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20/92

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I. INTRODUCTION:

WETLANDS: An Overview:

Constructed wetlands are small, on site systems that possess three of the most desirable components of an industrial wastewater treatment scheme: low cost, low maintenance and upset resistance. Operationally, a wastewater stream is passed through shallow water containing an assemblage of emergent plants growing in organic soils. An underwater layer of plant litter covers the soils. The plant leaves and stems, together with the litter, provide for physical filtration of suspended solids. Water velocities are low, and there is adequate time for sedimentation to occur. The organic soils and sediments possess a large and demonstrated sorption capacity for a wide variety of waterborne contaminants. Metals, such as copper, are held by cation exchange and specific adsorption processes (1,2). Other pollutants, such as the agricultural chemical atrazine or the nutrient phosphorus, are bound by mechanisms, such as van der Waals binding (3,4). Plant uptake contributes to the immobilization of some contaminants; ammonium nitrogen for example.

Microbial degradation is quite effective in the wetland environment. Natural populations of microbes efficiently reduce nitrate to atmospheric nitrogen, for instance (5). The bacteria are found selectively on the submerged surfaces of soil, plant stems and leaves, and litter. Consequently, the very surfaces that are effective in sorbing contaminants are also the location of the bacteria which can cause degradation to non-toxic products. In other words, the wetland litter layer acts as a trickling filter and as an adsorption bed. A pictorial representation of a typical wetland is shown in Fig. 1.

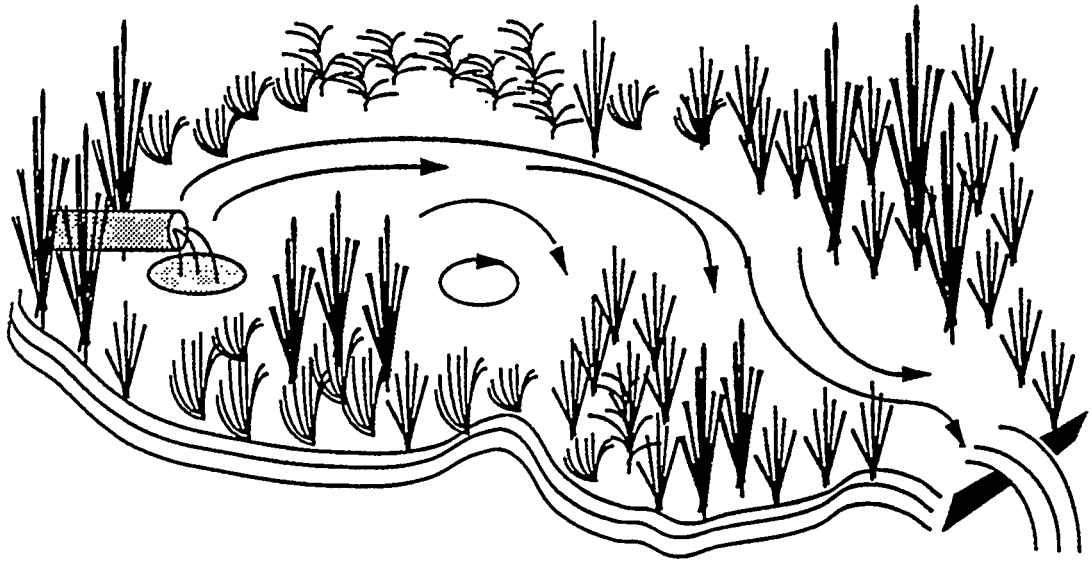
It may be discerned from Fig. 1 that wetlands are easy to build, requiring only earthmoving to create shallow impoundments, sealing to prevent leaks, rudimentary piping and ditches for water movement, and vegetation establishment. The innocula for the microbial populations are normally present in the soils and waters used for construction, but could be added for particular target compounds and organisms.

The capital cost of such systems is generally only a bit lower than other alternatives, but operating costs are much lower. Chemical additives are not used, and operators need training in hydrology, agriculture, aquaculture and ecology; not in chemical plant operation. Natural systems are resilient, and can withstand pulse inputs. The long contact times provide pulse damping, but do present high land costs. Natural systems are also somewhat chaotic compared to concrete and steel devices. They change performance in response to meteorology, seasonality and diurnal solar cycles. This feature currently causes discomfort for governmental regulators, who naturally prefer to deal in constancy.

