

EVALUATION OF RUNDLE SPENT SHALE AS AN ADSORBENT
FOR THE TREATMENT OF RETORT WATER.

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ABSTRACT

Adsorption and desorption tests were performed on a number of raw and spent shale samples to determine the ability of these solids to adsorb the organic components from retort waters. All solid samples were extracted from the Rundle deposit, Queensland, the most advanced of Australia's oil shale developments. Spent shales produced in the laboratory and in trial runs of two pilot retorts were utilised. The retort waters were generated by Fischer Assay techniques and from a pilot retort trial.

Preliminary results show that a significant amount of organic carbon is adsorbed onto Rundle shales. The adsorptive capacity was found to be significantly greater than that reported for Colorado shales, this being attributed to the larger internal surface area of the Rundle shales. The major non-adsorbable components in the retort water have been identified (by GC/MS) as being normal carboxylic acids. Also, it has been demonstrated that the adsorbed organic material is not easily desorbed and that the spent shale has a high capacity for retaining water.

The results of this work indicate that:

- . co-disposal of retort water with spent shale is a feasible proposition
- . there is potential for using spent shale as an organic adsorbent in a water treatment scheme.

INTRODUCTION

Oil shales range up to 20% moisture content. With wet shales, such as those in Queensland, Australia, a drying step is usually required before retorting. Even with such a step, the volume of water generated during the retorting process (i.e. the residual moisture plus water formed during the pyrolysis reactions) is significant. For a plant producing 50,000 barrels of oil per day, which is using as feed material shale at 2% moisture yielding 100 litres of oil per tonne, a retort water

stream of approximately 2500m³ per day must be treated. During many retorting and condensation processes, retort water comes into intimate contact with both the solid matrix (e.g. dust carryover) and the oil. This results in a large number of organic and inorganic compounds being mixed into the wastewater stream. The actual conditions existing during the retorting and condensation process have a perceptible but unknown effect on retort water quality. Initial work has shown that single step treatment of this waste stream is infeasible (Dobson, et al., 1984; Bell et al., 1983) and that biological treatment is subject to severe inhibition (Stephenson et al., 1982).

Previous work from this laboratory on retort water treatment has reported on the gross parameters of retort water quality (Stephenson et al., 1982) as well as on the detailed speciation of the organic fraction (Dobson et al., 1984). The results of this work are summarised in the next section. In the present study, the work has been extended to test the feasibility of using the spent shale and other solids as an adsorbent for the organic carbon contained in the retort water. If successful, this opens the way for an adsorption step prior to biological treatment and, possibly, even for co-disposal of the retort water with the spent shale. Summary of Characterisation and Treatment Studies To Date

A number of retort water samples were generated by Fischer Assay retorting of oil shales from the Rundle, Queensland deposit (Lower Ramsey Crossing Seam) while one sample was obtained from a pilot plant test on this same shale. These samples were analysed for a number of gross parameters as detailed in Table 1. The variation in quality of these waters is attributable mainly to the extent of pre-drying employed prior to retorting as well as the condensation system used. More detailed analyses of retort water samples generated from Rundle oil shales have previously been reported (Bell et al., 1983). In particular, it was noted that the COD:BOD5 ratio is very high and, hence, these waters are not amenable to direct biological degradation. The major organic constituents in the

retort water have also been identified and quantified by GC/MS/FID analysis (Dobson et al., 1984; Bell et al., 1983). The work to-date has shown the C2 - C12 carboxylic acids to be the dominant class, comprising 50-70% of the organic carbon identified and up to 95% of the acid fraction. Phenolic compounds are the other major constituents of the acid fraction. The basic fraction consists mainly of nitrogen heterocyclic compounds with pyridines and quinolines dominant. C5 and C6 cyclic ketones dominate the polar neutral fraction while the non-polar neutral fraction contains mainly alkyl substituted benzenes and straight chain alkanes in low (approximately 200 ppb) concentrations.

