

## OIL SHALE PROCESS WATER EVAPORATION

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### ABSTRACT

Evaporation research is being conducted on oil shale process wastewaters at Laramie, Wyoming using Class-A evaporation pans. Evaporation rates from the pans are measured at 30-minute to hourly intervals throughout the evaporation season. In addition, meteorological parameters are collected simultaneously.

Based on the analysis of evaporation and meteorological data, it was found that Class-A pan water temperatures were a good indicator of the relative evaporation rates between process waters and that the majority of pan evaporation occurred between noon and midnight.

Actual evaporation of two oil shale process wastewaters were found to evaporate 9.9 and 18.3 percent slower than freshwater on a daily basis. Regression models for the oil shale wastewaters were developed to predict hourly Class-A pan evaporation, using those meteorological parameters found to have the most significant effects on evaporation (air temperature, relative humidity, solar radiation and wind). Present studies are concerned with emission rates of the evaporation process and its possible pollution effect on the environment as well as evaporation rates of different oil shale process waters.

### INTRODUCTION

A significant environmental concern associated with the development of an oil shale processing industry relates to the handling, containment, and disposal of aqueous solutions associated with the processing methods used. Such effluents are generally heavily contaminated with organic and inorganic constituents. The published literature reveals that there is an acute lack of research data pertaining to containment and disposal of low-quality waste effluents.

Environmental data indicate that for each gallon of shale oil produced, approximately a gallon of effluent water is generated (Fox, 1980). Disposal

must, therefore, be managed in ways that minimize the introduction of constituent contaminants into the natural environment. The conventional procedure for preventing polluted water from entering the surface water and groundwater system in the arid west is to contain the water in lined retention ponds and allow it to evaporate. This procedure requires precise data on evaporation rates, on a local microclimate basis, to properly size the retention system and evaluate the contaminated waters for evaporative potential.

Past efforts at estimating evaporation rates have met with only partial success. Oils present in the water act as surfactants and high concentrations of dissolved solids (i.e., salts) drastically reduce vapor pressures, interfering with the natural evaporative processes. Therefore, sizing wastewater evaporation ponds becomes a guessing game without reliable estimates of evaporation rates. Use of evaporation rates obtained from present state-of-the-art fresh water evaporation models in pond design could result in a potential overflow with the release of toxic and undesirable substances into the environment.

Another aspect of evaporation which has received little attention in the past is the emissions being released during the evaporation process from the evaporation ponds. A literature search conducted on this item revealed that there is little information available on this subject. It is conceivable that the release of emissions from evaporation ponds could possibly be a source of pollution to the human and physical environment.

Research, therefore, is needed in both the evaporation and emissions areas to accurately assess the feasibility of using evaporation ponds or co-disposal for the ultimate disposition of oil shale process waters. If oil shale is to become a viable alternative for diminishing petroleum supplies, these problems should be addressed so that reliable

techniques for disposal of the wastewaters can occur with a minimum of environmental effects.

The research work reported on in the following pages is an attempt to initially address some of these critical questions. Future research has been planned to utilize these types of data to develop an evaporation model more suitable to predict evaporation rates from these waste effluents.

#### PURPOSE AND OBJECTIVES

The purpose of the research investigations which are reported in this paper are to investigate evaporation rates of oil shale wastewaters in comparison to fresh water. The comparisons were made on an hourly basis to identify daily trends in evaporation rates between the waters.

Specific objectives to achieve this purpose were:

1. Determine the effects of climatological parameters on the evaporation rate of oil shale process waters.
2. Determine the effect of chemical composition of process waters on evaporation rate.
3. Develop an evaporation model based on the significant climatological parameters to predict oil shale process water evaporation.

#### METHODOLOGY

A field research investigation site was established at Laramie, Wyoming which had climatological instrumentation to collect all important climatological parameters (air temperature, relative

humidity, solar radiation, barometric pressure and wind speed) on an hourly basis along with three Class-A evaporation pans to measure evaporation rate and amount. Evaporation rate and amount were measured using Belfort water level recorders mounted on filling reservoirs. A float valve system located in the Class-A pans released water from the reservoirs to meet evaporation demands of the pans. Figure 1 indicates the layout of the field research sites.