II. A CHEMICAL ENGINEERING DESCRIPTION:

The purpose of this study is to extend the knowledge base for wetland treatment to include processes and substances of particular importance to small, on site systems receiving oil and gas well wastewater. Collection of data on the sorption of heavy metals and the degradation of toxic organics commonly found in oil and gas wastewaters by typical wetland soil and biological assemblages is one of the key tasks of this study. The field implementation, however, involves design questions, such as wetland configuration, wastewater application rate, and the timing of intermittent discharges. These design considerations can be modeled using a reaction engineering approach to a wetland treatment scheme. Fig. 2 is an idealized, " flow sheet " type representation of the typical processes that occur in a constructed wetland.

The front end is visualized as a plug-flow reactor to take into account the delays in the breakthrough of contaminants. A series of completely mixed flow reactors (CMFRs) represents an unit operation involving a multi-stage adsorption process. The mass transfer of solutes in a



Idealization of the Pond and Island Wetland as Consisting of

open water channel with flow
vegetated and stagnant dead zone

Fig. 1 A schematic of a typical wetland

Network Model with Three Channel and Dead Zone Reactors

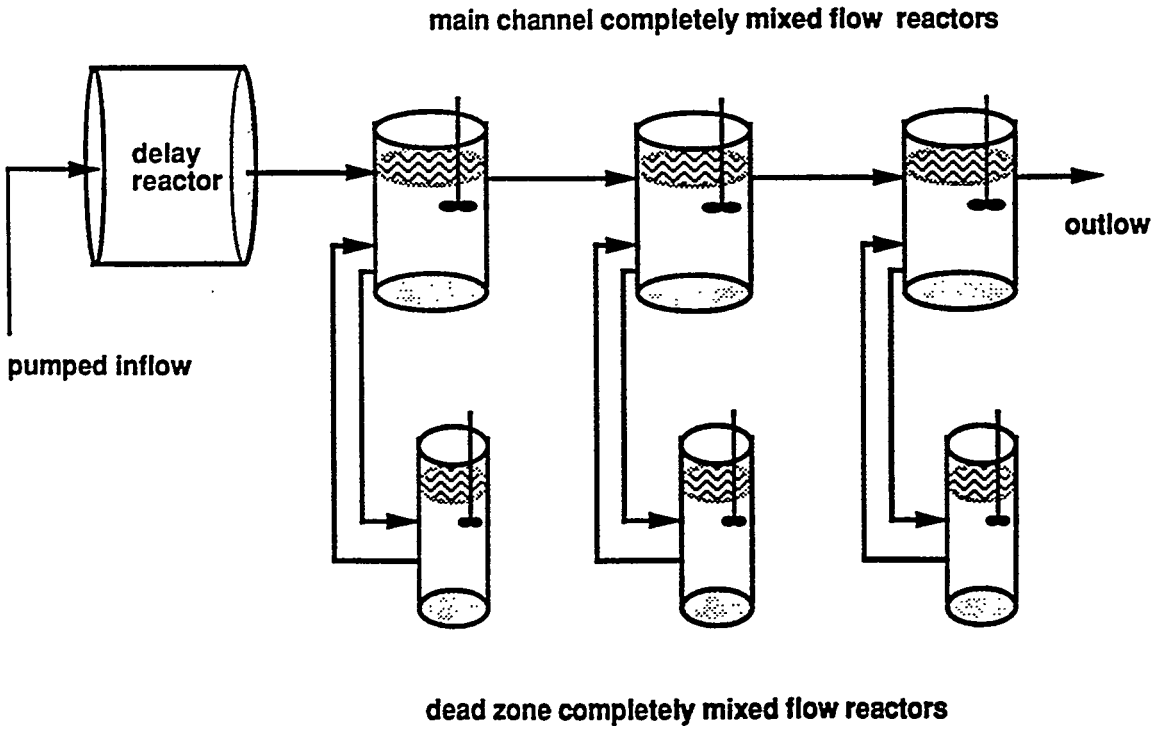


Fig. 2 A Chemical Engineering Approach to Wetlands

wetland is complicated by the occurrence of stagnant zones and the solute transport between these zones and the main flow channels occurs mostly by diffusion. Thus, the distribution of toxics in the effluent stream is a complicated function of the residence times of the convective and diffusive processes and " tailing" of the effluent concentration profile has been observed. This model of a wetland can be extended to describe an integrated treatment scheme that includes biodegradation of toxic organics in conjunction with the sorptive removal of heavy metals.

