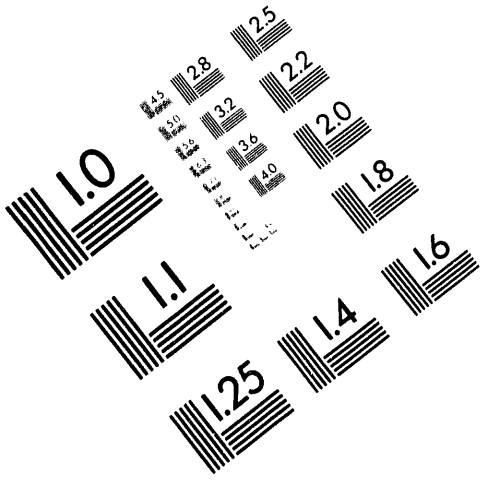

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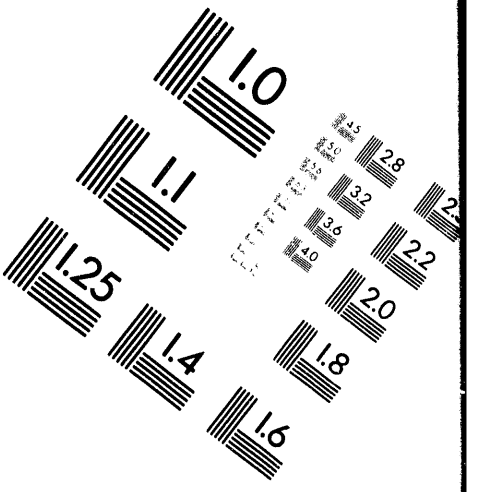

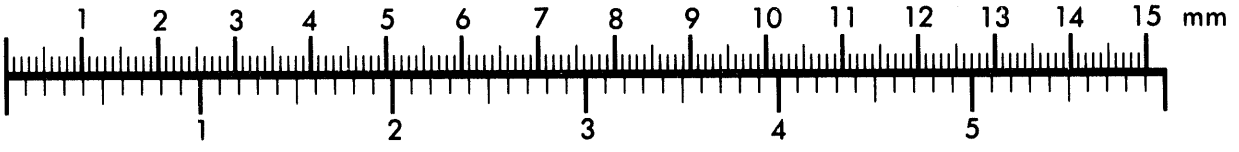

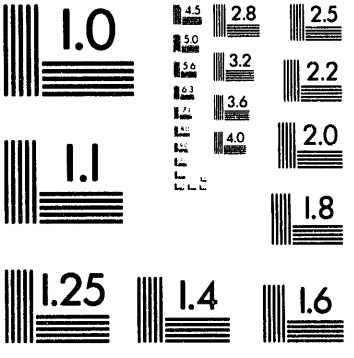

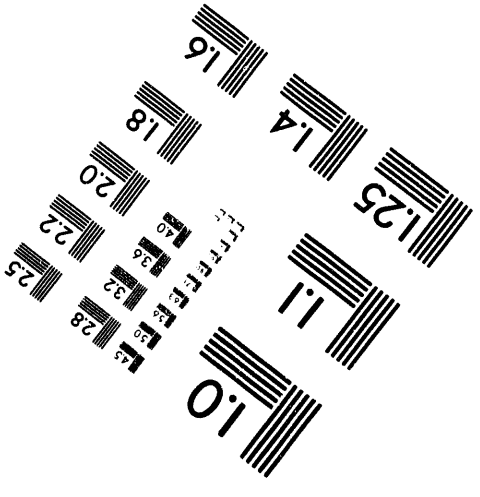

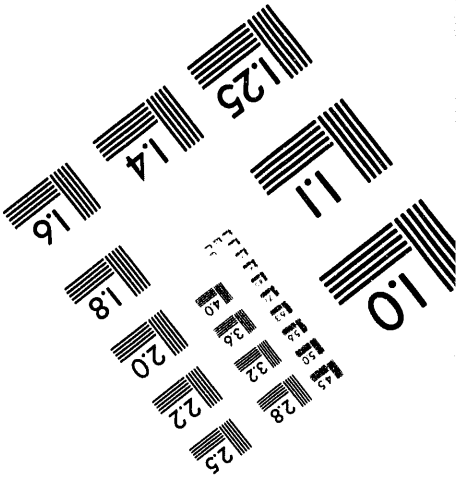

1 of 1

QUARTERLY TECHNICAL REPORT:

