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Microbial Recovery of Metals from Spent Coal Liquefaction Catalysts

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Catalyst Treatment.

During April and May we began the rather laborious task of crushing each of the solvent-extracted catalyst samples for the determination of the effect of crushing on leaching rate and per cent metal recovered. We searched for an alternative method which could save time. We believed that a Retsch mill or other electric powered device might allow us to more efficiently process these samples. However, this device produces material of only one particle size. The crushing of these catalyst samples employed a ball mill and it took approximately 1 week to crush each sample. All catalyst samples, after crushing, were sieved to a particle size of >100 mesh. Samples of 10, and 40 mesh were also collected, but only the >100 mesh was subjected to bacterial leaching. These samples were tested using denitrifying bacteria for their ability to release Ni and Mo from these samples. The data are shown in the attached figures as well as comparisons for rates of Ni and Mo released in relation to catalyst solvent pretreatment. These data were obtained with citrate as a carbon and energy source for the microorganisms. It is quite clear that crushing the catalyst allows for a more rapid release of these metals from the catalyst samples, regardless of the organic solvent used to pretreat the catalyst. However, the effects of the different solvents are still evident, although not as striking, after the catalysts are crushed (see previous reports). There also still appears to be a greater ease in removing Mo over Ni, a case particularly prevalent if ethyl acetate, methanol or xylene is used as the pretreatment solvent. In any case, it appears that a variety of solvents will be useful and that an optimized system could yield >90% release and recovery of both Ni and Mo in as little as 10 days of treatment.

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Characterization of the Mo in the Leachate.

G.P. Huffman, Director of the Consortium for Fossil Fuel Liquefaction Science at the University of Kentucky examined a sample of our leachate by XAFS spectroscopy analysis for the state of the Mo. The following is a report on the sample. It clearly shows that the Mo is in the +6 (molybdate) form.

"We obtained Mo $L_{2,3}$ edge XANES (edge energy = 2520 eV) spectra for a coal liquefaction catalyst leachate sample and an ammonium molybdate standard compound in fluorescence geometry. Top figures compares these two spectra. From the position of the peaks and their relative heights, we can conclude that the Mo exists in +6 state in the leachate sample.

To further confirm these findings, we also obtained a sulfur K edge (edge energy = 2472 eV) spectra for the leachate sample. The position of the main peak in this spectra at around 10 eV confirms that the sulfur is in the sulfate (+6) state and that there is no evidence of any sulfide phases.

A minor peak at around -3 eV in Mo XANES could be due to lower Mo oxidation state. However, from the sulfur XANES it appears that is most probably due to a background signal from sulfur edge. Since we do not have any Mo XANES for standard compounds with +5 and +5.5 oxidation states, we have not shown their spectra for comparison. If such phases exist, based on this XANES analysis, their concentration would be less than 10%."

Solvent Pretreatment.

As reported earlier, the use of a solvent helps in the microbiological release of metals from the spent catalyst. Depending on the solvent, varying efficiencies of release of bot Ni and Mo are obtained. These are summarized below in Table 1. Table 2 shows the solvents tested. Previous work had centered primarily on tetrahydrofuran, but it appears from the data below that other solvents may be superior to tetrahydrofuran.

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Table 1

Quality of Solvents for Coal Pretreatment

Solvent	Relative Efficiency (100 = best)		
	Ni	Mo	Ni+Mo
Tetrahydrofuran, 100 mesh	97	99	98
Pyridine	29	63	46
Dioxane	32	44	38
Acetic Acid	28	45	37
Toluene	24	42	33
iso-Propanol	25	37	31
Formic Acid	29	31	30
Methanol	15	38	27
Tetrahydrofuran	14	39	27
Acetone	15	38	27
Chloroform	15	37	26
Ethyl Acetate	13	38	26
Methylene Chloride	12	38	25
Hexane	14	33	24
Xylenes	11	36	24
Carbon Tetrachloride	22	21	22
Water	24	11	18

Table 2

Solvents for Catalyst Extraction

Methanol
 Hexane
 Toluene
 Ethyl acetate
 Acetone
 Water
 Chloroform
 Carbon tetrachloride
 Methylene chloride
 Acetic acid
 Formic acid
 Tetrahydrofuran
 Pyridine
 Isopropanol
 Acetonitrile
 p-Dioxane
 Xylenes

Publications.

A paper was presented at the American Society for Microbiology Annual Meetings in New Orleans in May 1992. *Microbiological Recovery and Removal of Molybdenum and Nickel from Spent Coal Liquefaction Catalysts*. Donald O. Hitzman, Penny L. Sperl and George T. Sperl. Bacteriol Proc. p. 346.

Patent.

