

# TREATABILITY STUDIES ON OIL SHALE RETORT SOUR WATER.

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## ABSTRACT

Oil from oil shale offers a potentially secure supply of fuel for Australia and other nations with oil shale deposits. However, the wastewater produced from retorting oil shale is contaminated and difficult to treat. High ammonia, sulphur, chloride and TOC concentrations can be expected. This paper describes bench scale treatability tests that were carried out on sour water produced by retorting oil shale from the Kerosene Creek deposit in Gladstone, Australia. Using a combination of acidification, air stripping, biological treatment, activated carbon and reverse osmosis, the water can be treated to a high standard whilst recovering valuable ammonium salts by crystallisation.

## INTRODUCTION

Oil reserves locked up as oil shale are estimated at close to three trillion barrels worldwide, which is enough to supply the current oil demand for about 100 years. However, there are significant barriers to oil shale development, mainly economic, but also environmental. Dealing with the waste streams that arise during shale oil extraction is one such hurdle, and the sour water produced during retorting of oil shale represents a particularly difficult challenge. Oil shale is typically mined and crushed, then processed in above-ground retorts to convert the organic kerogen bound within the shale to oil by pyrolysis. The vaporised oil is then cooled and condensed, but water that was associated with the raw shale is also condensed at the same time, becoming heavily contaminated in the process.

Approximately 1 litre of sour water is created per litre of oil produced, depending on the total moisture content fed to the retort.

A literature search for oil shale wastewater treatment techniques produces limited information. As with oil shale research in general, activity over the years has increased when a shortage of oil supplies looms on the horizon, then dies back when new reserves of traditional petroleum are developed. Some early wastewater treatment techniques were developed in the 1970's and are summarised by Fox (Fox et al 1980). Most of this work was carried out on Green River Shale in Colorado, one of the world's largest oil shale deposits.

Further work on bio-oxidation of oil shale organic contaminants (Healey et al, 1985) from a range of oil shale processes pointed out a key factor in this field - no two shale oil wastewaters will be the same. Each deposit has different mineralogy, and the mineral make-up determines the inorganic content of the water. For example, buddingtonite is found in some shales, and under the conditions of pyrolysis it decomposes to release ammonia gas (Oh et al 1992). Pyrite can decompose to release hydrogen sulphide in the high temperatures and high hydrogen partial pressures within the retort (Bhargava et al 2008). The temperature required for pyrolysis of kerogen is similar to that at which buddingtonite and pyrite decomposition commences. Thermal decomposition of carbonate in the shale also releases carbon dioxide. The inorganic matrix of the water is therefore dominated

by the ammonium salts of carbonate, bicarbonate, bisulphide, bisulphite and chloride.

As well as different mineralogy, the water content of the shale fed into the retort will influence the concentrations of the inorganic and organic species in the retort water. Some shales are very dry, such as Green River, whereas Australian shales tend to be wetter, and are typically partially dried before retorting. Overall, chemical oxygen demand can vary from a few thousand mg/l to over 150,000 mg/l (Healey et al, 1985), and conductivity from 15,000  $\mu\text{s/cm}$  to nearly 200,000  $\mu\text{s/cm}$  (Fox et al 1980). Some shale wastewaters are dominated by phenolic compounds, including those found in Estonia (Kamanev et al 2002) whereas others are dominated by carboxylic acids, hydrocarbons, and recalcitrant fulvic and humic acids.

Because of this variability, each shale wastewater must be characterised individually, and an appropriate treatment process designed and tested for it. The treatment plant must have the flexibility to cope with a changing wastewater as the shale seams being mined and processed change over the life of a project, and as subtle temperature variations in the retort produce variable inorganic constituent concentrations. This paper is dedicated to a particular shale processed with a particular retorting technology to generate a specific wastewater.