TABLE 1 RETORT WATER PARAMETERS

	RW1	RW2	RW2	RW3	RW4	RW5	RW6	RW7
pH	8.5	8.5	8.9	9.1	9.0	9.0	3.0	9.5
Cond. (µmho/cm)	8800	9700	31500	22000	22000	13700	17100	12500
TC (mg/l)	4350	3525	12800	11600	7750	6500	4250	7265
TIC (mg/l)	268	266	2600	845	700	1120	0	800
TOC (mg/l)	4082	3059	10140	10755	6850	5380	4250	6465

- RW1 - Fischer Assay Retort Water
- RW2 - Fischer Assay Retort Water
- RW3 - Fischer Assay Retort Water (other laboratory)
- RW4 - Fischer Assay Retort Water (other laboratory)
- RW5 - Fischer Assay Retort Water
- RW6 - Fischer Assay Retort Water
- RW7 - PP3 Retort Water
- RW8 - Fischer Assay Retort Water

A number of treatment options have also been evaluated, the most promising being combined stripping-adsorption-biodegradation (Dobson et al., 1984). Our studies to-date have shown the effectiveness of activated carbon in reducing the Total Organic Carbon (TOC) levels in retort water by up to 70%. In particular, the TOC level in the base/neutral fraction was reduced by approximately 80%. GC/MS analysis of the retort water after activated carbon treatment showed this fraction to be mainly alkyl pyridines, as before, but at much reduced concentrations. In addition, BOD test data showed that the non-adsorbable fraction was highly degradable, confirming that the use of activated carbon in the treatment scenario is definitely a technically feasible option. Due to the voluminous amount of retort water which would need to be

treated, the cost of this option would, however, be high. The use of less costly adsorbents such as spent shales, clays and overburden as possible supports for wastewater treatment have been suggested. The possibility of co-disposal of retort water and spent shales has also been proposed. It is the aim of the present study to investigate the feasibility of using spent shales, claystone and raw shale from the Rundle deposit as adsorbents for retort water.

Multicomponent Adsorption onto Spent Shale

The adsorption of retort water onto spent shale is a complex phenomenon. Not only is the composition of the water complex and highly variable, but also, the solid matrix is quite heterogeneous in nature. The application of available multicomponent adsorption theory to this system is not straightforward. However, some guidance to experimental design and to the interpretation of results can be gained from examining the theories developed from studies on simpler adsorption systems.

Influence of Solid Matrix

The composition of a typical spent shale is approximately 95% mineral and approximately 5% carbon residue, depending on the degree of combustion. The minerals vary from deposit to deposit but generally contain a significant proportion of clay materials which may possess important adsorptive properties. Adsorption takes place at the surface and, as such, the adsorptive capacity will be influenced strongly by the available surface area. However, access to this surface area is controlled physically by the pore size. This is particularly important for retort water treatment as we are dealing with some very large molecular weight compounds. Both physical and chemical adsorption would be applicable to a heterogeneous material such as spent shale, and many factors besides the physical dimensions of the adsorbent will be important in determining the adsorptive potential. For example, the surfaces of some minerals (e.g. Smectite) exhibit a constant surface charge through which either cation or anion (but not both) adsorption is possible. Other minerals (e.g. Kaolinite) exhibit a constant surface potential and the surface charge is therefore pH dependent with either cations or anions being adsorbed. The pH at which these solids change from a positive to a negative charge (iso-electric point) varies considerably from mineral to mineral and with the concentration of charge determining

ions such as Ca^{2+} and Mg^{2+} . Rundle shales contain both these types of minerals (Krol, 1984) and, as such, exhibit both a pH dependent and a pH independent effect of charge at various points in the shale matrix. Thus, ionic species in retort water will experience in addition to the normal physical attraction (due to Van der Waals forces) either electrostatic attraction or repulsion at the charged surfaces. The electrostatic forces will allow for selective adsorption of cationic or anionic species. Also the high levels of Ca^{2+} and Mg^{2+} known to occur in leached solutions from Rundle shale will tend to raise the iso-electric point into the more basic range. The raw and spent Rundle shales also possess considerable surface area and micropore structures (see below) and, therefore, are expected to exhibit significant physical adsorption even without the presence of charged surfaces. Another factor to be considered is that some dehydrated clays possess an expanding-lattice, and exhibit, on swelling, a far greater surface area than indicated by B.E.T. analysis (e.g. Montmorillonite, which has been detected in Rundle shales).