The two oil shale waste effluents used in this project are termed: retort water and stripped water. Retort water is produced directly from the retorting process and has high concentrations of oil, grease and ammonia. Stripped water is retort water which has been processed to decrease concentrations of these elements.

The measured results of evaporation were determined by a direct comparison of evaporation between the two oil shale process waters and the fresh water. Regression analysis was also used to verify the analysis and to develop the hourly modeling equations.

#### RESULTS

The two oil shale wastewaters were found to evaporate similarly to fresh water, but at a reduced rate. Figure 2 shows a comparison of hourly Class-A pan evaporation for fresh, stripped and retorted waters. Data for Figure 2 was compiled by averaging approximately seventy days of hourly pan evaporation rates collected between June 1 and October 4, 1982 from the Laramie, Wyoming research site.

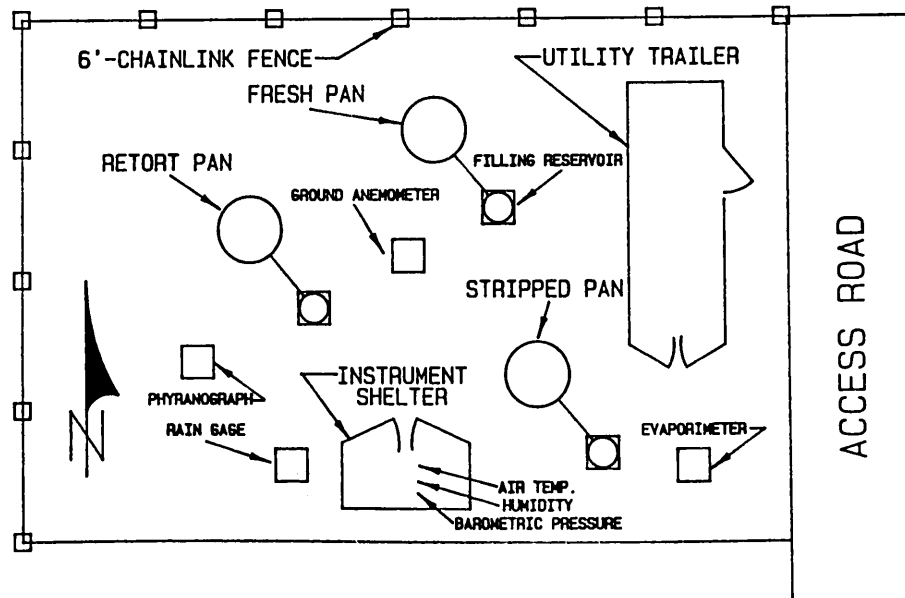


Figure 1. Layout of Field Monitoring Station (Laramie, WY)