QER is operating a technology demonstration plant (TDP), using the Paraho II<sup>TM</sup> technology to produce oil from the Stuart oil shale deposit in Queensland. A typical analysis of the sour water from the process is given in Table 1, along with expected treated water quality. Retort sour water generated at the TDP is currently steam stripped for removal of ammonia, hydrogen sulphide and volatile organic carbon (VOC) before being co-disposed onto the spent shale. The spent shale is highly hydrophilic and also has absorption properties similar to activated carbon. The water is absorbed and the remaining organics are bound to the char remaining

on the spent shale. However, steam stripping is energy intensive and requires a high caustic dose for ammonia removal, and the treated water is not of suitable quality for re-use or recycling. QER therefore explored options for treating the water to a much higher standard for re-use within the process, whilst using less energy and chemicals, and recovering valuable by-products at the same time. The concept design is briefly described here.

Sour water is first acidified using sulphuric acid (produced on-site from waste sulphur), then degassed and de-oiled in a 3-phase separator. Lowering the pH releases some of the dissolved oil, alongside carbon dioxide, hydrogen sulphide and sulphur dioxide. The dissolved salts in raw sour water are predominantly ammonium bicarbonate, and these are converted to ammonium sulphate by acidification and degassing. The water is then air stripped for final removal of acid gases and volatile organic carbon (VOC). Stripped water is treated in a moving bed bioreactor (MBBR) and a membrane bioreactor (MBR) for removal of bio-degradable COD. Non-biodegradable COD is mainly humic and fulvic acids, and these are removed by tight ultra-filtration followed by activated carbon polishing. The UF reject can be further concentrated by evaporation to produce a sludge which can be incinerated for energy recovery, or used as a soil improver in humic-poor areas. The remaining ammonium salts are then recovered by a combination of reverse osmosis, evaporation and crystallisation, to yield valuable salt products and very clean water for re-use.

Bench scale testing has been carried out to confirm the treatability of the water and the applicability of the methods. The methods and results are presented here.

## METHODOLOGY

### **Acidification and stripping**

Acidification and stripping were performed using a specially fabricated vessel with a liquid volume of

3.5l and a headspace of 7l. The sour water was filtered before stripping to remove solidified oil droplets. Acid was added gradually whilst monitoring pH with an in-situ analyser and off-gas was directed through a caustic scrubbing solution for sulphide capture. Air for stripping was supplied from a compressor via an air stone submerged in the vessel. Produced oil was decanted manually.

### **Biological Treatment**

An MBBR vessel of 2.1l and a 30% fill of Kaldnes K1 media was used with hydraulic retention times (HRT) between 2 and 5 days. The low fill % of Kaldnes media was due to the mixing limitations imposed by the small reactor. It was semi-batch fed with stripped sour water at hourly intervals with a peristaltic pump. A further test was carried out with 3 MBBR reactors in series, each 2.1l volume with 30% media fill.

An MBR vessel of 10.5l was fitted with a single 0.1m<sup>2</sup> Toray flat-sheet microfiltration membrane, and seeded with municipal activated sludge. It was semi-batch fed with stripped water at hourly intervals with a peristaltic pump. DO and pH were monitored and controlled by a PLC. Sulphuric acid was dosed to combat the pH rise as organic acids were digested. Treated water was withdrawn periodically by a peristaltic pump. HRT in the vessel varied from 7 (when the feed was diluted) to 21 days, MLSS was 14,000 to 20,000mg/l, and F:M ratio was 0.06 to 0.1 gCOD/g MLSS.d. Nutrients and antifoam were added daily to both the MBBRs and the MBR.

### **Ultra-/nano-filtration**

A range of nano- and ultra-filtration membrane coupons were tested using a Sepa-CF flat sheet test rig, with membrane coupons of 140cm<sup>2</sup>. The selection criteria were based on the maximum organics (colour) removal with minimum salt rejection.

### **Activated carbon**

PAC adsorption isotherms were generated using a jar test rig and a range of PAC types. This work

was used to help size GAC columns for further test work..

### **Reverse Osmosis**

A range of reverse osmosis membrane coupons were tested using a Sepa-CF flat sheet test rig, with membrane coupons of 140cm<sup>2</sup>. The selection criteria were based on the maximum ammonium salt rejection. Initial selection was on a synthetic mixture of ammonium salts.

### **Evaporation and crystallisation**

Evaporation and crystallisation were not tested at the bench scale, but tests are planned for the forthcoming pilot study.

