Microbial Recovery of Metals from Spent Catalysts

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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. This material was 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. The object of the contract is to treat these spent catalysts with microorganisms, especially *Thiobacillus ferrooxidans*, but also other *Thiobacillus* sp. and possibly *Sulfolobus*, 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).

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 This has since been replaced by 10 mesh or uncrushed material since microbial leaching appears to proceed just as well without crushing.

Microbial Leaching Studies.

During the fifth quarter of this contract we studied the actual effect of the growth of *T. ferrooxidans* on catalyst supported in a Soxhlet type reactor. The flushing action of this system allows for the collection of the fine microparticulate matter which contains much of the Mo released from the catalyst. The Ni is almost completely in a soluble form. As reported earlier, we have achieved approximately a ten fold decrease in the volume necessary to treat a gram of catalyst over our previous shake flask studies (275 ml/g for the soxhlet reactor vs 3275 ml/g for the shake flask studies employing the THF extracted material). It is quite clear that we could significantly reduce this volume with further work.

Table 1

Reactor Metal Release Studies

Reactor #	Catalyst Sample	% Ni Released	% Mo Released
1	Oily Wilsonville	72.46	64.31
2	THF-Extracted	93.22	81.56

Natural Isolates.

Samples were obtained in late November from three sources. First, a molybdenum mine in New Mexico was sampled. This mine is quite large and has been mining molybdenite for about 70 years. The site is quite well contained now, but samples were obtained from several sites around the property and at the base of the tailings piles. Since this area also contained some thermal springs, we also sampled them for potential thermophilic strains of *Thiobacillus*. The third site was the Curtis Tungsten mine in Upland, California. The form of tungsten in this mine is Scheelite (WO_3), which in solution would form tungstate. Samples were obtained from streams in the area of this mine and the tailings pond. The results from these studies are presented in Table 2. As can be seen, natural isolates of *T. ferrooxidans* do indeed exist which are more resistant to molybdate than previously tested isolates. However, the increase in the molybdate tolerance is not great. The best increase is from the typical approximate 100 μM of natural strains isolated from non-molybdenum containing sites to the 250 μM concentration of the molybdenum mine tailings isolate. While these isolates may prove useful, the molybdate resistance is not significant enough to make a significant impact on potential processes. We still believe that it is possible to increase this resistance through mutagenic measures in the future.

Table 2

T. ferrooxidans Isolates and their Molybdate Sensitivities

Isolate	Source	Maximum MoO_4^{2-} Tolerance, μM
Q-Mo1	Base of Mo Tailings Pile	250
Q-Mo2	River Across from Mo Tailings	200
Q-Mo4	Outside Mo Plant Gate	150
Q-Mo7	Upstream from Mo Plant Gate	100
J-Mo1	Soda Dam, Jemez Springs	175
J-Mo3	Soda Dam, Fe precipitated material	150
C-W3	W millings	200
DT-5	INEL	85

Strain Development.

We have begun the systematic mutagenic development of molybdate tolerant strains. So far these experiments have met with little success. We will also analyze the microbes from the soxhlet reactors for their abilities to tolerate increased levels of molybdate and tungstate. "Natural" more tolerant strains, typical lab strains and organisms from the soxhlet leach reactors will be the sources for the strains for the mutagenic studies. For the technologies to be developed and expanded to other types of catalysts and metal-containing waste materials, important process parameters such as volume and time necessary for successful leaching become of paramount importance, as well as the development of appropriate microbial strains.

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*, those which contain these two metals require special attention and highly tolerant strains of microorganisms 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.
2. To set up bench scale leach reactors and define the operating parameters for optimum metal recovery from the spent coal liquefaction catalyst from Wilsonville.
3. To obtain from these studies a good mass balance so that the systems developed can be adequately evaluated for their process efficacy and economics. In our latest studies, the mass balance is quite good, but further development of our methods would better refine the developing technology.

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