The carbon residue on the spent shale has some of the characteristics of "activated carbon"; as with activated carbon, however, the adsorptive properties will depend to a great extent on the processing conditions. For example, it has been suggested (Weber et al., 1980) that activated carbon produced below 500°C develops acidic surface oxides (e.g. carboxylic acid anhydrides) and negative surface potentials which promote the adsorption of basic compounds. The functional groups formed on the solid surface are highly specific in their adsorption potential (e.g. it is suggested that carbonyl groups of the quinone form will enhance adsorption of aromatics while carboxylic acid anhydrides will reduce adsorption of many aromatics). Similar patterns might be expected for Fischer Assay retorted shales or other non-combusted spent shales.

Carbon activated around $800\text{-}1000^{\circ}\text{C}$ is capable of adsorbing acids owing to the formation of basic surface oxides (and positive surface potential). Also, the presence of surface oxygen complexes imparts a polar character to the activated carbon, promoting the adsorption of polar organic solutes. This is likely to be the situation for partially combusted spent shales.

Solute-Solvent Interactions

As detailed above, retort water contains many inorganic and complex organic compounds. Major considerations in regard to the competitive adsorption of an organic species are its: solubility; hydrophobicity; affect on surface tension; overall classification (acid, base or neutral); degree of dissociation.

Species in the acid and base fractions will be subject to selective adsorption due to either/or both surface charge effects and to the degree of dissociation of the species. The non-dissociated neutrals should show good adsorption over a wide range of solution conditions, with adsorption increasing with the degree of hydrophobicity. Solution parameters which can significantly affect many of the above solute-solvent interactions are pH and ionic strength.

The pH can not only affect the surface charge but also the degree of dissociation of the dissolved organic species. For uncharged surfaces, both neutral and ionized forms of the organic species can adsorb, the latter adsorbing as salts. Melander and Horvath (1980) note that the adsorption of the neutral undissociated form is much stronger than that of the ionized forms, as the latter interact with the solvent water much more intensely. Manes (1980) notes that even very low concentrations of the undissociated form may still be preferentially adsorbed relative to the salt. Spent shale most probably contains both charged and uncharged surfaces with the charges being variably positive and negative, while the water consists of acids, bases and neutrals. For such a multicomponent system, the pH will change the selectivity of adsorption but at the same time may not necessarily vary the overall TOC removal. If, however, sites on the solid do exist for which molecules and ions do not compete, a maximum adsorption could occur at an intermediate pH, (Myers and Zolandz, 1980). It has been shown that the adsorption of humic acids onto activated carbon is reduced at low pH (Youssefi and Faust, 1980). This may be the case for the adsorption of the non-extractable portion (approximately 30% of TOC) of the Rundle retort waters, the characteristics of which suggest it is comprised largely of humic acids.

The effect of ionic strength on multicomponent adsorption is not as well delineated as for the pH

effect. Melander and Horváth (1980) conclude that the addition of salt increases retention onto non-polar sites for unionized solutes, attributing this to the increased surface tension. For ionized species, they showed that salt addition at low ionic strengths decreased retention. At high concentrations of salts, however, increasing the salt concentration increased the binding of the ionized organic solute. Other work has shown (Myers and Zolandz, 1980) that adsorption of nitrophenol and phenol at high pH values is enhanced by the addition of salt; this agrees with the above trends. Also, it is worth noting again that the salt content of the solution (e.g. Ca²⁺ and Mg²⁺ concentrations) can markedly affect the isoelectric point and hence the charge on the solid matrix at a given pH.

