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# Project Summary

# Biological Treatability of KRW Energy Systems Gasifier PDU Wastewaters

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**Bench-scale biological treatability tests with wastewaters produced from the KRW Energy Systems gasifier process development unit (KRW-PDU) were conducted to assess the biotreatability of these aqueous wastes and to develop data for correlations that establish a basis for designing a biooxidation process. An autotrophic activated sludge process was developed that utilized a mixed culture of nitrifying and sulfur-oxidizing bacteria for simultaneous thiocyanate biodegradation and nitrification. An ammonia-nitrogen concentration of greater than 250 mg/L and a thiocyanate concentration of 150 mg/L were biooxidized at a hydraulic residence time of 24 hours and at sludge ages between 60 and 150 days. Experimental testing at bioreactor temperatures below 20°C indicated that the nitrifying bacteria were severely impacted at a bioreactor temperature of 10°C, while the observed thiocyanate removal efficiency deteriorated at a mixed liquor temperature of 6°C. Elevated concentrations of chloride, fluoride, and boron in experimental wastewaters did not inhibit either nitrifying or sulfur-oxidizing bacteria in the activated sludge process. However, heavy metals were concentrated in the activated sludges: this was thought to be a consequence of the long sludge ages of the experimental process.**

***This Project Summary was developed by EPA's Air and Energy Engineering Research Laboratory, Research Triangle Park, NC, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).***

## Introduction

Biological treatability studies were conducted on wastewaters from the KRW Energy Systems gasifier, formerly called the Westinghouse gasifier, process development unit (PDU) as part of a characterization program to develop design and environmental data for synthetic fuels plants based on KRW-type coal gasification technology. This report gives results of the biooxidation study, conducted through the cooperative efforts of Radian Corporation and Engineering-Science, Inc., to provide engineering and environmental data for designing wastewater treatment systems for this and other similar coal gasification technologies.

In 1982 the Department of Energy's Morgantown Energy Technology Center (METC), the Gas Research Institute (GRI), and the Environmental Protection Agency (EPA/AEERL) recognized the need for a program to provide wastewater treatment process design data for a ash-agglomerating fluidized-bed gasification process. In response to this need, METC, GRI, and EPA entered into a joint program to develop wastewater treatment performance data, design parameters, and environmental characterization data from a series of bench-scale treatability tests with wastewaters from the KRW-PDU coal gasification process. The program produced a series of wastewater characterization and treatability documents which established the basis of design data for several wastewater treatment and reuse unit operations/processes:

- coagulation/clarification for removal of small diameter (<2 μm)

carbon particles (fines) present in the wastewaters after bulk settling of dense solids suspensions found in the PDU quench liquors/gas cooling condensates;
- chemical conversion and fixation of cyanide to less toxic forms;
- steam stripping for removal of dissolved acid gases and ammonia;
- activated sludge for ammonia, thiocyanate, and organic carbon removal; and
- concentration of treated effluents by low- and high-temperature evaporation processes.

This report is the basis-of-design document for an autotrophic activated sludge process, developed to treat process wastewaters from an ash-agglomerating fluidized-bed gasification process. The technology, also generally applicable to the treatment of process wastewaters from entrained-bed gasifiers, should be viewed as a technology innovation for treatment of low tar, oil, and phenol coal gasification quench liquors and gas cooling condensates.

## Objectives

The biological treatability tests were performed using wastewater from the KRW gasifier PDU. Primary objectives of the study were:

- To determine the feasibility of biological treatment of KRW-type gasifier wastewaters using mixed populations of heterotrophic and obligate autotrophic bacteria for degradation of organic carbon, ammonia, and thiocyanates.
- To obtain data for the determination of preliminary design parameters for an activated sludge process to treat KRW-type gasifier wastewater.

Bench-scale laboratory studies using continuous-flow bioreactors were conducted with the KRW wastewater. The studies were preceded by an initial period of activated sludge acclimation that established a representative microbial population for treatability testing. The continuous-flow biooxidation reactors were operated at different biological solids retention times and substrate loadings in order to establish the biokinetics of the activated sludge process. The impact of any toxic or inhibitory substances that may have been present in the KRW wastewater was investigated during treatability testing.

The effects of temperature and non-substrate ions on microbial activity were investigated using biooxidation test reactors and activated sludges acclimated during continuous-flow testing. Alkalinity and pH considerations also were investigated during continuous-flow testing.