AVERAGE HOURLY PAN EVAPORATION  
 JUNE 1 - OCTOBER 4, 1982

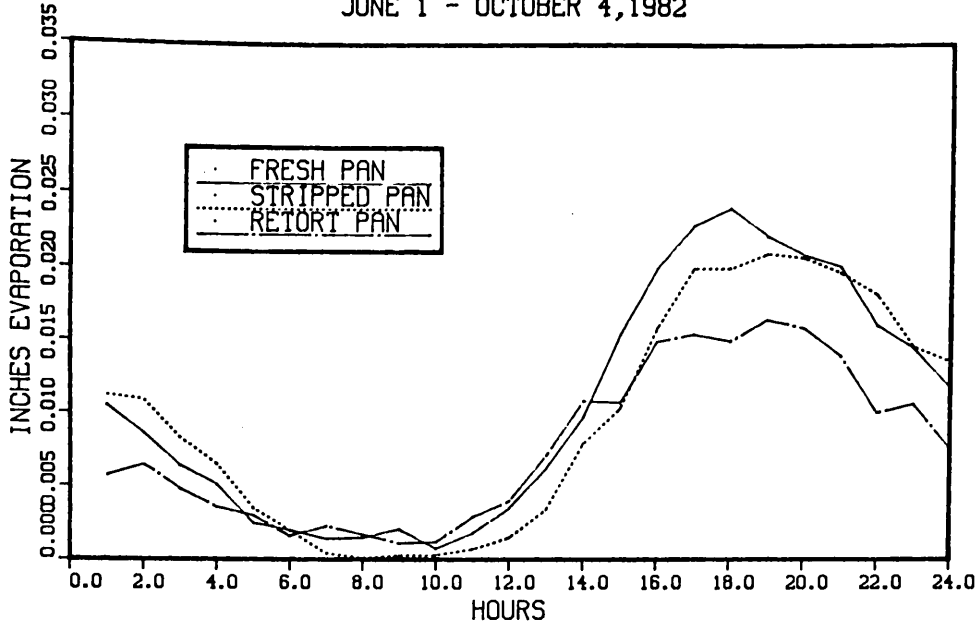


Figure 2. Average Hourly Pan Evaporation

As a means of comparing evaporation rates, mass curves were prepared by summing hourly evaporation data. Data were eliminated from the curves unless they existed simultaneously for all pans. The mass curves depicted in Figure 3 show a linear relationship between all three waters. Based on the slope of the mass curves, the stripped water evaporation rate was

9.9 percent less than the fresh water, while the retort water was 18.3 percent less. Table 1 lists the regression equations between the mass curves in Figure 3. To further analyze trends in evaporation, Figure 4 was prepared to illustrate a percentage breakdown of daily evaporation into six-hour periods. Inspection of Figure 4 shows that there are

