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Quarterly Report
July - September 1991

**Microbial Recovery of Metals from Spent Coal
Liquefaction Catalysts**

Contract No. DEAC2289PC89881

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Abstract/Summary

Introduction.

This project was initiated on October 1, 1989, for the purpose of recovering metals from spent coal liquefaction catalysts. Two catalyst types are the subject of the contract. The first is a Ni-Mo catalyst supported on alumina (Shell 324) as is used in a pilot scale coal liquefaction facility at Wilsonville, Alabama. This plant is run and operated by Southern Clean Fuels. A large sample of spent catalyst from this facility has been obtained. The second material is an unsupported ammonium molybdate catalyst used in a pilot process by the Department of Energy at the Pittsburgh Energy Technology Center and has been subsequently dropped as a part of the work. This material was first obtained in late February 1990 but has not been pursued since the Mo content of this particular sample is too low for the current studies and no new catalyst has since been obtained or produced by PETC. The object of the contract is to treat these spent catalysts with microorganisms, especially *Thiobacillus ferrooxidans*, but also other *Thiobacillus* sp. and possibly *Sulfolobus*, and other potentially useful microorganisms to leach and remove the metals (Ni and Mo) from the spent catalysts into a form which can be readily recovered by conventional techniques.

Cultures.

Cultures of *T. ferrooxidans* and *T. denitrificans* and related organisms were obtained from INEL, the American Type Culture Collection, and isolated from natural sources. The INEL medium for the cultivation of *T. ferrooxidans* was used with an initial pH of 2.0; this pH was later changed to 2.5 when better and more reproducible results were obtained at that pH. *Thiobacillus denitrificans* was cultured in the ATCC medium of choice (usually medium 450). Denitrifying bacteria were isolated from various soil samples and from water samples collected from Alaskan oil fields. These organisms were isolated in mixed culture and maintained as mixed cultures for use in these experiments. Depending on the carbon source they may be very different phylogenetically. However, for the carbon sources so far tested most of the microorganisms belong to the genus *Pseudomonas*. Denitrifying bacteria were cultured in medium 337 of Hirsch and Conti with the addition of 10 g/l NH_4NO_3 and which was modified to remove any extraneous sources of nutritional sulfur. This medium formulation is shown below.

Medium 337

Chemical Component	g/l
KH_2PO_4	1.4
Na_2HPO_4	2.1
$\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$	.2
NH_4NO_3	10.0
$\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$	.01
SL-4 Trace Metals	20 ml

SL-4 Trace Metals

Chemical Component	mg/l
EDTA, di Na salt	500
$\text{FeCl}_2 \cdot 5\text{H}_2\text{O}$	100
$\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$	25
$\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$	10
$\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$	20
$\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$	20
$\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$	30
Na_2WO_4	5
Na_2SeO_3	5
H_3BO_3	25

Both the salt solution and the trace metal solution have been reformulated to remove all salts containing S and replace them with chloride salts. This forces growing organisms to scavenge S from the catalyst. We know from other experiments that these denitrifying bacteria are capable of utilizing sulfide as a source of nutritional sulfur and that the "insoluble" sulfides such as FeS may serve as a nutritional S source.

Catalyst Treatment.

The spent catalyst from Wilsonville was treated initially by extensively washing the material with tetrahydrofuran in a soxhlet extractor and evaporating the THF from the residual catalyst and the oil/THF-containing liquid. The dried catalyst was then crushed in a ball mill, producing fractions from 10 to smaller than 100 mesh. Minus 100 mesh material was initially used to assay metal release. This has since been replaced by 10 mesh or uncrushed material since microbial leaching appears to proceed just as well without crushing when utilizing *T. ferrooxidans*. However, we do not know the effect of mesh size has on the ability of denitrifying bacteria to release metals from the spent catalyst. These studies are currently under way.

Microbial Leaching Studies.

During this quarter we studied both the composition of the leachate from the *T. ferrooxidans* studies as well as the ability of denitrifying bacteria to leach both Ni and Mo.

Leaching Experiments with Denitrifying Bacteria.

In this quarter we approached the general problem of recovering metals from spent catalysts microbiologically from a completely different direction. In work unrelated to this contract, we noticed that denitrifying bacteria which are regularly found in oil fields are capable of utilizing FeS as a source of S and can solubilize the Fe and use this chemical as both a source of nutritional Fe and S. Since the spent coal liquefaction catalyst contains both Ni and Mo sulfides, this ability might be used to recover both Mo and Ni from the spent catalyst. In addition these organisms would have many more advantages not available with the typical leaching microorganisms exemplified by *Thiobacillus ferrooxidans*. These include:

1. High resistance to molybdate
2. Good Ni tolerance.
3. These organisms are anaerobic, making simple leaching piles easy to operate without the constraints imposed by the necessity of supplying oxygen.
4. The organisms are apparently very resistant to the toxic effects of the coal liquids.
5. The products of their metabolism, CO₂, N₂ and water are environmentally innocuous.