III. PREVIOUS WORK:

About 500 wetlands systems exist in North America for treating a variety of wastes, including municipal wastes, mine water waste, stormwater, and various industrial wastewaters. Wetlands treatment can take place in natural or constructed wetlands sites. Principal categories of constructed wetland systems include densely vegetated overland flows, underground systems, pond and island systems, and channels with floating plants. In addition, there exist accidental wetland treatment systems, and forested wetlands as natural treatment systems. The largest existing wetlands treatment system is Iron Bridge, serving part of the Orlando area, which currently treats about 13 MGD (6). It is also designated as Orlando Wilderness Park. Columbia, Missouri, has designed a system to treat 19.5 MGD.

Despite a huge amount of research and published information, design procedures have been somewhat primitive in most instances. This is due to the fact that most information is quite recent, and has not yet been "picked up" by design organizations. The design reference list in the references section documents the primary sources of information.

The key economic features of the design are the required land area, water containment, water transport, and vegetation.

Three approaches to design are presently in use, for determination of system size. The reduction of a specific water quality parameter, such as BOD, may be presumed to be first order, and thus obey exponential decrease with increasing detention time. This procedure is illustrated in the USEPA Design Manual (see reference list). Or, the data from a number of wetland systems may be regressed to provide correlations between the principal variables, typically including loading rate and inlet concentration. This procedure is illustrated in the Water Pollution Control Federation Manual of Practice for Natural Systems (see reference list). Or, scatter plots may be used to assess the probability of a given design performing a specified task.

Water containment is normally achieved by construction of low level dikes or levees. Protection of groundwater requires some form of sealant if native soils are permeable. A few systems infiltrate into ground water, but most systems do not. Where natural soils do not provide a seal, liners of compacted clay, bentonite or plastic are used. In most natural systems, the wetlands formed because there is a natural seal. Water transport requires traditional pumps, piping and structures, and thus pose no problems in most designs.

Vegetation may be established by planting, or by permitting volunteer growth. Typical plants include cattails, bulrushes and reeds. These may be obtained from local wetlands via excavation or from wetland plant nurseries. Transplanting has been done by hand, but mechanized planters are beginning to be used. Plant establishment has been demonstrated to require some attention, and proper hydrologic conditions.

The extent of previous work is quite large, and we only attempt to give a general feel for its nature here. Nitrogen processes are among the best understood. Wetlands are efficient in performing several wastewater treatment functions, including reduction of suspended solids, BOD, and the various forms of nitrogen. They are very effective in the reduction of nitrates under a wide variety of operating conditions for many different ecosystem types, both natural and constructed. The

complex fluxes, storages and interconversions of nitrogen compounds in wetlands may be diagrammed in a variety of ways.

The basic chemistry involves the reduction of nitrate in anoxic zones, possibly accompanied by its formation by nitrification or nitrogen fixation. Denitrification is principally caused by diverse heterotrophic microflora, which are associated primarily with solid surfaces such as litter or soil particles. Thus, a carbon source is required, and a diffusion step may be required for the nitrate to reach the organisms. It is widely recognized that redox potential must be below about 200 mV to cause utilization of nitrate as the oxygen source.

In municipal wastewater treatment wetlands, the emphasis has been on BOD and TSS as well as nutrients. Effectiveness of the treatment has been well documented, though tempered by a fair amount of natural variability.

Mine waste treatment wetlands have focussed interest on various metals, and consequently there is information available. For example, peat has been shown to adsorb copper through a cation exchange process (7). The major literature on metals results from coal mine drainage wetlands (8).