Desorption

Although adsorption is not necessarily reversible, the various factors noted to be important for adsorption will affect to some extent the desorption process. Of particular interest to the co-disposal option of retort water and spent shale is the effect of flushing with rain water, which will introduce a large variation in the pH and ionic strength and their associated effects.

The above discussion indicates that spent shales and raw shales from the Rundle deposit would be expected to exhibit specific, selective and non-selective adsorption and desorption. It is also probable that the overall adsorption and desorption and selectivity will be dependent both on the pH and on the ionic strength of the solution. Temperature is also likely to have a significant effect as it will affect the rate of chemisorption, the surface tension, activity coefficients and the solubility products.

SURFACE AREA MEASUREMENTS

As noted above, the adsorption capacity is to some extent dependent on the pore structure of the adsorbent. The surface area and micropore size distribution of the following Rundle samples were measured:

	Code
Lower Ramsay Crossing (LRX) raw shale	RS1
Claystone	RS2
Pilot Plant 1 (PP1) spent shale	RS3
Pilot Plant 2 (PP2) spent shale	RS4

Pilot Plant 3 (PP3) spent shale	RS5
LRX spent shale ex Fischer Assay	RS6
Kerosene Creek (KCK) spent shale ex Fischer Assay	RS7
LRX 1 Laboratory Reactor	RS8

A Quantasorb Sorption System, essentially a B.E.T. nitrogen adsorption process, was used in the analysis. Triplicate measurements were made for each sample. The results are summarised in Table 2 together with results for Colorado shales (Fox et al., 1980). These results show that all of the Rundle spent shales exhibit a micropore structure, and have a relatively large surface area compared to Colorado spent shales. It is interesting to note that both the raw shale and claystone also have significant internal surface area, whereas Colorado raw shales have essentially no microporous structure or internal surface area (Tisot, 1962). A comparison of the specific surface area for LRX raw and LRX spent shale ex Fischer Assay indicates a significant increase in surface area on retorting.

TABLE 2 SPECIFIC SURFACE AREA AND MEAN MICROPORE SIZE MEASUREMENTS

	Sample	Particle Size Range (µm)	Specific Surface Area (m ² /g)	Mean Pore Size (Å)
Rundle Shales	Raw Shale RS1	<120	14.5 ± 1.8	40
	Spent Shale RS6	<120	21.0 ± 3.5	53
	Claystone RS2	<120	8.3 ± 0.5	48
	Spent Shale RS4	<120	21.7 ± 3.3	29
	Spent Shale RS5	<120	11.8 ± 0.8	31
	Spent Shale RS7	<120	29.6 ± 0.6	52
	Spent Shale RS3	<120	28.0 ± 0.7	53
	Spent Shale RS8		14.4 ± 0.7	
Colorado Shales		63-250	4.77	
		<63	4.76	
		<63	6.63	
		63-250	9.20	
		<63	3.50	
		63-250	3.37	

ADSORPTION STUDIES

The adsorption tests were performed by mixing 50g of solid with 50 ml of retort water in a 250 ml conical flask and allowing the mixture to equilibrate in a shaker bath (25°C) for periods of 1 hour, 1 day, 2 days and 5 days. After these periods, the samples were analysed for pH, conductivity, total carbon and total organic carbon (TOC).

The results for the TOC adsorption tests are summarised in Table 3 together with results from similar studies done with Colorado shales (Fox et al., 1980). The capacity of the shale to absorb and retain water was also measured using the method outlined in ASTM (1979). The 'maximum' water absorption results are also presented in Table 3. This method does not in fact give the maximum possible water retention. A better estimate of the maximum holdup is obtained by carrying out a capillary pressure versus saturation analysis for both wetting and drying conditions. This analysis has been done for PP1 spent shale. The saturated

water content measured by this method indicated a water hold-up capacity of around 0.50 ml/g, i.e. 20% higher than the value presented in Table 3. It should be noted that all the above hold-up tests were performed with distilled water and may not be directly applicable to retort water. This is because the organics and salt content of retort water will significantly affect its surface tension. This will affect the absorptive capacity. Water absorption curves need to be developed for actual retort water. Also, the hold-up will be a function of the packing density of the waste shale.