MASS CURVES  
 CLASS-A PANS

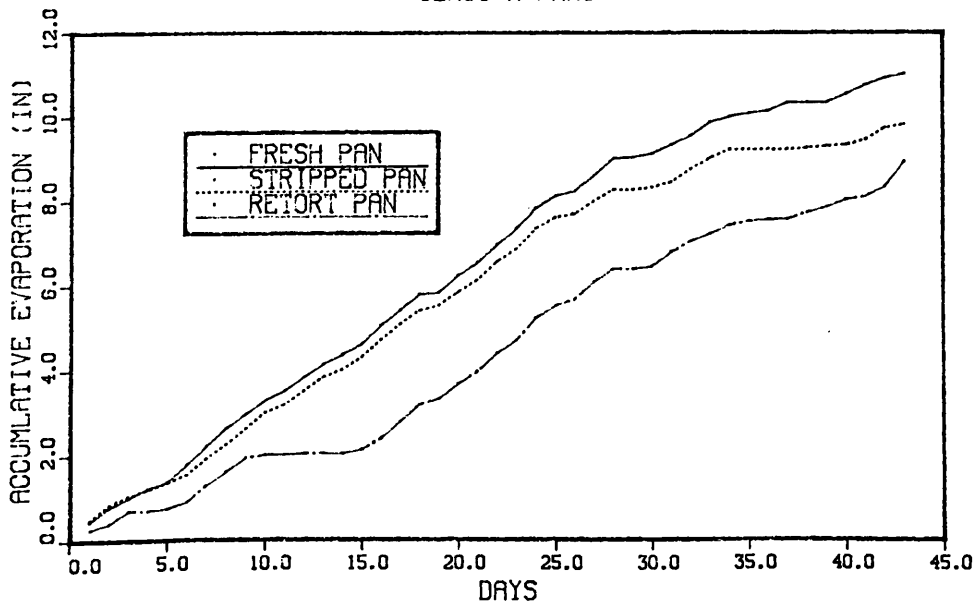


Figure 3. Mass Curves of Pan Evaporation

## COMPARISON OF PAN EVAPORATION

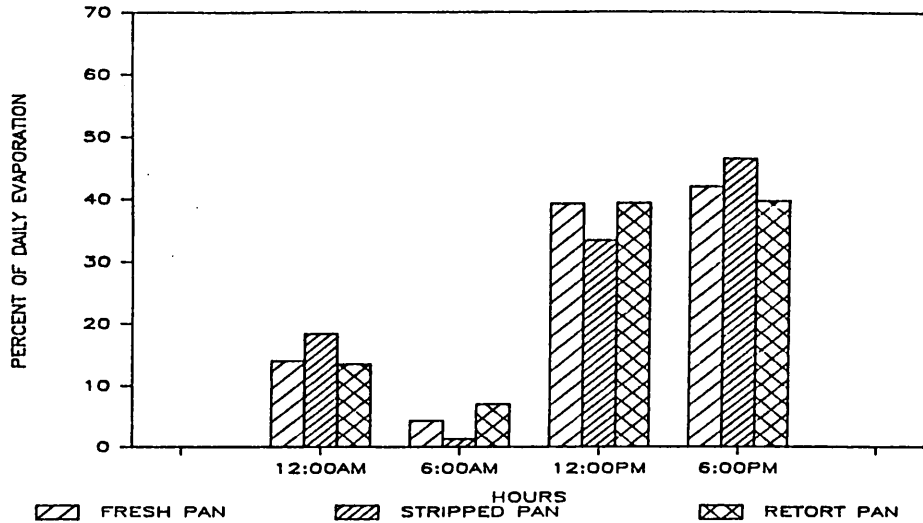


Figure 4. Percentage Comparison of Pan Evaporation in Six-Hour Intervals

Table 1. Regression Analysis Between Pan Mass Curves.

Y (in)	X (in)	y = mx P b R <sup>2</sup> (%)
FRESH PAN	STRIPPED PAN	y = 1.11 X -0.111 99.8
FRESH PAN	RETORT PAN	y = 1.22 X +1.11 97.4
FRESH PAN	EVAPORIMETER	y = 0.692 X +1.15 98.7
STRIPPED PAN	STRIPPED TANK	y = 1.43 X +1.48 96.3

essentially no differences in the timing of rates between evaporation periods for the three waters. Further examination of Figure 4 also shows that the bulk of daily evaporation occurs between noon and midnight. Details on other similar evaporation devices (large tank and evaporimeter) can be found in Haass (1985).

A literature search of the main parameters affecting the evaporation process was done. The main parameters for evaluation on a microclimate basis were found to be solar radiation, temperature (air to water)-vapor pressure deficit, humidity, wind speed, and chemical composition of the water.

The results of this literature search were used along with the collected hourly data on evaporation and climatological parameters to develop hourly evaporation rate equations for each type of water. The model evaporation rate equations were based on four of the climatological parameters felt to be most important: air temperature, relative humidity, solar radiation and wind velocity. The model equations were

developed using multiple linear regression analysis on the four climatological parameters. The model equations use calibrated coefficients for the different types of process waters.

The primary difficulty involved in developing an hourly model is relating changes in evaporation rates to meteorological parameters. More specifically, changes in evaporation rates generally lag behind changes in meteorological conditions. Further complicating the development of a model is the fact that meteorological parameters have cyclic trends which are not in phase on an hourly basis.

In developing the model equations, it was important to determine the hourly interrelationships of meteorological parameters. Approximately 90 days and 50 days of hourly data were averaged and typical plots of daily solar radiation and wind speed are indicated in Figures 5 and 6, respectively.

Coefficients of determination (R<sup>2</sup>), obtained from linear regression analyses, were used to determine lag time differences between meteorological parameters. Table 2 shows a comparison of (R<sup>2</sup>) values for various lag times between relative humidity and air temperature. Likewise, Table 3 shows a typical situation for the regression fit between air temperature and solar radiation. The regression analysis determined that air temperature and wind velocity lag relative humidity by one hour while solar radiation