Title:	WETLAND TREATMENT OF OIL AND GAS WELL WASTEWATERS
Contract No.	DE-AC22-92MT92010
Institution:	University of Michigan, Department of Chemical Engineering
Date:	April 15, 1994
Contract Date:	May 25, 1992
Anticipated Completion Date;	May 24, 1994
Government Award:	($ 89,560 for the Second Year)
Project Director:	Prof. Robert H. Kadlec
Project Manager:	Dr. Keeran R. Srinivasan
PIs:	Prof. Robert H. Kadlec and Dr. Keeran R. Srinivasan
Technical Project Officer (COR):	Dr. Brent W. Smith
Reporting Period:	November 25, 1993 - March 24, 1994.

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I. Executive Summary:

During the first quarter of the above contract, all the elements of Task 1 were completed. The first quarterly report (1) presented an overview of a wetland and its increasing use in industrial waste water treatment. An idealized, reaction engineering description of wetlands was presented to demonstrate how the various processes that occur in a wetland can be modeled. Previous work on the use of wetlands to remove BOD, TSS, Phosphorus and Nitrogen was reviewed. Recent literature on the application of wetland technology to the treatment of petroleum-related waste water was critically evaluated and an outline of the research plans for the first year was delineated. Further, our literature search (nominally completed under Task 1) unearthed more recent studies (some unpublished) and a summary was included in the second quarterly report (2). In the second quarterly report, results of our efforts on the construction of a laboratory-type wetland were also reported. Initial studies on the use of wetland amendments such as modified-clays and algae cells were presented and discussed (2). In the third quarterly report (3), adsorption of heavy metals ions such as Cu(II) and Cr(VI) onto soils drawn from the laboratory-type wetland (LW) was shown to be weak. On the other hand, it was shown that modified-clays did adsorb Cr(VI) ions strongly at pH 4.5. Further, studies on the pH dependence of the adsorption of β-naphthoic acid, (NA), a well-documented contaminant in many oil and gas well waste waters (4), onto modified-clays were undertaken and it was shown that uptake of NA by modified-clays was of the high affinity type at pH 4.5 and 7.0, but weak at pH 9.0. Adsorption of heavy metal ions, Cu^{2+}, and Cr(VI) onto algae, a proposed wetland amendment, was carried out and the results were presented and discussed in the fourth quarterly report (5). Uptake of NA by the soil component of LW was monitored as a function of pH. The adsorption of NA onto modified-clays was studied in greater detail and these data were described and analyzed in an earlier quarterly report (5). Studies on the dynamics of uptake of phenol and NA by laboratory-type wetlands (LWs) were initiated and preliminary results indicated that both phenol and NA were sorbed onto components of LWs (6). It was also observed that phenol volatilization from supernatant water contributed to phenol disappearance. This was attributed to high water temperature during the Summer months when these studies were conducted. On the other hand, there was minimal loss of NA through evaporation even during Summer months(6). Further results from studies on the uptake of Cu(II) and phenol by laboratory-type wetlands (LWs) designed and built during the earlier phases of this study have also been considered. The uptake of Cu(II) by laboratory-type wetland was shown to follow a tri-phasic behavior attributed to partial hydrolysis and precipitation , sorption onto wetland components and a slow dispersion into underlying pore water of the laboratory-type wetland (7). The addition of peat was observed to have only a minimal effect on Cu(II) uptake. On the other hand, phenol sorption was favorably modified by the addition of peat. Furthermore, a lower water depth in the laboratory-type wetland resulted in slightly higher evaporative loss of phenol, but the major removal mechanisms of phenol appeared to be sorption to various components of a laboratory-type wetland and degradation by micro organisms inherent to the wetland.

