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QUARTERLY TECHNICAL REPORT:

Title:	WETLAND TREATMENT OF OIL AND GAS WELL WASTEWATERS
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PIs:	Prof. Robert H. Kadlec and Dr. Keeran R. Srinivasan
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Reporting Period:	August 25, 1992 - Nov. 24, 1992.

3/2/92

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DISCLAIMER

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 wastewater 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 wastewater was critically evaluated and an outline of the research plans for the first year was delineated.

In this quarterly report, results of our efforts on Tasks 2 and 3 are presented and discussed.

- Construction of a laboratory-type wetland (green house) has been begun and the this undertaking is described in this report.

- Our literature search has shown that clay amendments to wetlands are beginning to be used in Europe for P removal in agricultural drainage systems. We have undertaken similar studies on the use of inexpensive amendments to wetlands such as **modified-clays** and algae to enhance the performance of a constructed wetland for the treatment of oil and gas well wastewaters. The results from these studies are presented and analyzed in this report.

- Further, our literature search (nominally completed under Task 1) unearthed more recent studies (some unpublished) and a summary is included in this quarterly report.

II. Task 1: Information Search: Petroleum Wetland Projects

Further information on the interaction of wetlands and metals and hydrocarbons has been located. One pilot research project is in progress in Wyoming under the auspices of the Marathon Oil Company, Wyoming Department of Environmental Quality and the Colorado School of Mines. Several conference papers have been obtained which deal with metal and hydrocarbon removal in wetlands.

Wyoming/Marathon Project

The following information has been extracted from draft manuscripts in progress, and should be considered confidential until released by the authors; such permission has yet to be obtained.

The State of Wyoming is the 6th largest oil producer in the USA. About 40% of the produced water is surface discharged, in the amount of approximately 80 million gallons per day. Thousands of acres of wetlands are sustained by this produced water.

The concerned agencies (Marathon Oil Company, Wyoming Department of Environmental Quality and the Colorado School of Mines) entered into a cooperative pilot project to assess the potential of wetlands to treat produced water. The system was constructed in summer 1991. It consists of four overland flow cells, a rock lined channel and a 0.75 acre wetland.

The wetland was constructed by placing cow manure and straw in a shallow basin, and transplanting cattail. By fall, 1991, an 80% cover of cattail had been achieved. Sampling locations include the inlet and the outlet of the wetland, as well as other points in the complex. Samples from four monthly samplings were analyzed, during the period of vegetation establishment. Radon was reduced 40% by the wetlands. Phenolics were reduced by 25%. Benzene was reduced to below 1 µg/l at the wetland outlet, but no inlet data were collected for benzene. The wetlands were found to have a very beneficial effect on the biotoxicity of the water.

The detention time in the wetland was quite short: on the order of less than one day.

We are in the process of establishing communications with this research project.

Paraffinic Hydrocarbon Degradation

Brian Shutes of Middlesex University, London, UK has completed a study of the degradation of individual members of homologous series of hydrocarbons in wetland environments. His reports have been requested.

Hydrocarbon Adsorption Utilizing Clay Amendments

Reference:

Ghosh, R. G. and T. M. Keinath, 1992. "Effect of Clay Mineralogy on the Adsorption of Hydrophobic Organic Compounds onto Aquifer Soils," Preprint AC92-006-005, Water Environment Federation, Alexandria, VA.

Key Results: Expandable clays montmorillonite and vermiculite had a significant effect on naphthalene partitioning.

Chromium Sorption and Precipitation

Reference:

Azizian, M. F. and P. O. Nelson, 1992. "Hexavalent Chromium Adsorption and Reduction in Natural Soils," Preprint AC92-040-004, Water Environment Federation, Alexandria, VA.

Key Results: Iron (Fe+2) oxidation provides an electron source for reduction of hexavalent chromium, and provides a route to the co-precipitation of iron and chromium oxy-hydroxides. Significant binding to soils occurs via ion exchange, which is reversible in the presence of displacing cations.