## **RESULTS**

### **Acidification**

Acidification was shown to remove 75% of the total petroleum hydrocarbons. As expected, adding acid to a carbonate solution resulted in the evolution of carbon dioxide bubbles. This tended to cause a certain amount of foaming, although the oil slick which formed acted as a natural anti-foam agent. Hydrogen sulphide and sulphur dioxide were also released from the water by acidification, with the carbon dioxide bubbles acting as a stripping gas. Removal of oil and stripping of sulphurous gases and VOC's combine to reduced the COD of the water by up to 15%. Thiosulphate in the sour water reacts with sulphuric acid to produce sulphur dioxide and elemental sulphur, giving the acidified water a cloudy yellow tinge – at first this was mistaken for an oil-in-water emulsion.

### **Air stripping**

Air stripping removed 80% of carbonate alkalinity. 97% of hydrogen sulphide, and >90% of volatile organics such as benzene and acetone. Aerating the acidified water also caused a marked increase in colour of up to 200%. It is thought that the colouration is caused by oxidation of certain organics, including phenols and cresols which are oxidised to quinones. Humic and fulvic acids may also be in a highly reduced state exiting the retort,

and oxidise rapidly to their more typical dark brown/orange colouration. Colour was also seen to increase through the bioreactors, becoming stronger with increasing retention times in the aerobic environment.

### **Biological Treatment**

The MBBR was able to remove up to 55% of COD at an HRT of 5 days, dropping to just 10% at 2 days. Upon dilution of the feed, the MBBR performance improved back to >55%, indicating concentration inhibition at short HRT. The maximum attainable organic loading rate was around 30g COD/m<sup>2</sup>.d. The best recorded performance, using diluted feed, was a COD removal rate of 68%.

With 3 MBBR's in series, the total COD removal possible was close to 80%. The third reactor only removed about 1% of the COD, with the first taking 55% and the second the difference. The performance of the final reactor demonstrated that 20 to 25% of the COD in retort sour water is not biodegradable.

The MBR COD conversion rate peaked at 80% with a HRT of 20 days, indicating once again that about 20% of the COD is not biodegradable. Different sour water samples produced removal rates of between 75 – 80%, showing that the recalcitrant portion of the COD varies considerably. As with the MBBR, at one point in the testing a very strong sample of sour water was used, with a COD of over 40,000 mg/l. Without dilution, this caused a noticeable drop in performance of the MBR, and a sudden elimination of higher life forms (protozoa etc). Upon diluting the feed, the performance quickly recovered to >70% COD removal.

It is worth noting that at no time did the high ammonium concentration in the feed (up to 6,500 mg/l) affect the organic removal rate. Prior to the trials there was concern that a high ammonium concentration may cause inhibition, though this was not the case. The pH in the reactors was controlled to be < pH7.0 at all times, to ensure the ammonia

remained in its less toxic ionized form, NH<sub>4</sub><sup>+</sup>. Nitrification was not evident during the tests. There are many compounds in the water which are known inhibitors of nitrification, including phenol and pyridine. The pH was kept deliberately low to discourage nitrification.

### **Ultra/Nano-Filtration**

The most efficient membrane for removing non-biodegradable COD was Osmonics 1,000 MWCO, with a colour rejection of 55% and a salt rejection of just 10%.

### **Activated Carbon**

PAC dose required for final COD removal was of the order of 3g PAC per g of TOC and 1g PAC per g of COD.

### **Reverse Osmosis**

The best membrane for concentrating ammonium salts was Dow SW-HRLE with a salt rejection of >99% at 20 bar. The final permeate quality had an ammonia concentration of <10 mg/l, certainly suitable for re-use as cooling tower make-up water or similar.

## CONCLUSION

It is possible to treat retort sour water from oil shale processing without the need to use energy and chemical intensive steam stripping processes. The revised process necessarily involves multiple steps due to the highly contaminated nature of the water. At the same time as producing high quality permeate for recycling in the facility, valuable ammonium salts can be recovered for sale as fertilizer or chemical feedstock. The value of the captured by-products more than compensates for the high cost of treating retort sour water, making the process economically attractive. The RO permeate used for recycling is a vital resource in a water-scarce environment such as Australia.