- A mass balance model has been developed to quantify the fate of phenol in LWs. The model is based on the postulate that the fate of phenol in LWs can be attributed to a combination of (1) evaporation of solute and solvent, (2) adsorption of phenol onto various components of LW and (3) its biodegradation, both in solution and at solid-liquid interface. As an initial approximation, the latter two processes have been lumped together and incorporated into the model as an unit operation. Both zero order and first order kinetics for the disappearance of phenol have been considered. Evaporative losses of water and phenol have also been taken into account and this model is presented and discussed in this quarterly report.

- The dynamics of the uptake of Cr(VI) by laboratory-type wetland systems (LWs) has been studied and the results are presented and discussed.

II. Tasks 4: Modeling of the fate of phenol in Laboratory-type Wetlands (LWs).

Phenol and water mass balance equations were simultaneously solved as described below. The water balance accounts for evaporation, while the phenol balance accounts for phenol evaporation, adsorption and degradation. The mass balance equations (eqns 1 -3 and 6 -8) are given below.

Fate of Phenol in a laboratory-type Wetland: Zero Order Kinetics:

$$d(VC_P)/dt = -K_A S_A - E_P C_P A \quad (1)$$

$$AC_P(E_P - E) + V.\, dC_P/dt = -K_A S_A \quad (2)$$

$$V = (V_0 - EAt) \quad (3)$$

$$c_p = \left\{ \left[-k_A SA - Ac_{p0}(E_p - E) \right] \left(\frac{V_0 - EAt}{V_0} \right) \left(\frac{E_p - E}{E} \right) + k_A SA \right\} \frac{-1}{A(E_p - E)}$$

zero order solution (4)

$$c_p = \frac{(c_{p0} V_0 - k_A SAt)}{(V_0 - EAt)}$$

zero order--simple (5)

Fate of Phenol in a laboratory-type Wetland: First Order Kinetics:

$$d(VC_P)/dt = -K_A S_A C_P - E_P C_P A \quad (6)$$

$$AC_P(E_P - E) + V.\, dC_P/dt = -K_A S_A C_P \quad (7)$$

$$V = (V_0 - EAt) \quad (8)$$

$$c_p = c_{p0} \cdot \left\{ \frac{V_0 - EAt}{V_0} \right\} \left(\frac{k_A SA + A(E_p - E)}{EA} \right)$$

1st order (9)

$$c_p = c_{p0} \cdot \exp\left\{ \frac{\left[k_A SA + A(E_p - E)\right]}{EA} \cdot \ln\left(\frac{V_0 - EAt}{V_0} \right) \right\} \qquad (10)$$

1st order --same as above but w/o exponent

An analytical solution for phenol concentration as a function of time was obtained assuming zero or first order dependence of phenol degradation. Equations 1 - 3 represent mass balance equations for the overall process driven by zero order kinetics. Similar equations for the first order degradation kinetics are numbered 6 -8. The solutions are given in eqns. 4 - 5 and 9 - 10 respectively for zero and first order processes. The notation for various terms in the equations is given below.

Notation:

C_p	Phenol Conc. (g/in^3)
E	Evaporation Rate Constant for water (in/hr)
E_p	Evaporation rate constant for phenol (in/hr)
A	Surface Area of water in LW (in^2)
V_0	Initial Volume (in^3)
t	Time (hr)
K_A	Specific rate constant for phenol Disappearance (g/in^2/hr; zero order) (in/hr ; first order)
S_A	Surface area of reactive components of LW (in^2)

Using the solver function on an Excel spreadsheet, the experimentally observed phenol concentration vs. time data were used to solve for the specific rate constant with the geometric surface area of the wetland, initial phenol concentration, and initial water volume as input parameters. The difference between the calculated and the observed values of phenol concentrations for each data set was calculated and this difference was minimized to obtain an optimal solution.

In some cases, a simplification of mass balance equations was attempted by neglecting phenol evaporation rate in relation to water evaporation rate due to the low vapor pressure of phenol at ambient temperatures. These equations (eqns 5 and 10) were solved in an identical manner except that the value of E_p was set to zero. Both zero order and first order kinetics were used to model the stoichiometry of phenol disappearance. A typical set of results is shown in Figs 1 and 2 respectively for zero and first order degradation kinetics. The values of input and calculated parameters are listed in Table 1.

