MASTER

Bio-oxidation of Aqueous Cyanogens Typical
of Synthane Gasifier By-product Water

Progress Report

for Period September 1, 1977 - November 30, 1977

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Abstract

Acclimated biological cultures were developed from activated sludge taken from coke plant biological wastetreatment facilities. These cultures are capable of degrading potassium thiocyanate from an original concentration of 500 mg/l SCN to less than 1 mg/l in an aeration period of 24 hours pH inhibition appears to be significant at values greater than 7.6. Preliminary assessments indicate that aerobic biological organisms may play a major role in the removal of aqueous thiocyanate as found in the wastewaters from the gasification of certain coals.

Progress Report

Bio-oxidation of Aqueous Cyanogens Typical of
Synthane Gasifier By-product Water

Contract EY-77-5-02-4502.A000

Start Date: 9/1/77

Expiration Date: 2/28/78

Date of this Report: 11/30/77

Principal Investigator: Dr. Ronald D. Neufeld, Associate

Professor, University of Pittsburgh

As indicated above, this progress report and attached renewal proposal is submitted after only 3 months into the contract period. The scope of this contract is to develop biological cultures capable of degrading thiocyanate (cyanogen) compounds typical of those found in the Synthane gasification of certain coals, and to provide data illustrative of such degradation.

In accordance with the proposal, a final report in triplicate is due 30 days after the termination of this 6 month effort. This report, however, is a requirement which is to accompany a request for project renewal 3 months prior to the contract termination.

All contract requirements regarding the development of a thiocyanate degrading biocultures and assembly of bench sized bio-reactors are complete at this time. Sketches and photographs of the bioreactor shall be included in the final report. As a deliverable for this contract, approximately 1 gram of thiocyanate degrading sludge shall be packaged and hand delivered to Mr. W. P. Haynes, the Technical Project Officer of the Pittsburgh Energy Research Center. This sludge is now available but shall be delivered within 30 days after the termination of the contract.

The principal investigator has devoted at least 10% of his time to the contract and expects to increase this percentage as time progresses. This level is in excess of the 8% for 6 months time commitment indicated in the contract. A graduate research assistant has been employed for 1/2 time for the duration of this project. A technician has been employed for about 50 hours for assistance in the construction of bench scaled reactors.

Discussion of Technical Results to Date

Prior research indicates that thiocyanates are produced in an amount of about 0.07 lb per pound moisture ash free coal gasified from the Synthane and Lurgi processes (1), and in amounts of about 2.5 lb per pound moisture ash free coal gasified from the Hygas Process. Concentrations of thiocyanate on the order of 20 to 200 mg/l have been reported from the Synthane gasification of certain coals (2).

At present, several states including Pennsylvania have a "zero discharge" requirement for cyanogens (and cyanides). Thus, cyanogen removal is a requisite for the environmentally acceptable operation of SYNTHANE and other coal gasification processes.

For larger scale coal gasification processes to come on stream by the mid 1980's, wastewater treatment processes must be developed from essentially currently available best treatment alternatives. The traditional approach to thiocyanate (and cyanogen removal) is batch chlorination. This approach, while viable for the metal plating industry, is not applicable to coal conversion processes due to the phenolic nature of gasifier effluents and the inherent tendency to form toxic chlor-phenolic by-products. Chlor-phenolics exhibit tastes, odors, and toxicities to animals in waters at the parts per billion level.

The steel industry has utilized biological processes for the treatment of the phenolic content of coke plant wastewaters. These facilities are not specifically designed for thiocyanate removal and such removal is reported to occur in a somewhat unpredictable fashion. Accordingly, while proof of principle data exists in the literature for thiocyanate biodegradation little data exists regarding kinetic and other design parameters necessary for prediction of process applicability and stability for use by SYNTHANE and other coal conversion processes.

The purpose of this six month contract is to demonstrate that biological cultures in significant quantity could be developed that are capable of thiocyanate degradation in concentrations typical of SYNTHANE effluents. In September, 1977, approximately 20 liters of activated sludge were obtained from the Clairton, PA plant of United States Steel Corp. This plant has a coke manufacturing facility and treats its liquid waste biologically. The activated sludge received was amber in color, had significant floating oils, and exhibited strong phenol and cresol odors.

The sludge was brought to the Environmental Engineering Laboratories of the University of Pittsburgh and allowed to aerate for two days for stripping and removal of soluble volatile organic materials and skimming of surface oily materials. Acclimation of the culture to thiocyanate (SCN) was begun by feeding the system a daily diet of 100 mg/l SCN and 100 mg/l dextrose with appropriate levels of phosphate nutrient buffer solution. Dextrose was utilized during this phase because its use is reported to result in shortened times for thiocyanate acclimation (3). This period of acclimation lasted for about 1 month during which time an attempt was made to develop continuous cultures systems with no cell recycle. Organisms capable of growth on the media provided were retained in the continuous reactors while others were washed out. Detention periods of 24 hours resulted in effluent SCN levels of 1 mg/l or less while reactors with detention time of 16 and 21 hours providing poorer quality effluents.