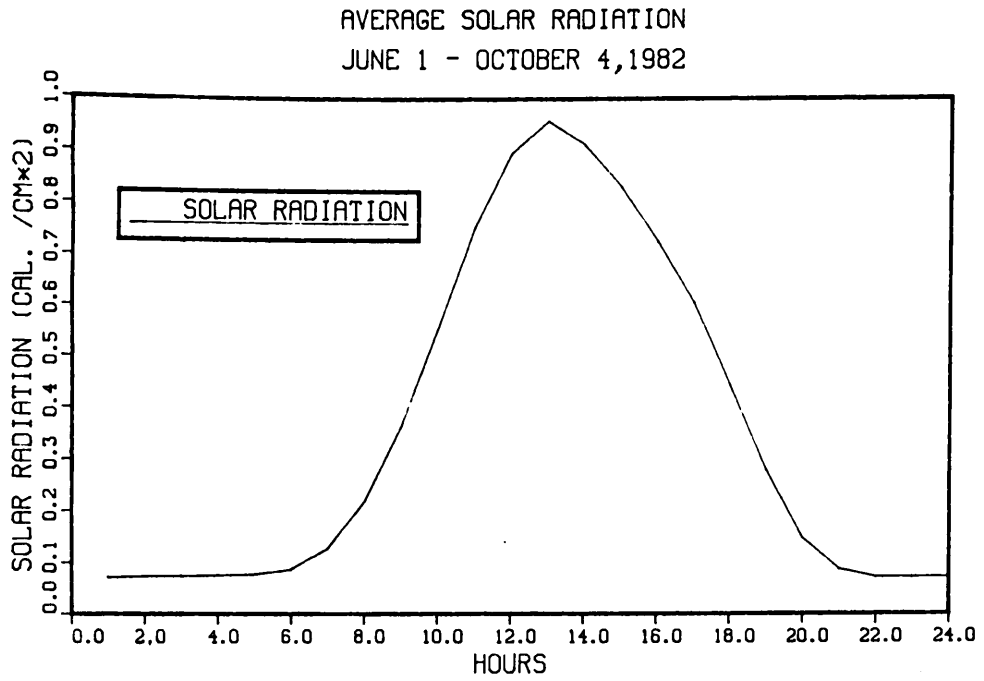


Figure 5. Average Incident Solar Radiation (Laramie, WY)

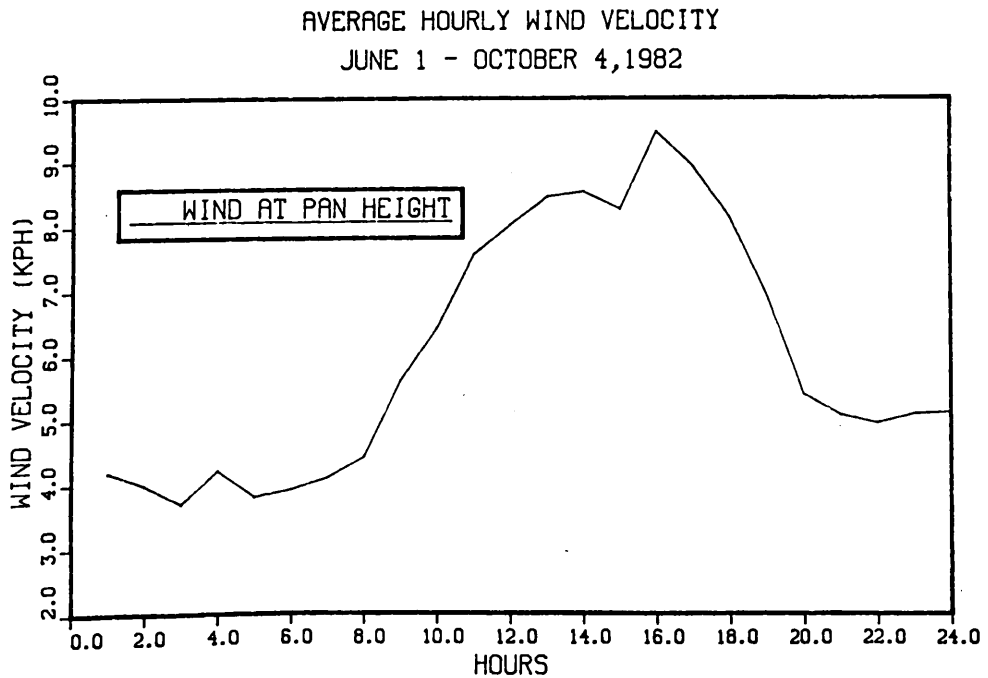


Figure 6. Average Hourly Wind Velocity (Laramie, WY)

Table 2. Regression Analysis of Humidity Versus Air Temperature\*

TIME LAG (hours)	R <sup>2</sup> (%)	REGRESSION EQUATION y(RH) = mx (temp - F°) + b
0	95.9	y = -2.04 X +179
1	98.8	y = -2.07 X +181
2	86.1	y = -1.92 X +172

\*Lagged Time Variable

Table 3. Regression Analysis of Air Temperature Versus Solar Radiation

TIME LAG (hours)	R <sup>2</sup> (%)	REGRESSION EQUATION y(temp - F°) = mx (solar - ly) + b
0	75.9	y = -22.1 X +51.2
1	89.6	y = -23.5 X +50.7
2	86.0	y = -23.0 X +50.9

\*Lagged Time Variable

lags relative humidity by two hours. An almost perfect inverse relationship exists between relative humidity and air temperature even without a time lag.