III. Task 2A: Construction of a Laboratory-type Wetland:

A laboratory-type green house has been designed and built during the reporting period and cattails (*Typha latifolia*) are being grown in 50 liter lysimeters. A total of 90 lysimeters have been constructed. Each lysimeter was filled with approximately 8 " to 12" of wetland soil (obtained from an operating wetland in Michigan) and four cattails were planted per lysimeter. An indoor lighting system was designed and put in place in one of the laboratories of the chemical engineering department at this University. The construction of lysimeters was undertaken so that cattails can be closely monitored and their environment carefully controlled. A 200 sq.ft area was illuminated by twelve 400 watt lights with an average light intensity of 1740 foot-candles. The area was sufficient to hold 80 microcosms or lysimeters. The remaining 10 are housed at the University of

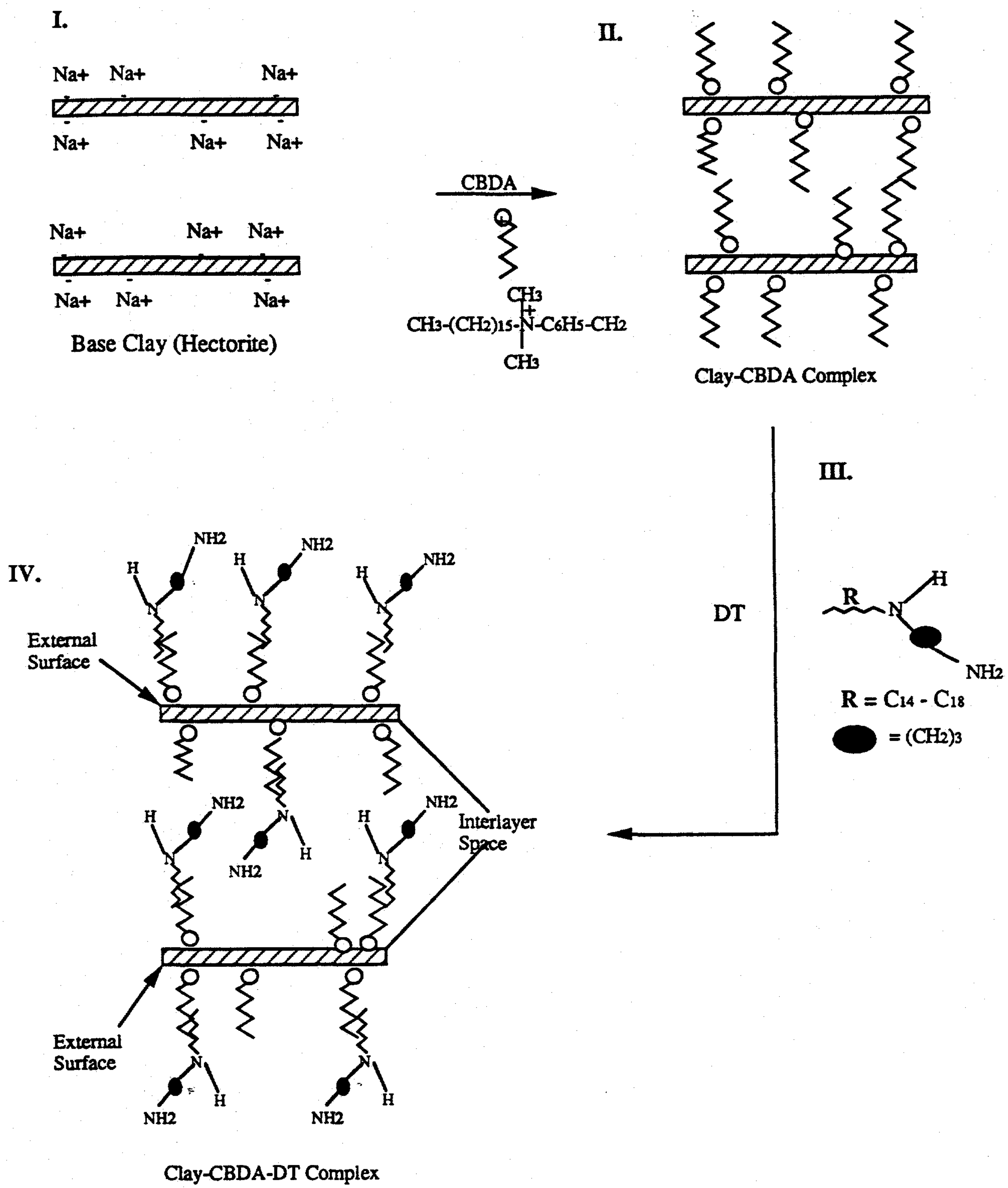


Fig. 1 Preparation scheme of Clay-CBDA-DT Complex

Michigan botanical gardens. The indoor microcosms (lysimeters) have shown signs of stress. The cattails developed tan tips and many started to droop. The average light intensity and the power spectrum of the indoor lighting system were examined. It was found that the indoor luminescence in the visible part of the electromagnetic spectrum was roughly one half of the ambient outdoor intensity on a summery day. More importantly, the emission spectrum of the indoor lights (high pressure sodium light bulbs) was found to peak around 540 nm, while photosynthetic pigments of cattails (Chlorophyll A) have absorption maxima at 430 and 680 nm. The cattails were moved outdoors and they seemed to recover within days and grow normally. Further modification of light bulbs in the indoor area where lysimeters are being prepared for future experiments has been undertaken. Half of the high pressure sodium light bulbs were replaced by metal halide bulbs which have a fairly uniform emission spectrum in the visible light range. A number of microcosms were moved back to the indoor area to monitor the effect of the new lighting system on their growth. Preliminary indications are that the cattails are starting to turn brown at the tips and are showing other signs of distress. It is not clear as to why the an indoor setting is not as helpful for the robust and are continuing our work on trying to create a proper indoor environment for the optimal growth of cattails.