Table 1: Calculated and Input model parameters for phenol disappearance in LWs:

Model Parameter	Zero Order	First Order
$K_A S_A$	1.79 - 2.1 E-03 (g/hr)	8 - 10 (in^3/hr)
E_P	4.0 - 9.2 E-07 (in/hr)	3.6 E-07 (in/hr)
E	4.53 E-03 (in/hr)	4.53 E-03 (in/hr)
A	213 .8 (in^2)	213.8 (in^2)

Fig. 1 Modeling the fate of Phenol in LWs:
Zero Order Disappearance Kinetics

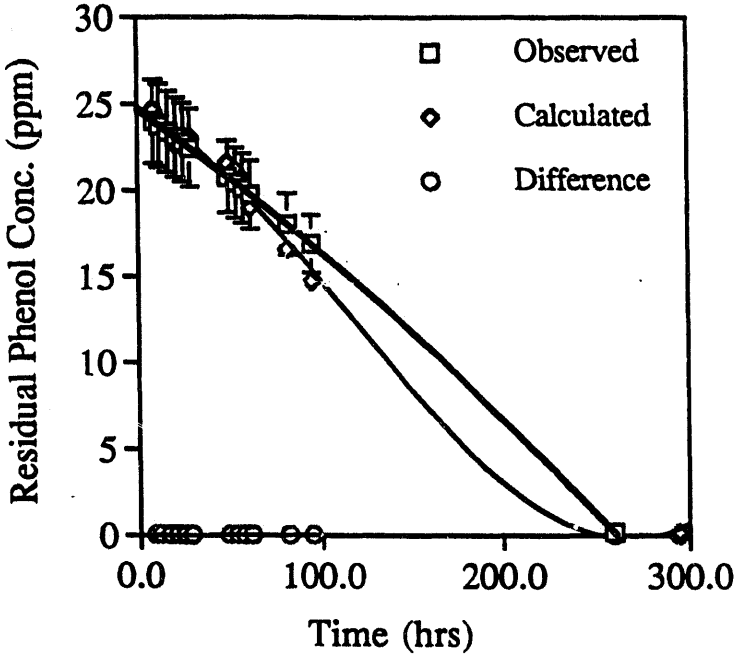
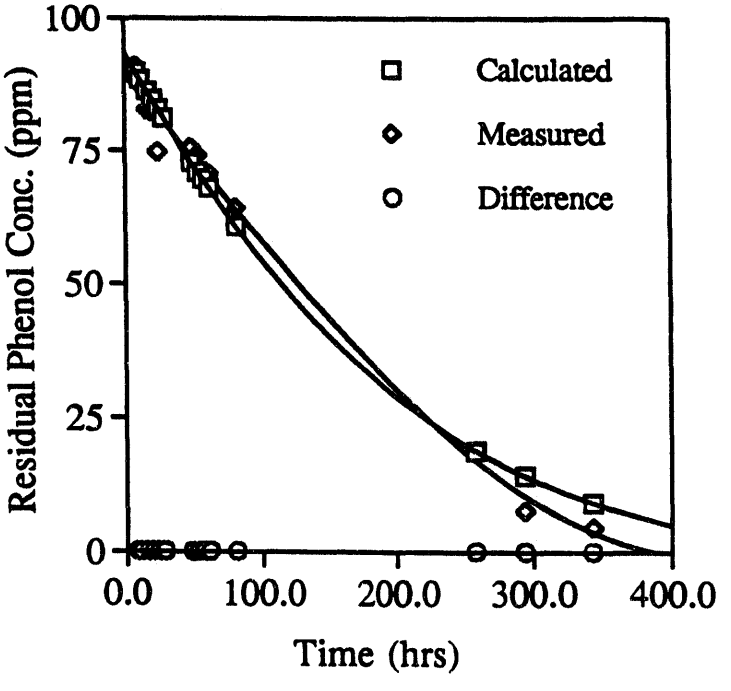


Fig. 2 Modeling the fate of Phenol in LWs:
First order disappearance Kinetics



The values listed in Table 1 represent the initial results of model calculations that produced minimum error between the observed and fitted data. Further model calculations are in progress and we expect to develop a full scale correlation encompassing all the observed data. For example, the frequency distribution of the values of $K_A S_A$ will be obtained from a large number of LWs.