After establishing relationships between the meteorological parameters, it was necessary to determine how evaporation rates lag meteorological parameters. Arbitrarily choosing temperature as the test parameter, regression analysis was used again to determine the lag time differences between the fresh pan and air temperature. Table 4 shows the best fit occurs when air temperature is lagged four hours ahead of pan evaporation.

Table 4. Regression Analysis of Fresh Pan Evaporation Versus Air Temperature

TIME LAG (hours)	R <sup>2</sup> (%)	REGRESSION EQUATION y(in) = mx (temp - ly) + b
0	17.9	y = 0.000416 X -.0142
2	65.1	y = 0.000795 X -.0366
3	86.2	y = 0.000914 X -.0436
4	96.7	y = 0.000697 X -.0468
5	92.9	y = 0.000949 X -.0457

Using the above determined lag times, a correlation matrix was calculated between the pans and four meteorological parameters. This matrix depicted in Table 5 shows an extremely high correlation between all of its elements. Based on this finding, an hourly evaporation model was calculated using multiple regression analysis techniques.

A stepwise multiple regression was used to determine the significance of each meteorological parameter

Table 5. Correlation Matrix Between Class-A Pans and Lagged Meteorological Parameters

	*F-PAN	*S-PAN	*R-PAN	TEMP	HUMID.	SOLAR
S-PAN	.967					
R-PAN	.973	.924				
TEMP	.983	.941	.982			
HUMIDITY	-.976	-.981	-.945	-.979		
SOLAR	.962	.891	.958	.947	-.910	
WIND	.936	.958	.989	.936	-.964	.898

\*F = FRESH

\*S = STRIPPED

\*R = RETORT

in the model. Table 6 shows the results of an analysis for each pan. The regression analysis determined that air temperature, humidity and solar radiation were, respectively, the most significant factors for the fresh pan and stripped pan models, while temperature, solar radiation and wind were the most significant factors for the retort pan model. Table 7 shows the results of regression analysis which uses all four climatological parameters. The fresh pan regression equation from Tables 6 and 7 were both compared to measured evaporation from the fresh Class-A pan. It was found that the hourly four-variable evaporation models listed in Table 7 are an excellent prediction of hourly evaporation rates. The fresh pan regression equation has a coefficient of determination of 0.99. The residual errors in the fresh pan equation were found to fall within ±1.8, which is considered acceptable. The four-variable regression was the best prediction of pan evaporation but over-predicted it by 11 percent. The 11-percent error in the regression equation appears to be linear throughout the study period and hence can be corrected by introduction of a constant. The three-variable equation over-predicted evaporation by 22 percent.

The average evaporation curves in Figure 2 show an excellent linear relationship between the three pans. Based on this finding, an equation was

Table 6. Stepwise Linear Regression Analysis of Hourly Evaporation Model

REGRESSION EQUATION*	
R <sup>2</sup> EVAP(IN)	= A(Temp°F) + B(RH) + C(Solar-ly-hr) + D(WIND-mph) +E
.98 FRESH PAN	= .0015(T) + .00038(RH) + .0063(S) - .02570
.98 STRIPPED PAN	= .00341(T) + .00112(RH) - .0053(S) - .25558
.98 RETORT PAN	= .00059(T) + .0045(S) - .00034(W) - .02524

\*Variables which do not significantly improve the accuracy of the model have been eliminated.

Table 7. Regression Model Based on Four Variables

REGRESSION EQUATION\*

R <sup>2</sup>	EVAP(IN)	= A(Temp°F)	+ B(RH)	+ C(Solar-ly-hr)	+ D(Wind-mph)	+ E
.99	FRESH PAN	= .00453(T)	+ .000182(RH)	+ .0110(S)	- .00068(W)	- .00309
.98	STRIPPED PAN	= .00296(T)	+ .00303(RH)	- .00278(S)	- .000186(W)	+ .0106
.97	RETORT PAN	= .000591(T)	- .00005(RH)	+ .000453(S)	- .000318(W)	- .0260

developed to estimate the evaporation rate of stripped and retort water from more readily available fresh water data. Haass (1985) found that there was a good relationship between changes in pan water temperatures and reduced evaporation rates. Based on this finding, two assumptions can be made: 1) there is no temperature gradient in the fresh pan and 2) the amount of energy stored in the pan is totally dissipated by night. Based on these two assumptions, the fresh pan is assumed to be in thermal equilibrium with the environment, while the stripped and retort pans are not.