IV. Task 2B: Development of Wetland Amendments:

Our literature search has revealed that clay amendments are beginning to be used in Europe for P removal in agricultural drainage systems. We have undertaken studies on the use of inexpensive amendments to wetlands such as **modified-clays** and **algae** to enhance the performance of a constructed wetland for the treatment of oil and gas well wastewaters.

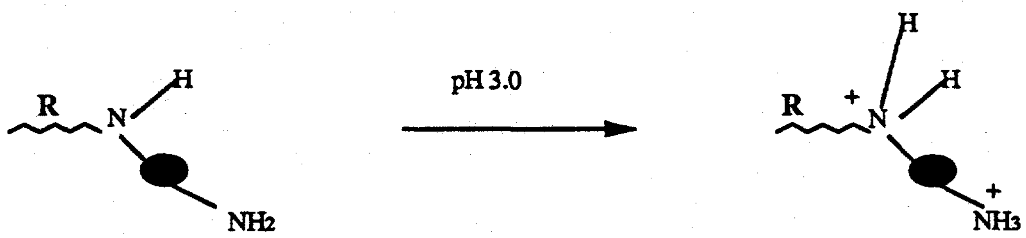
Modified-clays:

The scheme is shown diagrammatically in Fig. 1. The base clay is a smectite, specifically Na-hectorite (part I, Fig. 1) This is treated initially with quaternary ammonium surfactant, cetyl benzyl dimethyl ammonium (CBDA) ion. Previous studies have shown that this cationic surfactant binds "irreversibly" to the interlayer and the external surfaces of the base clay (part II, Fig. 1) (2,3). As a consequence, the CBDA-clay becomes hydrophobic and, if the adsorption density of CBDA is high, all of the cation exchange sites on the clay are " irreversibly " blocked.

The next step is to contact CBDA-clay with a dialkyl amine Duomeen-T, (DT), a dissociable surfactant, which has been shown to be a potential complex agent for metal ions such as Cu in solution around pH 8.0 (4).

Duomeen-T, (DT), is a commercially available, aliphatic diamine of the type ($R\text{-}NH\text{-}(CH_2)_3\text{-}NH_2$) and the size of the alkyl group ranges from C_{12} to C_{18}. The apparent molecular weight based on hydrocarbon assay is 350 g/mole (4). Duomeen-T, (DT), is insoluble in water and a solution of DT was prepared in isopropanol for use. As shown in part III of Fig. 1, the " anchoring" of DT to CBDA-clay surface would occur via hydrophobic bonding. The net result would be to have the active end of DT to be pointing towards the solution side of the interface where it is most likely to encounter heavy metal ions.

In practice, the amount CBDA was fixed at 23% by weight of the CBDA-clay adduct. At this adsorption density of CBDA, bulk of the interlayer and the external surface of the clay is coated with this surfactant and the surface charge was also minimal, as evidenced