Characterisation of a number of retort waters after adsorption onto the solids was performed by GC/MS analysis, following methylene chloride extraction into acids, neutral and basic fractions. The result for one such analysis is presented in Table 4. This is the analysis of the adsorbate of retort water RW8 on spent shale sample RS8. The analysis of three other adsorbates produced by adsorbing this same retort water RW8 onto three other Rundle spent shales produced almost identical chromatograms.

TABLE 3 SUMMARY OF TOC ADSORPTION DATA

Solid Support (Adsorbent)	Maximum Water Absorption (ml/g)	Retort Water (Adsorbate)	Specific Adsorption (mg TOC/g)	Equilibrium Adsorbate Concentration (mg/l TOC)	pH	Conductivity (μ mho cm^{-1})
Raw shale RS1	0.31	RW2	1.9	1154	8.0	20,300
		RW4	6.4	4387		
		RW6	3.2	2180		
Claystone RS2	0.34	RW2	1.7	1409	7.9	18,800
		RW4	6.2	4550		
		RW6	2.9	2510		
Spent shale RS3	0.41	RW2	2.2	875	7.8	11,500
		RW3	0.9	9220		
		RW6	3.1	2320		
Spent shale RS4	0.39	RW3	3.7	6445	8.3	35,000
		RW4	5.1	5675		
		RW6	3.4	1940		
Spent shale RS5	0.25	RW3	0.7	9400	9.1	38,000
		RW4	4.0	6800		
		RW6	2.7	2650		
		RW7	2.1	2200		
		RW7	2.1	2133		
Spent shale RS6	0.34	RW1	3.0	1115	9.1	12,900
		RW3	3.5	6690		
Spent shale RS7	0.40	RW5	5.5	1350	8.6	20,000
		RW4	5.4	5400		
Spent shale RS8	0.34	RW8	4.0	2450	9.6	13,300
Colorado Shales			0.0-1.6			

TABLE 4 MAJOR ORGANIC CONSTITUENTS IN ADSORBATE (RW8 on RS8)

Acid Fraction	Conc. mg/1	Basic Fraction	Conc. mg/1	Neutral Fraction	Conc. mg/1
Ethanoic acid	1294	Pyridine	7	Cyclopentanone	11
Propanoic acid	305	2-methyl pyridine	6	Methylcyclopentanone	11
2-methyl propanoic acid	33	3-methyl pyridine) 4-methyl pyridine)	2	Ethyl Cyclobutenone	3
Butanoic acid	143			Cyclohexanone	6
3-methyl butanoic acid	30	4-ethyl pyridine	1	C ₂ Cyclopentanone	6
Pentanoic acid	108	2,4-dimethyl pyridine	1	C ₂ Cyclopentanone	2
CA*	1	2,6-dimethyl pyridine	1	Methylcyclopentenone	0.6
CA	3	Aniline	-	C ₂ Cyclopentenone	6
Nitrophenol	1			C ₂ Cyclopentenone	2
4-Methyl pentanoic acid	8			Cycloheptanone	2
Hexanoic acid	108			Unknown 1	1
CA	5			Unknown 2	2
CA	6			Phenol	1
CA	5			Unknown 3	1
Heptanoic acid	165			Unknown 4	1
Phenol	66			C ₂ N-substituted piperidine	3
CA	4				
CA	25			Unknown 5	1
CA	6			Unknown 6	2
Octanoic acid	116				
Cresol	12				
CA	9				
CA	19				
CA	8				
CA	5				
Nonanoic acid	42				
CA	4				
CA	8				
CA	4				
Decanoic acid	8				
Undecanoic acid	14				
2-methyl benzoic acid	5				

CA* unidentified carboxylic acid

Discussion of Adsorption Studies

Table 3 contains a summary of all the adsorption data, together with details of the particular retort water used. Because of the variety of retort water used to generate the data, the temptation to construct continuous isotherm curves and label them as such was resisted.