A list of the most relevant <u>comprehensive</u> publications (29 in all) on the design of wetlands for water quality improvement has been compiled. This list generally does not include individual papers. The list is appended to this report. The numbering of the list is chronological; but the most recent entries are listed first.

IV. INFORMATION SEARCH: PETROLEUM WETLAND PROJECTS

Oil refinery waste treatment wetland systems exist at Mandan, ND (Amoco)(9, 10) and Richmond, CA (Chevron)(11). A vegetated submerged bed has been operated at Natchitoches, LA (Tenneco)(12). It is also known that British Petroleum has conducted research on wetlands and their interactions with petroleum-containing waters. Preliminary conversations have produced some guidance on selection of model compounds for our study, and indicate some possibility of data sharing from these private sector projects. A brief summary of information obtained follows.

Amoco: Mandan, ND

Don Litchfield, refinery manager, is the principal spokesperson for this project. All the wastewater from the refinery goes through conventional treatment, and is then passed through a series of wetlands (78 acres) before river discharge. This system is over fifteen years old. The performance of the system has won several awards as an outstanding, environmentally sensitive project. Technical details are summarized in references 9 & 10.

As part of this project effort, contact has been made to obtain recent results and advice on model compounds for our study. Amoco currently monitors for BOD, COD, TSS, TDS, DO, pH, ammonium nitrogen, sulfides, oil and grease, phenol, total chromium, and hexavalent chromium. All these parameters are reduced significantly by the wetlands. Benzene is controlled in the conventional treatment elements. Chromium and lead are the two metals of most concern in the refinery effluent. There is a possibility of obtaining detailed monitoring records at the refinery, but data books cannot be copied or released.

Chevron: Richmond, CA

Peter Duda, refinery environmental manager, is the spokesperson for this project. As at Mandan, the entire wastewater stream from the refinery goes through conventional treatment, and is then passed through wetlands (90 acres) before discharge to San Francisco bay. This project has been operational for about three years (portions started in fall 1989). Chevron currently monitors for BOD, TOC, ammonium nitrogen, total phosphorus, chromium, and selenium. All these parameters are reduced significantly by the wetlands.

Publication of results is expected soon; in the from of data tables and a report to the State Water Board. We are on the list to receive this information.

The model compounds suggested for our study by Peter Duda include: selenium, chromium; benzene, phenolics, pyrenes, anthracenes, and high molecular weight organic acids.

British Petroleum: location confidential

A request for information has been unofficially made, and we are awaiting developments. However, the current posture of BP is one of complete secrecy.

Conversations with Janice Farmer of BP have produced some suggestions for model compounds. Selenium was mentioned as a troublesome "metal", as well as chromium.

A bibliography of literature focused on petroleum-related wetland papers is being assembled.

V. PLANS FOR THE FIRST YEAR AND PRELIMINARY RESULTS:

Based on the work described in Part IV, toxic organics such as phenolics, and anthracene and metals such as Chromium and copper have been selected as the target adsorbates. A laboratory-type green house has been designed and built and cattails (*Typha latifolia*) are being grown in 50 liter lysimeters. Surfactant-modified clays have been prepared and preliminary batch studies on Cr uptake are under way. **A bibliography of literature focused on petroleum-related wetland papers is being assembled.**

VI: SUMMARY

This is the first quarter of the above contract and all the elements of Task 1 have been completed. This reports presents an overview of a wetland and its increasing use in industrial wastewater treatment. An idealized, reaction engineering description of wetlands is 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 is reviewed. Recent literature on the application of wetland technology to the treatment of petroleum-related wastewater has been critically evaluated and an outline of the research plans for the first year has been delineated. An appendix to this report is a compilation of recent literature on various aspects of wetlands and their design.

VII: Report Distribution List:

Document Control Center
U. S. Department of Energy
Pittsburgh Energy Technology Center
P. O. BOX 10940, MS 921-118
Pittsburgh, PA 15236-0940.

VIII. REFERENCES:

1. Kadlec, R.H and Keoleian, G.A. "Metal Ion Exchange on Peat." In: The Relationship of Water with Peat. Ch.H. Fuchsman, Ed., May 1986. Elsevier, pp. 61-94.