Initial experiments showed very good growth in the presence of the spent catalyst and the presence of the coal liquids. Although the denitrifying bacteria grew very well in the presence of the coal liquids, in contrast to *T. ferrooxidans*, they did not efficiently leach either Ni or Mo from the oily spent catalyst. This is greatly different from the effects noticed for *T. ferrooxidans* earlier. In addition very good growth occurred in the presence of THF-washed catalyst (10 mesh). More complete results than those originally reported in August are shown in Table 1.

Table 1

**Release of Mo and Ni from THF-Washed Spent
Coal Liquefaction Catalyst by Denitrifying Bacteria**

Catalyst Sample	C Source	Initial		Released		% Released	
		g Mo	mg Ni	mg Mo	mg Ni	Mo	Ni
THF-Washed	Succinate	1.00	207	545	13	64	6.4
THF-Washed	Lactate	1.04	215	702	29	68	29
THF-Washed	Lactate-EDTA	1.27	262	791	200	62	76
THF-Washed	Adipate	.95	197	639	18	67	9.1
THF-Washed	Malonate	.99	204	789	78	80	38
THF-Washed	Citrate	.98	202	789	96	81	48
THF-Washed	Oxalate*	.98	203	518	83	53	41
THF-Washed	EDTA	1.00	205	502	126	50	62
THF-Washed	none	1.01	205	422	11	42	5.4

* - There was very poor growth under denitrifying conditions with oxalate as a source of carbon and energy.

In 26 days up to 81% of the Mo was released, utilizing a volume only 8% of that required by *T. ferrooxidans* for a similar release of metals. As can be seen the presence of the chelator appears to facilitate the release of Ni from the spent catalyst, but does not seem to affect the release of Mo. All of the carbon and energy sources were chosen because of the ability of the carbon compound to serve two functions 1) to act as carbon and energy sources for the denitrifying bacteria and 2) to act as chelators of divalent cationic metal ions. In addition there appears to be some selectivity for Mo, the targeted metal of this contract, depending on the organic growth substrate. We still do not know the extent of this specificity. It may be possible to selectively release either of these two metals, although our previous studies have shown that the metals are readily recovered, specifically, from a mixed solution. We also do not know the effect of mesh size on metal release. These experiments were performed with 10 mesh THF-washed catalyst and finer material may very well release more of the metal. In the remaining time on the contract we will pursue these experiments to see if we can make the economics and feasibility of the process attractive enough for further work. For a graphic representation of these data please refer to Figures 1 and 2 attached to this report.

Conclusions.

We have defined critical areas for further study. These arise out of the basic nature of both the microorganisms and the nature of catalysts. Whereas other catalysts not employing Mo or W would probably be readily leached by *T. ferrooxidans* and

denitrifiers, those which contain these two metals require special attention and highly tolerant strains of *T. ferrooxidans* but not the denitrifiers to be realistically treated microbiologically. The alternative is to develop methods for the continuous removal of Mo as it is removed from the catalyst. We have preliminary data that show this to be technically feasible. The following are areas which need detailed study in the coming years.

1. To increase the molybdate tolerance of *T. ferrooxidans*. This increase could realistically also confer higher tolerance to W containing coal liquefaction catalysts. It is also clear that a major biochemical and genetic effort will be necessary to make this goal a success. This effort is beyond the scope of the current contract.

2. To employ the metabolic actions of other microorganisms which may be better adapted to metal tolerances and sulfide scavenging. Clearly the use of denitrifying bacteria for leaching meets these requirements. However, the "hybrid" selection of *T. denitrificans* (a thiobacilli which can utilize sulfide as an energy source and grow anaerobically with nitrate as a terminal electron acceptor) does not work. This organism appears to be both sensitive to most metals, not good at scavenging sulfides from minerals nor resistant to coal liquids.

Figure 1

**Release of Mo from Spent THF-Washed
Catalyst by Denitrifying Bacteria**

Catalyst Leaching by Denitrifying Bacteria

Figure 2

**Release of Ni from THF-Washed Spent
Catalyst by Denitrifying Bacteria**

Catalyst Leaching by Denitrifying Bacteria

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