Both amines are protonated and very little metal ion binds

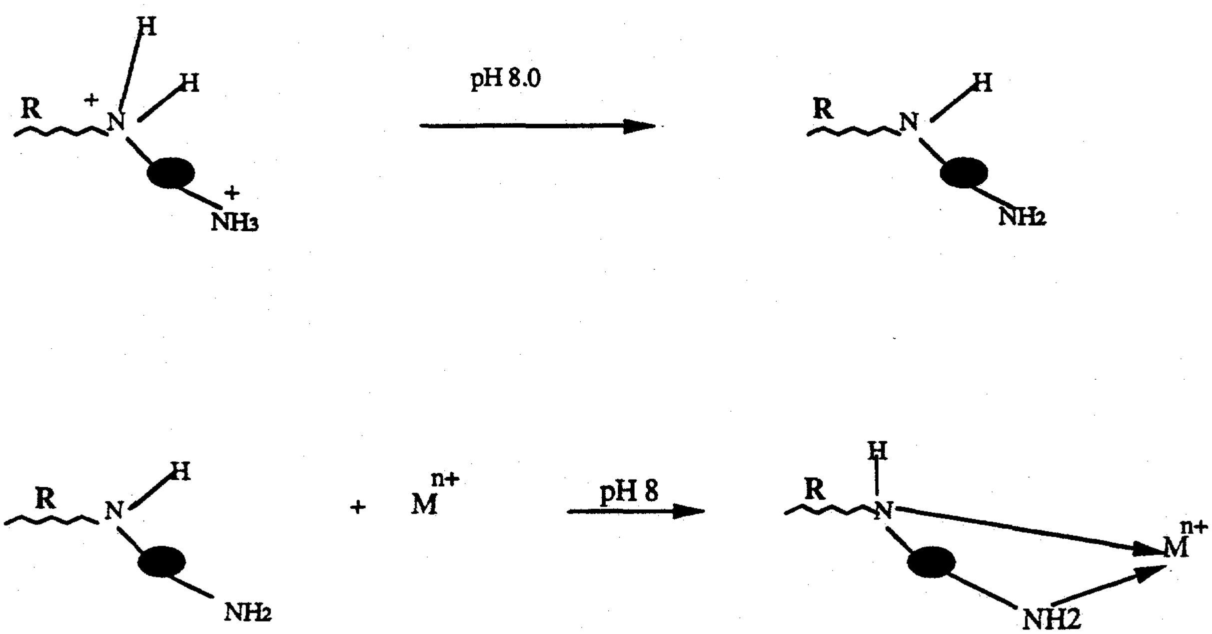


Fig. 2 Proposed mechanism for the adsorption of metal ions (M^{n+}) onto clay-surfactant complex

by a very low value of zeta potential (5). A four-fold (on a molar basis) excess of DT was mixed with the flocs of hectorite-CBDA to form hectorite-CBDA-DT complex. This was washed extensively with deionized water to remove unreacted DT.

The possible mode of operation of this complex is pointed out in Fig. 2. At low pH, (i.e. pH 3.0), the primary and the secondary amine groups of DT will be protonated. The resultant positive surface charge will repel metal ions from the surface and minimize the adsorption of metal ions (Upper panel, Fig. 2). At pH 8.0, both the amine groups will be significantly, in not fully, deprotonated. Under such conditions of low or zero surface charge metal ions can form a bidentate complex with both the primary and the secondary amine groups of DT (lower panels, Fig.2).

The resultant Hectorite-CBDA-DT complex adsorbed Cu^{2+} ions (in low ppm levels) strongly at pH 7.2 and desorbed the metal ions at pH 3.0. In the case of Cd^{2+} ions, a strong adsorption maximum occurred at pH 8.0 and the desorption of metal ions could be effected at pH 3.0.

Algae:

Experiments were conducted to study cadmium uptake by the unicellular green alga *chlorella vulgaris*.. These were 96 hour batch experiments with 50 ml triplicate cultures in 125 ml flasks. Algae was grown in media suggested for *chlorella vulgaris* with a minor modification of using $FeCl_3$ (2.5 mg/L) rather than Fe-EDTA to minimize the chelating effect of EDTA on Cd uptake by the algae. The pH of the medium was 5.8. It should be recognized that, in the absence of EDTA, bulk of Fe^{3+} would in insoluble form at this pH. But, it is our belief that algal growth was not limited by the possible precipitation of Fe^{3+} ions.

Exponentially growing cultures at an initial cell concentration of 2.5×10^8 cells/L were spiked with Cd in the form of $CdCl_2$. The initial Cd concentration was 3 mg/L. Biomass, final metal concentration, cell size distribution, and cell concentration were measured every 12 hours.