These data were used to develop a basis-of-design for an activated sludge process to treat KRW-type gasifier wastewater.

## Results and Conclusions

Biological oxidation treatability studies on KRW-PDU wastewaters were conducted to obtain data for the determination of design parameters for the treatment of contaminated quench liquors and gas condensates produced during coal gasification. The characteristics of the KRW-PDU wastewater were such that biological oxidation of nitrogen species (i.e., ammonia and thiocyanates) is the most important consideration because the organic pollutant content of the wastewater is low. The study involved examining aerobic chemoautotrophic cultures which were utilized for the biodegradation of ammonia and thiocyanate. The principal functions of the treatability study were to ascertain the degree of biodegradation possible by conventional activated sludge processes and to develop the basic criteria which would establish proper operation of an autotrophic biological treatment facility.

Coefficients to mathematical models which establish basic operation criteria were determined by operating bench-scale biological reactors at various substrate loadings and evaluating each system for substrate removal, sludge production, and oxygen requirements. Sludge settleability and thickening tests were performed throughout the treatability study to determine surface loading rates on secondary clarifiers which would provide both effective clarification and thickening during normal activated sludge process operation.

The treatment efficiency associated with the operation of a test bioreactor is indicated by the data presented in Table 1. The continuously fed, completely mixed bioreactor was evaluated at water temperatures of between 22 and 23°C. The steady-state period was generally characterized by excellent pollutant removal, with comparable effluent values observed for all test reactors with respect to ammonia, thiocyanate, TOC, COD, and $BOD_{20}$. Trace element data for the bioreactors indicated little apparent difference between the influent and effluent quality associated with biooxidation treatment because most of the trace elements were present at low concentrations in the KRW wastewaters. Sodium was present in the bioreactor effluent at elevated concentrations because of the addition of sodium hydroxide to the test reactors for pH control during biooxidation. Elements that were found at elevated concentrations in the sludge (relative to the water phase) were aluminum, barium, calcium, iron, potassium, magnesium, phosphorus, silicon, and zinc. Cadmium, chromium, copper, manganese, nickel, lead, and titanium were also bioaccumulated, but to lower levels. The presence of high concentrations of iron, copper, and nickel in the biosludge may indicate a potential for the accumulation of complexed cyanides in the sludge. These pollutants were at elevated concentrations in the sludges because of the long operational sludge ages of the autotrophic activated sludge process.

The GC/MS results for biotreated wastewaters indicated little apparent reduction during biooxidation of the low levels of extractable/chromatographable organics found in the KRW wastewater. The data relative to biosludge characteristics are inconclusive because a new group of compounds were found in the sludges that had not been detected in the wastewater. This may have resulted from the production of metabolic intermediates generated during

***Table 1.*** *Steady-State Bioreactor Average Treatment Performance*

| *Parameter* | *Influent (mg/L)* | *Effluent (mg/L)* |
|---|---|---|
| *TOC* | *38* | *2.7* |
| *COD* | *178* | *18* |
| *$BOD_{20}$* | *1,163* | *5* |
| *$NH_3$-N* | *253* | *<1* |
| *$NO_3$-N* | *<0.5* | *286* |
| *$NO_2$-N* | *<0.1* | *<0.1* |
| *SCN* | *130* | *<1* |
| *Total CN* | *1.19* | *0.86* |
| *Total P* | *4.95* | *2.8* |
| *TDS* | *294* | *2,976* |
| *Alkalinity (as $CaCO_3$)* | *57* | *36* |

the biodegradation of the low level of organics in the wastewaters.

A series of tests were performed with a continuously fed, completely mixed bioreactor to identify the effects of operation at lower ambient temperatures on substrate removal performance. These tests were conducted at equilibrium bioreactor temperatures of from 22 to 5.6°C. The effects of low temperature operation on bioreactor effluent quality are summarized in Table 2. These data indicate an apparently severe impact on removal efficiency at a mixed liquor temperature of about 10°C. The results presented show that nitrate formation was strongly inhibited at temperatures below 10°C under the conditions of the experiments. The microbial washout rate increased during this period, perhaps due to cell lyse. At no time during the study did nitrite build up in the mixed liquor of the test bioreactor.

The observed thiocyanate removal efficiency deteriorated below a 6°C bioreactor temperature. There was no apparent reduction in thiocyanate biodegradation: the temperature was reduced until this temperature was reached, despite elevated levels of ammonia in the bioreactor.

