue from Kuwait Crude	4.16	4.37	1.30	34
85/100 pen paving bitumen manufactured by air blowing the Kuwait residue	4.85	5.11	2.01	37

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Report written by:

Report reviewed by:

534034

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1. Technical Memorandum CRC/TM/16/83
Comalco Research Centre.

2 CRAE Report 12081 I.M. Clementson

3. Proposals for further Investigations of Tasmanite shale. E.J. Dickson