2. Eger, P., Lapakko, K. and P. Otterson. "Trace Metal Uptake by Peat: Interaction of a White Cedar Bog and Mining Stockpile Leachate," Proc. 6th Int. Peat Cong., Duluth, MN, 1980.

3. Hammer, David E. and Kadlec, Robert H. "Orthophosphate Adsorption on Peat." 6th International Peat Congress, Duluth, Minnesota, 1980.

4. Kadlec, R. H. and H. H. Alvord, Jr. "The Role of Wetlands in Agricultural Non-Point Pollution Control," Paper presented at Conf. on Biogeochemical Cycling in Wetlands, LSU, Feb. 1991.

5. Kadlec, R. H. "Denitrification in Wastewater Wetlands," Paper presented at WPCF Conf., Dallas, TX, 1989.

6. Jackson, J. "Man-Made Wetlands forWastewater Treatment: Two Case Studies," in: Constructed Wetlands for Wastewater Treatment, Lewis, Chelsea, MI 1989.

7 Kadlec, R.H. and Rathbun, M.A. "Copper Sorption on Peat." In: Proceedings of the International Symposium on Peat Utilization, S.A. Spigarelli and C.A. Fuchsman, Eds., Bemidji State University, Minnesota, pp. 351-364, February 1984.

8 Weider, R. K. " A Survey of Constructed Wetlands for Acid Coal Mine Drainage Treatment in the Eastern United States," Wetlands, Vol. 9, No. 2, 1989.

9 Litchfield, D. K. and D. D. Schatz " Constructed Wetlands for Wastewater Treatment at Amoco Oil Company's Mandan, North Dakota, Refinery," in: in: Constructed Wetlands for Wastewater Treatment, Lewis, Chelsea, MI 1989.

10 Litchfield, D. K. " Constructed Wetlands for Wastewater Treatment at Amoco Oil Company's Mandan, North Dakota, Refinery," in: Constructed Wetlands for Water Pollution Control, Pergamon, New York, 1990.

11 Duda, P. Chevron Oil Company, Richmond, CA, Personal communications and site visit, 1989.

12 Honig, R. "Tenneco's Use of a Rock-Reed Filter at a Natural Gas Pipeline Compressor Station," Poster Session Paper at Conference on Constructed Wetlands for Wastewater Treatment, Chattanooga, TN, 1988.

IX: Publications: None

APPENDIX A:

MAJOR LITERATURE SOURCES
WETLAND TREATMENT OF WASTEWATER

A list of the most relevant comprehensive publications on the design of wetlands for water quality improvement has been compiled. This list generally does not include individual papers.

The numbering of the list is chronological; but the most recent entries are listed first.

[A29] **Constructed Wetlands for Water Quality Improvement**, G. A. Moshiri, Editor, Proceedings of an International Symposium, in preparation, 1992.

[A28] Hammer, D. A. **Creating Freshwater Wetlands**, Lewis Publishers, Chelsea, MI, 1992, 297 pp.

[A27] **North American Wetlands for Water Quality Treatment Database**, Phase I Draft Interim Report, R. L. Knight, R. H. Kadlec and S. C. Reed, prepared for USEPA, July 1991, 228 pp.

[A26] **An Inventory of Constructed Wetlands used for Wastewater Treatment in the United States**, S. C. Reed, prepared for USEPA, March 1990, 163 pp.

[A25] **Moerassen voor de Zuivering van Water (Wetlands for the Purification of Water)**, Post Academic Course, published as The Utrecht Plant Ecology News Report, University of Utrecht, Lange Nieuwstraat 106, 3512 PN Utrecht, The Netherlands, No. 11, October 1990, 269 pp., (about 50% in English).

[A24] **Behandlung von hauslichen Abwasser in Pflanzenbeeten**, ATV, Gesellschaft zur Föderung der Abwassertechnik e.V., Postfach1160, Markt 71, D-5205 St. Augustin 1, Germany. English translation of this design guideline document available, 1989, 12 pp.

[A23] **European Design and Operations Guidelines for Reed Bed Treatment Systems**, P. F. Cooper, Editor, prepared by EC/EWPCA Emergent Hydrophyte Treatment Systems Expert Contact Group, Water Research Centre, Swindon, UK, 1990,

33 pp.