From the data shown in Figs 1 and 2 it appears that zero-order degradation applies to lower initial phenol concentrations (17-25 ppm), and first-order degradation applies to higher initial phenol concentrations (90-112 ppm). Further modeling work is continuing and is expected to shed more light on these preliminary observations.

Task 3: Cr(VI) Uptake by LWs:

In a previous report (2), we had described the design and the construction of a laboratory-type wetland. Briefly, 18-gallon plastic containers containing 4 cattails/container were prepared in a suitable soil matrix and grown at the Botanical Gardens operated by The University of Michigan. The following are steps used to quantify Cr(VI) uptake. by LWs.

(1) Removed the overlying water and replaced with fresh tap water. In some cases, 2 -3 gallons of peat in the form of a thick paste were layered before adding tap water. Water depth was set to 7 inches from the surface of the soil matrix.

(2) After 24 -hr equilibration, the height of the water column was monitored again and the overlying water was spiked with Cr(VI) to a pre-determined nominal concentration. Following the addition of the heavy metal, the water was mixed manually with a paddle, and was left undisturbed thereafter.

(3) Collected water samples prior to the start of the experiment and periodically during the experiment. The temperature, water depth and the pH were noted.

Concentrations of Cr(VI) were measured using Perkin Elmer AA Spectrometer. Cr(VI) uptake experiments were studied in triplicate, i.e. three LWs per experiment. The effect of peat addition was also monitored in triplicate. Water depth was maintained at 7 inches and the initial concentrations of Cr(VI) was nominally **16** ppm. pH was between 5.5 - 6.5 and did not change during the course of the experiment. The results are shown in Fig. 3 and 4.

The uptake of Cr(VI) appears to be an exponential function of time. During the first 100 hours the extent of Cr(VI) removal ranges from 60 - 85%. It should be noted that the data shown in Fig. 3 have been normalized with respect to initial Cr(VI) concentration in each LW. Thus, the observed variations in Cr(VI) uptake may be related to the pH in different LWs. It may be noted that pH varied from 5.5 - 6.5 and Cr(VI) adsorption may be quite sensitive to pH in this range.

The addition of peat had no effect on Cr(VI) uptake. In this respect Cr(VI) removal results correspond closely to similar finding on Cu(II) uptake reported previously. Further work to verify this finding is in progress.

III. Future Work:

Based on the results described above, simultaneous uptake of Cu (II) and Cr(VI) by LWs will be considered. To minimize interactions between the two multivalent ions, non stoichiometric mixtures of the two ions will be used. The model for phenol uptake will be