After 4 weeks of culture acclimation and purification, a second phase of acclimation was begun whereby the residual biomass was collected, concentrated, and placed into one 8 liter reactor operated on a batch basis. This reactor was fed 500 mg/l SCN daily with no

dextrose or other supplemental organic carbon sources. The system was fed and aerated for 23 hours. Air was then turned off and organisms were allowed to settle for 1 hour. Samples were taken of solids, pH, NH_3 , SCN, and alkalinity as needed. One liter of supernate was wasted each day and replaced with tap water and sufficient potassium thiocyanate so that the SCN concentration at the beginning of the next 24 hour cycle was 500 mg/l. At this point in the experimental program, the 500 mg/l SCN was chosen as the maximum SCN level due to published reports of substrate inhibition occurring at higher levels (4). As shown below SCN degradation at 1000 mg/l were demonstrated as being feasible.

During the course of fill and draw operation, the sludge assumed a light brown color and gave off no odor. A light pin-point floc became evident which is typical of young rapidly growing sludge. Specific thiocyanate removal rates rose from 0.5 lb SCN removed/lb biomass-day to 2.1 lb SCN removed/lb biomass-day during the course of this phase of experimentation. The pH was held at 6.7 to 7.0 and the alkalinity was about 300 mg/l as CaCO_3 . A small increase of about 15-25 mg/l was noted in the NH_3 concentration during the course of aeration. This is consistent with observations that oxidation of SCN leads to CO_2 , protoplasm and NH_3 . NO_3 may similarly be formed by the biological nitrification of NH_3 . Further research is proposed to complete the material balance for nitrogen in the process and to account for possible simultaneous biological nitrification.

A third phase of experimentation was started on October 28 when about 3800 mg of non purified but acclimated U. S. Steel thiocyanate degrading organisms were placed in a 6 liter batch bio reactor. This system was compared side by side to 2000 mg of the previously developed purified culture for specific rates of thiocyanate degradation. The non-purified culture exhibited a rate of 0.67 mg SCN removed/mg biomass-day. Thus either the purified culture was better acclimated to SCN

or the non purified culture contains biomass or organic inerts that lower the apparent biological activity of the entire macrosystem. In either case, this experimental phase highlights the importance of utilizing a purified and acclimated culture of microorganisms for SCN removal. Microorganism may be developed over time from coke plant wastewater treatment facilities, but a direct utilization of these organisms without an appropriate period of acclimation and purification will lead to unsatisfactory performance.

During the course of experimentation, the pH of each bioreactor was allowed to reach 7.6. At this pH the specific rate of removal dropped to 0.36 and 0.28 mg SCN removed/mg biomass-Day for the purified and non purified cultures respectively indicating inhibition.

This level of inhibited activity was maintained in-advertently for a period of about 7 days. Subsequent pH depression to the range 6.8 to 7.0 with H_2SO_4 in each reactor resulted in renewed activity indicated that the alkaline pH level acted as an inhibitor to the system and not as a toxicant.

During the second week in November, the two batch bio reactors were converted to semi-continuous systems with imposed cell wasting rates of 1/20 per day, pH was monitored and held to the range 6.8 - 7.1. Thiocyanate was reduced from 500 mg/l to less than 1 mg in the 23 hour aeration time indicating specific removal rates of 1.14 mg SCN removed/mg biomass-day for the purified culture and 0.653 mg SCN removed/mg biomass-day for the non-purified culture.

For comparative purposes, a rate of 1.14 is translatable to a COD basis as follows.

$$\frac{1.14 \text{ mg SCN removed}}{\text{mg Biomass-Day}} \times \frac{12 \text{ mg Carbon}}{58 \text{ mg SCN}} \times \frac{32 \text{ mg O}_2}{12 \text{ mg Carbon}} = 0.63 \frac{\text{mg COD removed}}{\text{mg Biomass-Day}}$$

when the sludge age is 20 days for this batch system. As shown by Valiknac (5) SCN is not stripped off to the atmosphere in the pH range by cell free systems. Thus, all thiocyanate removals must be attributed to active biomass using SCN as the sole carbon source.

In interests of stressing the system a few days prior to writing this progress report, the two semicontinuous systems were operated at imposed cell wasting rates of 1/15 and 1/20 per day respectively. Thiocyanate was removed from the initial 1000 mg/l to about 800 mg/l in 24 hours in the 15 day sludge age system and from 1000 mg/l to 600 mg/l in 24 hours in the 20 day sludge age system. It is possible that either the 1000 mg/l is inhibitory to these organisms or, most likely, an insufficient mass of biota is in the system at this time to effect virtual complete removal over a 24 hour aeration period. These experiments are continuing and will be reported on in the final report.

Conclusion

1 - Mixed cultures have been developed from coke plant biological wastetreatment facilities that are capable of degrading thiocyanate from levels of 500 mg/l to 1 mg/l in a 24 hour aeration period.

2 - Thiocyanate biodegradation appears to be inhibited at pH levels of 7.6 and higher. Maximum biodegradation rates were observed in the pH range of 6.7 to 7.2.

3 - Ammonia appears to be a by product of SCN biodegradation. A nitrogen balance however, has not as yet been done.

4 - Organisms taken directly from a coke plant biological wastewater treatment facility should be acclimated and purified prior to use to assure satisfactory performance.

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