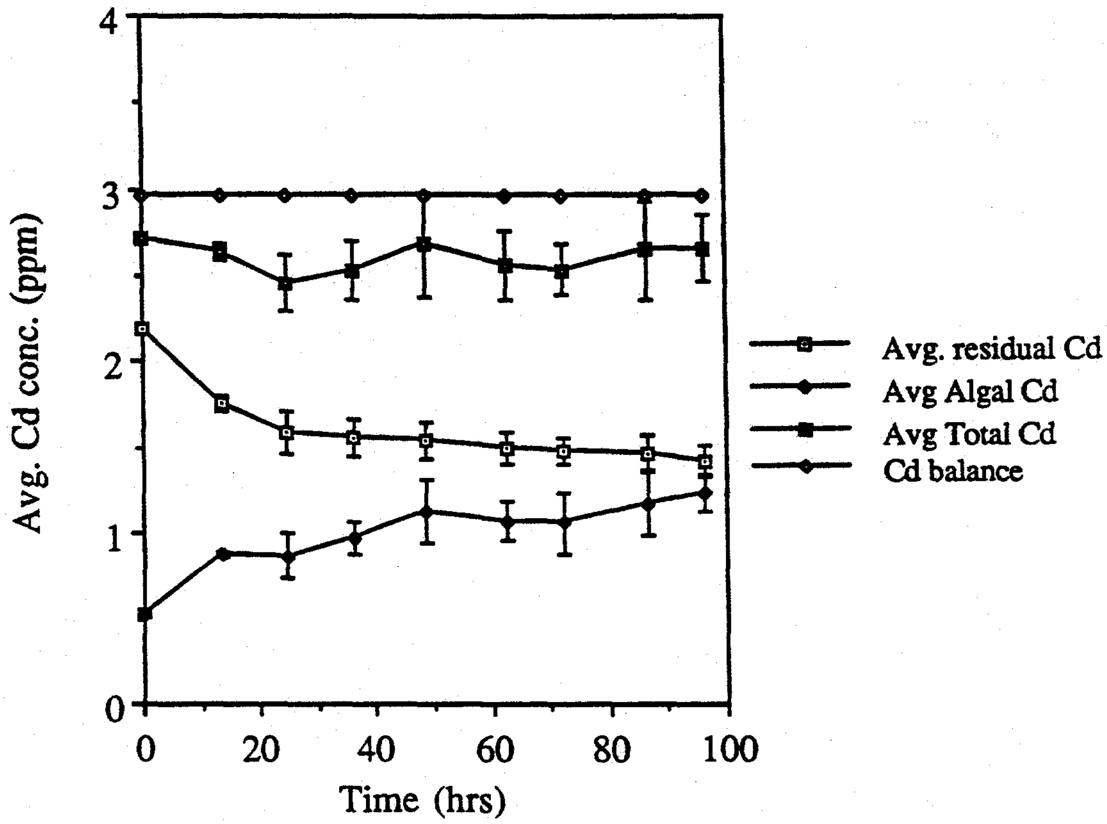
The results are shown in Figs. 3. An instantaneous uptake of Cd^{2+} ions amounting to around 30% of the final value is observed. This initial fraction is thought to arise from sites on the external surface of the cells. The metal accumulation continues for 96 hours , and the amount of metal ion adsorbed is greater than 0.1 g Cd/g dry wt. biomass. It is to be noted that 90% of the total accumulation occurs within the first 24 hours. The adsorption profile appears to be tri-phasic in time, comprising of an instantaneous, gradual, and a very slow process.

An increase in the average cell size with little or no increase in cell concentration is noted in presence of Cd. Thus, it is concluded that Cd inhibited cell division, but it did not kill the algal cells.

V. Future Work:

Immobilization of toxic organics and heavy metals by modified-clays, uptake of different types of heavy metals by algae, biodegradation of toxic organics by the microorganisms inherent to a wetland and the sorption of heavy metals by the soil and the sedimentary components of a wetland are some of the study areas for the next reporting period.

Fig. 3 Adsorption of Cd ions onto Algal cells



VI: SUMMARY

This quarterly report presents recent (as yet unpublished) literature on the use of wetlands for the treatment of process wastewaters from operations relating to oil and gas wells. Thus, Task 1 of the contract has been completed. Construction of a laboratory-type wetland has been commenced and cattails are being grown for future experiments. Studies on the use of modified-clays and algae as wetland amendments to promote a more cost-effective and efficient immobilization of heavy metals by wetlands have been undertaken. It is shown that modified-clays strongly adsorb both Cd^{2+} and Cu^{2+} ions from solution at pH 8.0 and 7.2 respectively. On the other hand, uptake of Cd^{2+} ions by algae occurs at pH 5.8. Our results also indicate that Cd^{2+} ions in solution (at an initial concentration of 3.0 mg/L) inhibit cell division, but do not kill algal cells.

VII: Report Distribution List:

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VIII. REFERENCES:

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IX. Publications: None