The lowest adsorption occurred with retort water RW3. This water was provided from a Fischer Assay analysis carried out at an outside laboratory,

and it is evident from Table 1 that its composition is significantly different from the other waters. In particular, a much higher conductivity and inorganic carbon concentration are noted. It was noted earlier that ionic strength can affect multicomponent adsorption. Since this laboratory Fischer Assay water appears anomalous for Rundle shales and since it was collected from a multitude of assays, it is postulated that some random contamination has occurred. However, the effect is

of interest.

The organic carbon in all other retort waters tested was significantly adsorbed on all supports. The levels of adsorption are higher (up to 4 times) than those reported for U.S. shales (Fox et al., 1980). This increased adsorption is in part attributed to the large surface areas of the Rundle shales, but as noted above, there are many other complicating factors. Indeed, the highest loadings were achieved with raw shale and claystone, the surface areas of which were significantly less than some of the spent shales. In all cases, adsorption was rapid with greater than 90% occurring in the first hour. The change in all other parameters followed the same trend, remaining essentially constant after the first hour. All adsorbates were found to be basic, even those produced with the acidic retort water (RW7). The conductivity of the adsorbates was generally higher than that of the retort waters, indicating leaching of salts from the shales, the extent of this increase varying with the processing method.

The specific water absorption tests indicated that spent Rundle shale can retain up to half its weight in water before drainage will occur. It should be noted though that these tests were carried out with distilled water and, hence, need to be repeated with retort water. It is expected that both organic content and ionic strength will affect the surface tension and, therefore, water absorptive capacity.

The compounds presented in Table 4 are the major identifiable components in retort water following adsorption onto the spent shale. Comparison of this data with that of untreated Rundle retort water (Bell et al., 1983; Dobson et al., 1984) indicates that a significant proportion of the base and neutral fractions have been removed by adsorption onto the spent shale. A significant fraction of the higher molecular weight acids is also removed. The major portion of this adsorbate consists of lower molecular weight normal carboxylic acids. This data is encouraging in that the more environmentally significant and refractory compounds are contained in the adsorbed fraction while the major compounds in the non-adsorbable fraction are readily biodegradable. These results are in agreement with those reported by Fox et al., (1980) for the adsorption of in-situ retort waters onto Colorado spent shales, and with those from work done

in our laboratory on the adsorption of Rundle retort water onto activated carbon.

The results of Stuber and Leenheer (1978), however, show an opposite trend to the above, in that the principal retort water components adsorbed are from the acid fraction. It would appear in the work of Stuber and Leenheer that the salts of the acids were adsorbed preferentially over the undissociated bases. A possible explanation for such a phenomenon is that selective adsorption took place due to a positively charged mineral or positively charged basic surface oxides associated with the residual carbon. Various other effects due to pH, ionic strength and actual dissociation of the organic species also need to be considered. It is important to note that in the present study, a significant amount of the acid fraction is also adsorbed, with only the lower molecular weight, more soluble species, being excluded. Hence, it would be necessary to look at the actual compounds in the study of Stuber and Leenheer to see which were or were not adsorbed.

These apparently conflicting results illustrate that spent shale exhibits selective adsorption and, from the earlier discussion, it is clear that this selectivity and the adsorption capacity will vary with the composition of the raw shale and with the method and degree of processing. It appears feasible that for a given shale the adsorptive capacity and selectivity could be optimised. For example, from the earlier discussion on activated carbon, it may be deduced that spent shale combusted at more elevated temperatures could decrease the ability of the residual carbon to adsorb the more environmentally important compounds. Combustion also has the potential to change the mineral forms and surface charge and, hence, selectivity of adsorption. Combustion could also reduce the surface area of the residual carbon and possibly that of the minerals, thereby reducing the overall adsorptive capacity. It must be noted that two of the Rundle Pilot Plant shales in this study were at least partially combusted during the retort processing. Thermal history of the spent shales, however, was not disclosed.