[A22] **Constructed Wetlands in Water Pollution Control**, P. F. Cooper and B. C. Findlater, Editors. Pergamon Press, London, 1990, 605 pp.

[A21] Water Pollution Control Federation. **Manual of Practice: Natural Systems, Wetlands Chapter**. February 1990, MOP FD-16 WPCF, 270 pp.

[A20] **Water: Laws and Management**, F. E. Davis, Ed., AWRA, Bethesda, MD, 1989, >600 pp.

[A19] **Wetlands: Concerns and Successes**, D. W. Fisk, Ed., AWRA, Bethesda, MD, 1989, 565 pp.

[A18] **Constructed Wetlands for Wastewater Treatment**, Conference Proceedings, D. A. Hammer, Editor, Lewis Publishers, Chelsea, MI , 1989, 831 pp.

[A17] **Design Manual: Constructed Wetlands and Aquatic Plant Systems for Municipal Wastewater Treatment**, USEPA 625/1-88/022, September 1988, 83 pp.

[A16] Reed, S. C., Middlebrooks, E. J. and R. W. Crites. **Natural Systems for Waste Management and Treatment**, McGraw-Hill, NY, 1988, 308 pp.

[A15] **The Ecology and Management of Wetlands**, D. D. Hook & Others, Eds., Timber Press, Portland, OR, 1988, 992 pp.

[A14] **Report on the Use of Wetlands for Municipal Wastewater Treatment and Disposal**, USEPA 430/09-88-005, October 1987.

[A13] K. R. Reddy and W. H. Smith, eds. **Aquatic Plants for Water Treatment and Resource Recovery**, Magnolia, Orlando, 1987, 1032 pp.

[A12] Kaynor, E. R., P. J. Godfrey and J. Benforado. **Ecological Considerations in Wetland Treatment of Municipal Wastewaters**, Van Nostrand, 1985, 473 pp.

[A11] **Freshwater Wetlands for Wastewater Management Handbook**, USEPA 904/9-85-135, September 1985, 507 pp.

[A10] **The Ecological Impacts of Wastewater on Wetlands: An Annotated Bibliography**, USEPA 905/3-84-002, February, 1984, 257 pp.

[A9] Hyde, H. C., Ross, R. S. and F. Demgen. **Technology Assessment of Wetlands for Municipal Wastewater Treatment**, USEPA 600/2-84-154, NTIS No. PB 85-106896, November 1984, 98 pp.

[A8] Hammer, D. E. and R. H. Kadlec. **Design Principles for Wetland Treatment Systems**, USEPA 600/2-83-026, April 1983, 243 pp.

[A7] **Phase I Report: Freshwater Wetlands for Wastewater Management**, USEPA 904/9-83-107, 1983.

[A6] **The Effects of Wastewater Treatment Facilities on Wetlands in the Midwest**, USEPA 905/3-83-002, September 1983, 377 pp.

[A5] Eisenberg, D. M. and J. R. Benneman. **An Overview of Municipal Wastewater Aquaculture**, USEPA, Draft Final Report, Contract No. DM41USC252(C), March 1982, 84 pp.

[A4] Chan, E., Bursztynsky, T. A., Hantsche, N., and Y. J. Litwin. **The Use of Wetlands for Water Pollution Control**, USEPA 600/2-82-036, September 1982, 261 pp.

[A3] Proceedings of the Seminar on **Aquaculture Systems for Wastewater Treatment,** R.K. Bastian and S.C. Reed, Eds., USEPA Publication No. MCD-67, September 1979, 485 pp.

[A2] **Wetland Functions and Values: The State of Our Understanding**, P. E. Greeson, J. A. Clark and J. E. Clark, Eds.,AWRA, Minneapolis, MN, 1979, 674 pp.

[A1] **Freshwater Wetlands and Sewage Effluent Disposal**, Proceedings of NSF/RANN Conference, D. L. Tilton, R. H. Kadlec, and C. J. Richardson, Eds., The University of Michigan, Ann Arbor, Michigan, May 10-11, 1976, NTIS PB259305, 343 pp.