Using water temperatures of the fresh pan to represent equilibrium conditions, two equations were developed to predict the relative evaporation rates of other low quality waters. The first equation (1) is for use when a low quality water reaches thermal equilibrium with the environment at night. This equation gives a percentage estimate (C),

$$C = \frac{(T_{SH}^{\circ F})_{\text{Fresh Pan}}}{(T_{SH}^{\circ F})_{\text{Waste Water Pan}}} \times 100 \quad (1)$$

of how much slower the waste water pan evaporates in comparison to the fresh water pan where  $T_{SH}$  is the surface high water temperature.

The second equation (2) is for use with a waste water that does not reach thermal equilibrium with the environment at night.

$$C = \frac{(T_{SH}^{\circ F})_{\text{Fresh Pan}}}{(T_{SH}^{\circ F})_{\text{Waste Water Pan}}} \times 100 \quad (2)$$

It was found that Equation (1) estimates that the stripped pan will evaporate 7.8 percent slower than the fresh pan, while measured results were found to be 9.9 percent. Equation (2) estimates that the retort pan will evaporate 23 percent slower than the fresh pan, while measured results were found to be 18 percent.

A further study of evaporation rates, chemical composition and emissions released from oil shale wastewaters was started in 1985. Data from the summer of 1985 was analyzed in some detail to determine the effects of meteorological and chemical effects on evaporation rates for fresh water and 3 different oil shale waters.

All possible subsets multiple regression, using Mallows  $C_p$  and Adjusted  $R^2$  criteria for model selection, was used to identify significant meteorological variables affecting the evaporation rates of the waters. Results for oil shale wastewater #1 are presented in Table 8. In general, relative humidity, wind speed, and energy-type variables were found to significantly affect evaporation rate for all wastewaters. These data confirm results of the literature review indicating that these factors are significant. It is interesting to note that for fresh water and the #1 wastewater, a curvilinear relationship between evaporation rate and relative humidity was significant. Analysis of coefficients for relative humidity show increasing evaporation rate with a curvilinear decrease in relative humidity. Water temperature (measured at the base of the pan) showed significant effects on the evaporation rate of fresh water and the #1 wastewater. The energy-related effects, however, were expressed as net radiation measured from the process water and were significant for #2 and #3 process waters. It is believed that these energy-type effects on evaporation rate are the same, however, the variables identified (i.e., water temperature or net radiation) show more accurate predictive capability for the evaporation rates of the process waters.

A one-way analysis of variance and Scheffe multiple range tests were used for statistical comparison between the evaporation rates of fresh water and the three oil shale process waters from Class A pans. Mean evaporation rates, standard deviations and coefficients of variation for the means are presented in Table 9. No significant difference

Table 8. Meteorologic Variables Significantly Effecting Process Evaporation Rate Results from All Possible Subsets Regression Analysis

PROCESS WATER	R <sup>2</sup>	ADJ. R <sup>2</sup>	VARIABLE	REGRESSION COEFFICIENT	T-STATISTIC
#1	0.78	0.76	% RH	-0.001734	-3.54
			% RH <sup>2</sup>	0.000014	2.69
			BASE H <sub>2</sub> O TEMP	0.000879	1.54
			WIND SPEED (3 m)	0.002430	5.04
			WIND SPEED (2 m)	-0.000569	-1.66
			INTERCEPT	0.049558	

between mean evaporation rates could be determined between fresh water, #1 and #2 oil shale process waters (P=.01). Mean evaporation rates for these waters are 0.037, 0.036 and 0.041 cm/hr, respectively. The mean evaporation rate from the #3 process water (0.016 cm/hr) was significantly lower than all other waters (P=.01), however, this mean evaporation rate exhibits higher variation than the other waste waters.

Table 9. Descriptive Statistics for Process Water Evaporation Rates - Julian Day 218-166 1985

PROCESS WATER	SAMPLE SIZE	MEAN		COEFFICIENT OF VARIATION
		EVAP RATE (cm/hr) /1	STANDARD DEVIATION	
FRESH WATER	87	0.037 a	0.027	0.73
#1	68	0.036 a	0.023	0.64
#2	61	0.041 a	0.038	0.93
#3	87	0.016 b	0.022	1.38

Mean concentrations (ppm), standard deviations, and coefficients of variation for chemical constituents of the process waters progressively sampled for the entire 1985 summer field season are presented in Table 10. On several occasions, the automatic water-level controllers allowed the evaporation pans to completely drain and refill, resulting in a significant dilution of the process waters in the pans. This factor has complicated analyses designed to test for significant effects of increasing chemical concentrations on evaporation rate.