DESORPTION STUDIES

Batch Desorption Tests

Desorption tests were carried out on the same solids samples as were used in the adsorption

by studies. In these tests, the adsorption of the retort water was carried out in a similar manner i.e. 150 g of solid sample was mixed with 150 ml of retort water in a 250 ml conical flask for 5 days at 25°C in a reciprocating shaker bath set at 60-70 shakes per minute. The adsorbate was vacuum filtered through a 0.30µ membrane filter and the filtered solid was then used in the desorption experiments. Separate 25g samples of this wet solid (onto which retort water compounds had adsorbed) were mixed with 100 ml of distilled water in 250 ml conical flask for periods of 1 hour, 1 day, 2 days, and 5 days at 25°C. After these periods the mixtures were then filtered through a 0.30µ filter. The adsorbates and desorbates were analysed for pH, conductivity, total carbon, total inorganic carbon and total organic carbon.

The adsorption and desorption results are summarised in Table 5. Some explanation is required on how the various specific values were calculated.

The specific release of carbon can be defined as the total mass of carbon released into the desorbate per gram of dry shale.

$$\text{Specific Release (mg/g)} = (\text{Cd}/\text{W}) \times \text{V}$$

where Cd = Concentration of carbon in desorbate (mg/l)

V = Volume of liquid in sample = Volume of desorbate + Vp (l)

Vp = Volume of liquid retained in pores at end of adsorption test.

W = Weight of dry shale (g)

The specific release consists of carbon previously held in the pores with the free water as well as carbon which has desorbed from the surface of the support. It is assumed that the concentration of carbon in the liquid in the pores is equal to that in the bulk solution at equilibrium and remains as such following filtration. i.e. there is negligible partitioning between the liquid in the pores and the bulk liquid. It is also assumed that this carbon, the specific pore content, re-equilibrates with the bulk solution on the addition of distilled water:

$$\text{Specific Pore Content (mg/g)} = \text{Cp} \times \text{Vp}$$

Cp = concentration of carbon in pores (mg/l)

From the above results we can calculate the specific desorption:

$$\text{Specific Desorption} = \text{Specific Release} - \text{Specific Pore Content}$$

TABLE 5 **DESORPTION TESTS**

Shale (Retort Water)	Specific Adsorption (mg/g)	Specific Pore Content (mg/g)	Specific Release (mg/g)	Specific Desorption (mg/g)	Desorption % ^{**}
LRX Raw					
RS1 (RW4)	6.4	1.4	2.0	0.6	9
Claystone					
RS2 (RW4)	6.2	1.6	2.1	0.5	8
Spent Shale					
RS3 (RW3)	0.9	3.5	3.0	-0.5	0*
Spent Shale					
RS4 (RW4)	5.1	2.2	1.65	-0.55	0*
Spent Shale					
RS5 (RW4)	4.0	1.9	4.2	2.3	58
Spent Shale					
RS6 (RW3)	3.5	1.5	2.4	0.9	26
Spent Shale					
RS7 (RW4)	5.4	1.8	4.3	2.5	46

* adsorption actually occurred **percent of TOC which was originally adsorbed

The above calculations require the knowledge of V_p . Because the filtered solids were not weighed this value was estimated. It was assumed that the volume of liquid contained in the pores was equivalent to the maximum water absorption as given in Table 3.

Sequential Desorption Tests

A number of sequential desorption tests were also performed to determine the effect of successive leachings with distilled water on the removal of the adsorbed organics. In the tests, three successive desorptions were carried out. 50 g of loaded wet solid were contacted with 100 ml of distilled water for 24 hours. The desorbates were removed by filtration and the solids recontacted with 100 ml of distilled water. This desorption procedure was then repeated. The results from this set of tests are given in Table 6.

