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QUARTERLY STATUS REPORT

CONTRACTOR: Geo-Microbial Technologies, Inc.
P. O. Box 132
Ochelata, OK 74051

CONTRACT NO.: DEAC2292PC92119

CONTRACT TITLE: Microbiological Recovery of Metals from Spent
Coal Liquefaction Catalysts

AUTHOR: Patrick Joffe and George T. Sperl

REPORTING PERIOD: January - March 1993

CONTRACT PERIOD: 9/30/92 - 9/30/94

PROJECT STATUS:

This project was begun on October 1, 1992. Its main objectives are:

1. To test non-growing cells for their ability to remove metals from spent coal liquefaction catalysts.
2. To optimize time and volumes necessary for efficient metal removal from spent catalysts.
3. To perform an economic evaluation based on the best case scenario from the other tasks.
4. To seek thermophilic bacteria which can leach metals from spent catalysts. Such organisms would undoubtedly increase rates of release.

In an earlier contract we studied the ability of *T. ferrooxidans* to release metals from spent coal liquefaction catalysts (Shell 324 from the Wilsonville pilot plant). This organism was good at releasing Ni from the Ni-Mo catalyst, but the toxicity of Mo for these organisms meant large volumes of liquid were required and long periods of time. We discovered at that time that heterotrophic denitrifying bacteria were capable of releasing both Ni and Mo at high rates and efficiently at small volumes. These organisms are the target of study in this project along with other potentially interesting microorganisms.

During the first Quarter of 1993 we studied the metallic content of catalyst samples through the use of the methods described in our two previous reports. This technology has allowed us to save both time and money in our efforts to obtain good, sound mass balances. An example of the data are shown in the following Table 1.

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Table 1
Metal Content of Solvent-Washed Catalysts

Solvent	% Ni	% Mo
Acetonitrile	2.6	8.1
Acetic acid	2.4	8.1
Carbon tetrachloride	2.5	7.0
p-Dioxane	2.3	7.3
Ethyl acetate	2.5	8.0
Formic acid	2.5	7.7
Hexane	2.5	7.7
Methylene chloride	2.6	8.3
Methanol	2.5	7.7
1-Propanol	2.3	7.1
Pyridine	2.9	7.8
Tetrahydrofuran	2.7	9.1
Toluene	2.5	7.2
Water	2.9	7.0
Xylenes	2.5	7.7

These data show the remarkable similarity between catalyst samples as compared with different solvents used to remove the contaminating coal liquids. Therefore, we can realistically choose solvents based on criteria other than on their ability to leave the metals undisturbed. We were surprised that the acidic solvents as well as the more polar ones did not remove some of the metals. We have noted earlier that solvents such as acetic acid and pyridine are very good at cleaning the catalyst. In our previous contract we noticed some selectivity based on carbon and energy source for tetrahydrofuran-washed catalyst samples. Although selectivity is not necessarily a focal point of this work, it may prove useful in future development work. The carbon sources and solvents which have proven to be the best at driving total metal (Ni + Mo) release are citrate:pyridine, citrate:acetic acid, malonate:pyridine, malonate:tetrahydrofuran, lactate:pyridine, lactate:acetic acid and lactate/EDTA:pyridine. The addition of a good chelator (EDTA or citrate) appears to help in rapid removal of metals from the spent catalyst.

We have been testing other carbon and energy sources. Initially, we did not think that fermentable carbon and energy sources would be good materials for the support of the metal releasing microorganisms. However, mixed cultures may well actually benefit from the sequential degradation of fermentable carbon sources first through compounds like ethanol, lactate and acetate by fermentative microbes and to CO₂ by the resident denitrifying bacteria. The initial fermentation may cause a decrease, initially, in the pH of the medium as acids are formed, but the utilization of these acids by the denitrifying bacteria will raise the pH back to neutrality. Thus fermentable substances, which are cheap may be used to support microbial metal release and recovery. Table 2 shows the fermentable carbon sources which we have studied and the ability of these to support denitrification by mixed cultures.

Table 2
Fermentable Carbon Sources for Denitrifying Bacteria

Glucose	Molasses
Starch	Glycerol
Acetate	Propionate
Butyrate	Vegetable Oil
Cellulose	Fructose
Sucrose	Galactose
Lactose	Gelatin
Glutamate	Aspartate
Ethanol	n-Propanol
n-Butanol	

A mixed source of microorganisms was inoculated into media with these substances (0.5% w/v or v/v) as sole source of carbon and energy (Medium 337 + SL-4 Trace metals, see below). All bottles showed good signs of growth except for that of cellulose. Since cellulose is not soluble, we discarded it from further study. We feel that the pH in many of these would drop initially and then rise as the denitrifiers used the fermentation products. For the most part this did not happen. Quite simply, the denitrifiers kept pace with the strict fermentative microorganisms. Because of the dynamics of these cultures, all of the above carbon and energy sources may be useful in metal release and recovery from spent coal liquefaction catalyst. These will be tested in future experiments. We have examined, separately, molasses and it does not appear to be an improvement over previously studied carbon and energy sources. Earlier studied substrates were all designed to have some chelation ability since, chelators were effective in helping to release metals in our previous contract. The substances of Table 2 have little or no chelation ability, but the balance of chelation with cost may be important factors in deciding which carbon and energy source will be needed in any process developed from this technology.

Table 3
Medium 337

Chemical Component	g/l
KH ₂ PO ₄	1.4
Na ₂ HPO ₄	2.1
MgSO ₄ •7H ₂ O	.2
NH ₄ NO ₃	10.0
CaCl ₂ •2H ₂ O	.01
SL-4 Trace Metals (see Table 6)	20 ml

Table 4
SL-4 Trace Metals, Sulfate Free

Chemical Component	mg/l
EDTA, di Na salt	500
FeCl ₂ •5H ₂ O	100
MnCl ₂ •4H ₂ O	25
CuCl ₂ •2H ₂ O	10
CoCl ₂ •6H ₂ O	20
NiCl ₂ •6H ₂ O	20
Na ₂ MoO ₄ •2H ₂ O	30
Na ₂ WO ₄	5
Na ₂ SeO ₃	5
H ₃ BO ₃	25

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