Linear regression analysis was utilized to determine chemical constituents showing significant coefficients (trends) for increasing concentration for the time period in which evaporation was obtained. It was found that only total organic carbon, total dissolved solids, total alkalinity, and sulfates were significantly increasing over time for the #2 process water. These effects can be explained by the fact

that problems with draining and refilling of the #2 process water did not occur for a significant portion of the time period in which evaporation data was obtained as it did with the other process waters. Because of these results, statistical analyses to analyze the effects of chemical concentration on evaporation rate was only conducted for the #2 process water and for the chemical constituents showing significant increasing concentrations over time. Multiple regression analysis for determination of significant effects on the evaporation rate of the #2 process water caused by increasing concentration of chemical constituents, however, indicated no significant effect. With future laboratory and field analyses in the 1986 season, however, it is expected that chemical effects on evaporation rates will be determined to be significant.

Studies on emissions from the process waters are currently being initiated. It is hoped that types of emissions and their rates can be determined.

#### SUMMARY

The results of work on evaporation rates and modeling of oil shale process waters has indicated that a linear relationship exists between the evaporation rates of oil shale wastewater and fresh water. This linear relationship was quantified through regression models to predict evaporation of stripped and retort wastewaters from climatological parameters. The important climatological parameters were found to be relative humidity, wind speed and energy-type variables (i.e., solar radiation and water temperature).

The results of this type of work will give new insight into environmental problems associated with the ultimate disposal of oil shale waste effluents. Based on these findings, further research may be needed to determine acceptable limits for emissions



Table 10. Descriptive Statistics for Chemical Concentrations of Oil Shale Process Waters - Time Period: Julian Day 183-312 1985

PROCESS WATER	CHEMICAL CONSTITUENT	SAMPLE SIZE	MEAN CONCENTRATION (ppm)	STANDARD DEVIATION	COEFFICIENT OF VARIATION
#1	TOTAL ORG. CARB.	16	40.1	8.00	0.19
	TOTAL DIS. SOLIDS	16	9145.6	1078.73	0.12
	pH	16	7.4	0.19	0.02
	TOTAL ALKALINITY	16	49.7	18.48	0.37
	CL <sup>-</sup>	16	51.5	10.35	0.20
	SO <sub>4</sub> <sup>=</sup>	16	9061.2	1699.10	0.19
#2	TOTAL ORG. CARB.	14	12167.1	3094.89	0.25
	TOTAL DIS. SOLIDS	14	23320.7	5715.61	0.25
	pH	14	6.7	0.15	0.02
	TOTAL ALKALINITY	14	3149.6	585.16	0.19
	CL <sup>-</sup>	14	1581.2	446.02	0.28
	SO <sub>4</sub> <sup>=</sup>	14	7207.9	1602.43	0.22
#3	TOTAL ORG. CARB.	12	3615.5	657.36	0.18
	TOTAL DIS. SOLIDS	12	26822.5	6154.30	0.23
	pH	12	8.9	0.17	0.02
	TOTAL ALKALINITY	12	15760.3	1813.23	0.12
	CL <sup>-</sup>	12	3517.2	1074.07	0.31
	SO <sub>4</sub> <sup>=</sup>	12	4900.8	1418.76	0.29

and evaporation rates from oil shale evaporation ponds. Research may also be needed to determine new processing methods to curb the release of emissions from oil shale process waters.

The use of this research may be an initial step in striving to answer some of the water balance questions which will be associated with codisposal of spent oil shale and process waters. Evaporation from spent shale piles and evapotranspiration from these same piles are keys to water balance and redistribution. Although this research should start to answer some of the water balance questions associated with codisposal, continued research will be required on evaporation and evapotranspiration from spent shale piles and the associated concept of codisposal.

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#### ACKNOWLEDGEMENTS

A large portion of this research was supported by the Department of Energy through the Laramie Project Office by DOE Contract No. DE-AC20-84LC11049.