TABLE 6 SEQUENTIAL DESORPTION TESTS

Shale (Retort Water)	Specific Adsorption (mg/g)	% Desorption *		
		Sequential Leach Batch No.		
		1	2	3
Raw Shale RS1 (RW6)	3.20	5.3	29	3
Claystone RS2 (RW6)	2.87	6	27	2
Spent Shale RS3 (RW6)	3.06	0	8	1
Spent Shale RS4 (RW6)	3.44	2	14	2
Spent Shale RS5 (RW6)	2.73	0	17	0

* percentage of TOC originally adsorbed

Discussion of Desorption Results

The values of conductivity, total organic carbon and total inorganic carbon in the desorbates all increased rapidly in the first hour of desorption and then did not change appreciably during the following five days of the test. This initial rapid change is attributed mainly to the attainment of equilibrium between the water occluded in the macropores of the solid and the bulk desorbate solution i.e. due to diffusion of the

carbon held in solution within the pores of the spent shale at the end of the adsorption stage.

Tables 5 and 6 show that there is significant variation in the desorption characteristics of the various loaded shales, indicating that the retention of organics is influenced by both the quality of the original retort water and the nature of the solid adsorbent. The nature of desorption in these heterogeneous systems is just as complicated as that of adsorption. Factors influencing the competing adsorption (e.g. pH, ionic strength, nature of solid) play an important role in the desorption as well. It is pointless at this early stage of our study to attempt to interpret the results in any detail; general observations only will be made.

The percentage of adsorbed organics, which were desorbed, varied considerably, from less than 0% (i.e. adsorption occurred) to 58%. However, the desorption from most shale samples was less than 10% in the first desorption run (see Tables 5 and 6). The variation of the results in Table 5 and Table 6 indicates that both the original retort composition and the nature of the solid support have a marked influence on the magnitude of desorption. For example, sample PP3 spent shale, (RS5) when adsorbed with retort water RW4, experienced 58% desorption, but experienced zero desorption, when contacted with retort water RW6. The sequential desorption tests showed that approximately 35-37% of the original adsorbed organic carbon was desorbed from the unprocessed shales, but only 9-18% was desorbed from the spent shales. This indicates that the spent shales exhibit more effective binding of the adsorbed organic fraction. It is interesting to note that for all solid samples most desorption occurred with the second sequential leach, with minimal amounts of desorption occurring for the first and third leachings. This indicates that desorption is not related simply to the equilibrium concentration of the solution other factors (e.g. ionic strength) are also important.

CONCLUSIONS

Rundle raw shale, claystone and spent shale all exhibited a high capacity for retaining water (up to 50% of dry weight) and for significantly adsorbing the organic carbon content of both Fischer

Assay and pilot plant (PP3) retort waters. In tests to-date, specific adsorption loadings from 0.7 to 6.4 mg of TOC/g shale have been achieved, although this does not represent the maximum capacity of the shale.

The major non-adsorbable components in the retort water have been identified (by GC/MS) as being lower molecular weight normal carboxylic acids. Comparison with the composition of untreated retort water indicates that a significant proportion of the base and neutral fractions are adsorbed. This data is encouraging in that the major identifiable compounds in the non-adsorbable fraction are readily bio-degradable and a significant proportion of the more environmentally significant and refractory compounds are retained by the solid material.

The heterogeneous nature of the shales containing various clays and carbon forms provides for a variety of possible specific or selective adsorption mechanisms. The method of retorting of the shale and the degree of combustion will affect both the selectivity and adsorption capacity.

It has also been demonstrated that the composition of the retort water - a function of shale type and processing conditions - has a significant effect on the adsorptive capacity of a particular waste shale.

Desorption studies have shown that most of the adsorbed organics are not easily desorbed, but again, there is considerable variation with the composition of retort water adsorbed, and the nature of spent shale adsorbent.

The preliminary results are encouraging in that co-disposal of retort water with Rundle waste and spent shale may be a feasible alternative to separate disposal concepts. However this will need further confirmation for specific processes because of the dependence of water composition and spent shale properties on the retorting process.

Our results also indicate a potential use for Rundle spent shales, as adsorbent for organics removal in the treatment of oil shale process waste water for re-use or release.

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