Pollutants which are common for most fluidized- and entrained-bed gasifier process wastewaters are chloride, fluoride, and boron. These elements may exist at elevated concentrations in gasifier quench liquors and gas cooling condensates and are considered a potential source of problems for biological treatment. A nonsubstrate ion toxicity study was performed with bioreactor activated sludges to document the impacts of increased concentrations of chloride, fluoride, and boron in the KRW wastewater on biooxidation treatment efficiency. A test bioreactor, operated at 3000 mg/L $Cl^-$, 285 mg/L $F^-$, and 150 mg/L $BO_2^-$ (as boron), produced a treated effluent quality comparable to the effluent generated from a bioreactor treating wastewaters with substantially lower concentrations of these pollutants. This indicated that the impact of these elements on biological treatment performance should be negligible.

Several conclusions can be drawn from the information obtained during steady-state and microbial stress testing of activated sludges used for the biooxidation of pollutants in the KRW-PDU wastewater:

- KRW wastewaters pretreated by steam stripping for ammonia reduction and acid gas removal can be successfully treated biologically with the activated sludge process. An ammonia-nitrogen concentration of 285 mg/L and a thiocyanate concentration of 150 mg/L can be biooxidized on a long-term basis at neutral pH conditions with a mixed culture of nitrifying and sulfur-oxidizing bacteria.
- Concentrations of 3000 mg/L chloride, 285 mg/L fluoride, and 150 mg/L boron in the KRW wastewater did not inhibit either the nitrifying or sulfur-oxidizing bacteria in the activated sludge process. The presence of low levels of free and complexed cyanide in the KRW wastewater did not have an adverse impact on ammonia or thiocyanate removal during biooxidation. Consequently, an autotrophic activated sludge process can be used to treat similar wastewaters derived from the gasification of different coals. The process may also be applicable to the treatment of wastewaters from other fluid- and entrained-bed gasifiers that produce aqueous wastes with chemistries similar to the experimental wastewater compositions.
- A study of temperature effects on the biodegradation of ammonia and thiocyanate indicated that the nitrifying bacteria were severely impacted at a bioreactor operational temperature below 10°C. This effect was thought to be largely the result of substrate (ammonia) inhibition. The observed thiocyanate removal efficiency deteriorated at a bioreactor operational temperature below 6°C. However, there was no apparent reduction in thiocyanate biodegradation: the temperature was reduced until this temperature was reached, despite elevated levels of ammonia in the test bioreactor.
- Although the settleabilities of the activated sludges were generally good, the apparent activated sludge settling quality (measured by the zone settling velocity and the sludge volume index) showed a deterioration at higher bioreactor sludge ages. Operational sludge ages for the experimental biooxidation process varied between 60 and 150 days. Generally, these sludge ages were considered necessary to maintain system stability for complete nitrification and to minimize sludge production.
- Heavy metals were concentrated in the activated sludges during experimental testing. However, the degree of bioaccumulation associated with the presence of metal-cyanide complexes in the wastewater could not be determined from the experimental data. The removal during biooxidation treatment of extractable/chromatographable organics identified by GC/MS analysis was inconclusive. The study did not determine the fate of organics in the autotrophic activated sludge process because of contradictory results regarding the nature of the organics in the aqueous and solid phases of the process.

**Table 2.** *Temperature Impact on Bioreactor Effluent Quality*

| | Average Effluent Quality | | | | | |
|---|---|---|---|---|---|---|
| *Average Temperature (°C)* | *$NH_3$-N (mg/L)* | *$NO_3$-N (mg/L)* | *$NO_2$-N (mg/L)* | *SCN (mg/L)* | *TOC (mg/L)* | *COD (mg/L)* |
| 18 | 0.12 | 269 | 0.15 | 1.05 | 4 | 13 |
| 15 | 0.07 | 284 | <0.1 | 1.03 | 5 | 23 |
| 12 | 0.08 | 270 | 0.16 | 1.13 | 4 | 30 |
| 10 | 209 | 68 | 0.22 | 1.15 | 3 | 27 |
| 8 | 252 | 3 | <0.1 | 1.1 | 2 | 33 |
| 6 | 278 | 2 | <0.1 | 11 | 6 | 23 |

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*The complete report, entitled "Biological Treatability of KRW Energy Systems Gasifier PDU Wastewaters," (Order No. PB 85-199 685/AS; Cost: $17.50, subject to change) will be available only from:*
*National Technical Information Service*
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