Fig. 3 The Fate of Cr(VI) in LWs

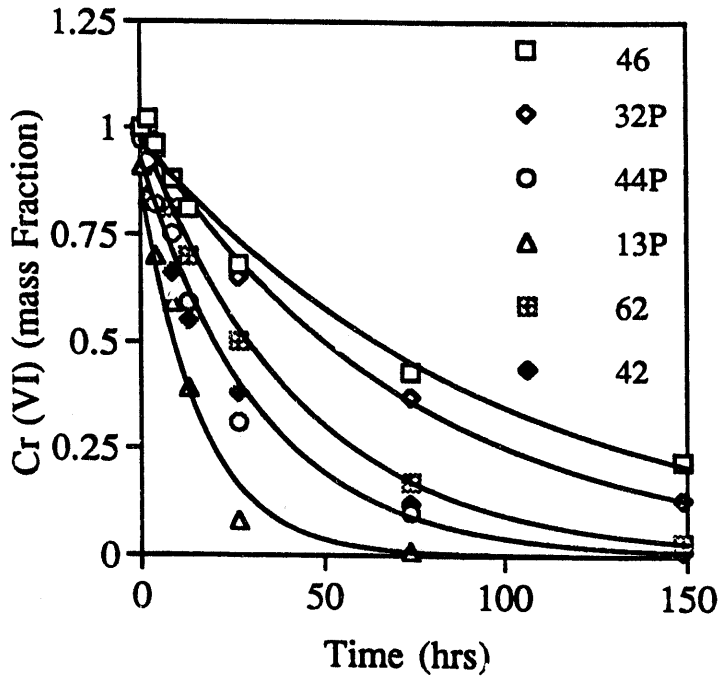
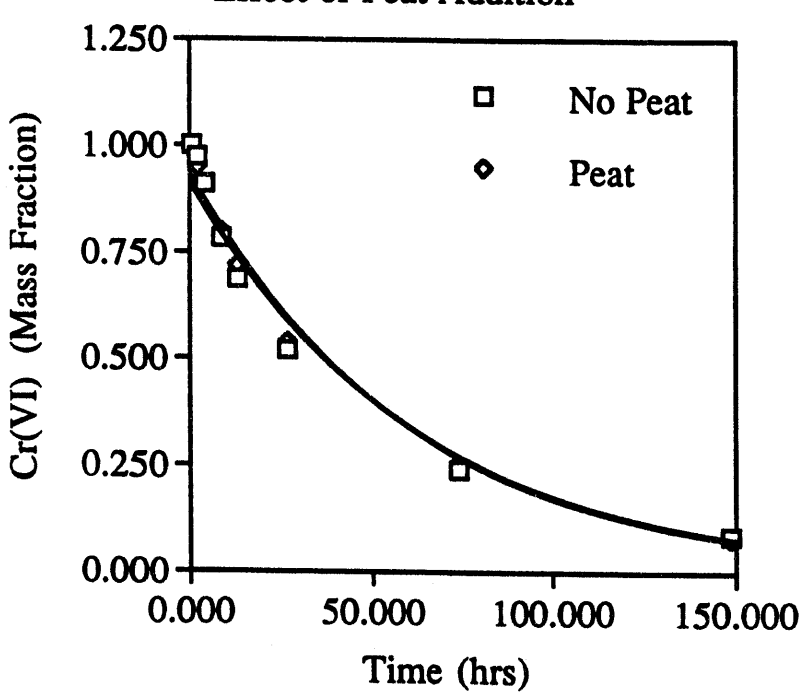


Fig. 4 Fate of Cr(VI) in LWs:
Effect of Peat Addition



further refined. For example, a frequency distribution of the values of $K_A S_A$ will be obtained from a large number of LWs. A mass balance model will be developed to quantify metal uptake. This latter model will include effects of dilution and dispersion and hydrolysis and precipitation.

IV: SUMMARY

This quarterly report presents results from modeling studies undertaken to quantify the fate of phenol in a laboratory-type wetland (LW). A mass balance model has been developed to quantify the fate of phenol in LWs. It has been assumed that the fate of phenol in LWs is determined by evaporation of solute and solvent, adsorption of phenol onto various components of LW and its biodegradation, both in solution and at solid-liquid interface. Both zero order and first order kinetics for the overall disappearance of phenol appear to fit the experimental data. Evaporative loss of water appears to be more important than the loss of phenol through evaporation.

The uptake of Cr(VI) by laboratory-type wetland systems (LWs) appears to be quite effective, but the addition of peat to the wetland produces only minor enhancement in Cr (VI) uptake.

V: Report Distribution List:

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VI. REFERENCES:

(1) R. H. Kadlec and Keeran R. Srinivasan: 1st Quarterly Report, U. S. DOE, PETC, August, 1992.

(2) R. H. Kadlec and Keeran R. Srinivasan: 2nd Quarterly Report, U. S. DOE, PETC, November, 1992.

(3) R. H. Kadlec and Keeran R. Srinivasan: 3rd Quarterly Report, U. S. DOE, PETC, March, 1993.

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(5) R. H. Kadlec and Keeran R. Srinivasan: 4th Quarterly Report, U. S. DOE, PETC, July, 1993.

(6) R. H. Kadlec and Keeran R. Srinivasan: 5th Quarterly Report, U. S. DOE, PETC, October, 1993.

(7) R. H. Kadlec and Keeran R. Srinivasan: 6th Quarterly Report, U. S. DOE, PETC, December, 1993.

VII. Publications: None

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