## FURTHER WORK

Further studies have commenced to confirm and improve the concept of this wastewater treatment

process. A pilot plant has been constructed to treat a nominal 25 litres per day of retort sour water. The pilot will be a continuous end-to-end representation of the bench scale processes outlined above. It consists of a feed water storage vessel, an acidification/stripping/de-oiling vessel, dilution, an MBBR followed by an MBR, a tight UF filter, GAC column (s) and an RO filter.

Brine from the RO will be collected and sent to an evaporator/crystalliser vendor, to carry out pilot studies on separation and purification of the ammonium salts. This step will demonstrate the commercial viability of the process in terms of by-product recovery.

UF reject liquid will be sent to a vendor specialising in wastewater concentrators. The maximum concentration factor of this stream will be determined, to forecast waste disposal volumes and costs. Samples of the concentrated material will be sent to agricultural specialists to identify whether it could be used as a soil improver, or has any commercial value.

Samples of acidified/de-oiled water will also be processed using MPPE technology (macro-porous polymer extraction). MPPE has the potential to remove and recover much of the hydrocarbons and alkylated phenols, as well as some of the phenol and other aromatics, which would substantially reduce the load to, and therefore size of, the bioreactors (Pars et al, 1998).

A range of organic resins such as Amberlite XAD, will be trialled for removal of humic and fulvic acids from MBR permeate, as an alternative to the use of UF and GAC.

## REFERENCES

Bhargava, S.K., Garg, N., Subasinghe, N.D. (2008) In situ high temperature phase transformation studies on pyrite. *Fuel*, 2008.

Fox, J.P., Phillips, T.E. (1980). *Wastewater Treatment in the Oil Shale Industry*  
Laurence Berkeley National Laboratory

Healy, J.B. Jr, Langlois, G.W., Daughton, C.G. (1985). Bio-oxidation of organic solutes in oil shale wastewaters. *Water research* Vol 19, No. 11

Kamenev, I., Munter, R., Pikkov, L. (2002). *Wastewater Treatment in Oil Shale Chemical Industry. Symposium on Oil Shale in Tallin, Estonia, 2002.*

Oh, M.S., Foster, A.A., Crawford, R.W., Taylor, R.W., Coburn, T.T. (1992). Thermal decomposition of buddingtonite in oil shales. *Fuel* 1993, Volume 72 No.4

Pars, H.M., Meijer, D.Th. (1998) Removal of dissolved hydrocarbons from production water by Macro Porous Polymer Extraction. *Society of Petroleum Engineers, SPE 46577.*

Table 1. Sour Water Analysis and expected treated water quality

Species	Units	Typical values (Heating mode)	Reverse Osmosis Permeate Expected Quality
TSS	mg/L	40	<1
TPH (C <sub>10</sub> -C <sub>28</sub> )	mg/L	1 512	<1
TDS	mg/L	6 000	<50
pH		8.7	6.5
NH <sub>4</sub> -N	mg/L	6 197	9.5
H <sub>2</sub> S	mg/L	500	0
TOC	mg/L	15 129	<5
TOC from humic substances	mg/l	3,000	<5
TIC	mg/L	3 127	<5
COD	mg/L	35 000	<5
BOD <sub>5</sub>	mg/L	14 100	<5
Total carboxylic acids	mg/l	6,070	<5
Acetone	mg/L	127	<1
BTEX	mg/L	30	<1
Total phenols	mg/L	250	<1
Bicarbonate as CaCO <sub>3</sub>	mg/L	18 100	<10
Carbonate as CaCO <sub>3</sub>	mg/L	3 593	<10
Total alkalinity	mg/L	21 729	<10
Chloride	mg/L	890	2
Sulphate	mg/L	1 940	31
Sulphide as S	mg/L	200	0
Sulphite	mg/L	400	0
Total Kjeldahl Nitrogen (TKN)	mg/L	7 829	10
Cyanide, total	mg/L	8.90	0