A patent was filed on May 22, 1992: Inventors: George T. Sperl and Donald O. Hitzman. *Method for Treatment of Catalysts Using Denitrifying Bacteria*. Serial No. 07/887,011

Figure Legends

1. Mo release from whole and crushed spent catalyst - Solvents: methanol, formic acid, dioxane and xylenes.
2. Ni release from whole and crushed spent catalyst - Solvents: methanol, formic acid, dioxane and xylenes.
3. Mo release from whole and crushed spent catalyst - Solvents: water, acetone, acetic acid and acetonitrile.
4. Ni release from whole and crushed spent catalyst - Solvents: water, acetone, acetic acid and acetonitrile.
5. Mo release from whole and crushed spent catalyst - Solvents: toluene, tetrahydrofuran, pyridine and methylene chloride.
6. Ni release from whole and crushed spent catalyst - Solvents: toluene, tetrahydrofuran, pyridine and methylene chloride.
7. Mo release from whole and crushed spent catalyst - Solvents: isopropanol, hexane, ethyl acetate and carbon tetrachloride.
8. Ni release from whole and crushed spent catalyst - Solvents: isopropanol, hexane, ethyl acetate and carbon tetrachloride.
9. Ni and Mo release from crushed and whole spent catalysts - Solvent: acetic acid.
10. Ni and Mo release from crushed and whole spent catalysts - Solvent: acetone.
11. Ni and Mo release from crushed and whole spent catalysts - Solvent: acetonitrile.

12. Ni and Mo release from crushed and whole spent catalysts - Solvent: carbon tetrachloride.
13. Ni and Mo release from crushed and whole spent catalysts - Solvent: chloroform.
14. Ni and Mo release from crushed and whole spent catalysts - Solvent: dioxane.
15. Ni and Mo release from crushed and whole spent catalysts - Solvent: ethyl acetate.
16. Ni and Mo release from crushed and whole spent catalysts - Solvent: formic acid.
17. Ni and Mo release from crushed and whole spent catalysts - Solvent: hexane.
18. Ni and Mo release from crushed and whole spent catalysts - Solvent: isopropanol.
19. Ni and Mo release from crushed and whole spent catalysts - Solvent: methanol.
20. Ni and Mo release from crushed and whole spent catalysts - Solvent: methylene chloride.
21. Ni and Mo release from crushed and whole spent catalysts - Solvent: pyridine.
22. Ni and Mo release from crushed and whole spent catalysts - Solvent: tetrahydrofuran.
23. Ni and Mo release from crushed and whole spent catalysts - Solvent: toluene.
24. Ni and Mo release from crushed and whole spent catalysts - Solvent: water.
25. Ni and Mo release from crushed and whole spent catalysts - Solvent: xylenes.

Figure 1 is a line graph showing the percentage of methanol released over 40 days for various whole and crushed plant materials. The y-axis is labeled '% Mo Released' and ranges from 0 to 100. The x-axis is labeled 'Time, Days' and ranges from 0 to 40. The legend lists the following materials and their corresponding symbols:

- Whole, methanol: filled circle
- Crushed, methanol: open circle
- Whole, formic acid: filled square
- Crushed, formic acid: open square
- Whole, dioxane: plus sign
- Crushed, dioxane: open triangle
- Whole, chloroform: plus sign with a dot
- Crushed, chloroform: open triangle with a dot
- Whole, xylenes: filled diamond
- Crushed, xylenes: open diamond

The graph shows that the release of methanol is generally higher for crushed materials compared to whole materials. The release rate is highest for crushed dioxane and crushed chloroform, reaching approximately 80% release by day 40. The release rate is lowest for whole materials, with most showing less than 20% release by day 40.

Ni Release from Spent Catalyst Crushed vs Whole, Solvent-Washed

Mo Release from Spent Catalyst Crushed vs Whole, Solvent-Washed

Ni Release from Spent Catalyst Crushed vs Whole, Solvent-Washed

Mo Release from Spent Catalyst Crushed vs Whole, Solvent—Washed

Ni Release from Spent Catalyst Crushed vs Whole, Solvent-Washed

Mo Release from Spent Catalyst Crushed vs Whole, Solvent—Washed

Ni Release from Spent Catalyst Crushed vs Whole, Solvent-Washed

Leaching of Crushed vs Whole Catalyst Acetic acid—Washed

Leaching of Crushed vs Whole Catalyst Acetone—Washed

Leaching of Crushed vs Whole Catalyst Acetonitrile—Washed

Leaching of Crushed vs Whole Catalyst Carbon Tetrachloride—Washed

Leaching of Crushed vs Whole Catalyst Chloroform-Washed

Leaching of Crushed vs Whole Catalyst Dioxane—Washed

Leaching of Crushed vs Whole Catalyst Ethyl Acetate-Washed

Leaching of Crushed vs Whole Catalyst Formic acid—Washed

Leaching of Crushed vs Whole Catalyst Hexane-Washed

Leaching of Crushed vs Whole Catalyst Isopropanol-Washed

Leaching of Crushed vs Whole Catalyst Methanol-Washed

Leaching of Crushed vs Whole Catalyst Methylene Chloride-Washed

Leaching of Crushed vs Whole Catalyst Pyridine-Washed

Leaching of Crushed vs Whole Catalyst
Tetrahydrofuran--Washed

Leaching of Crushed vs Whole Catalyst Toluene-Washed

Leaching of Crushed vs Whole Catalyst Water-Washed

Leaching of Crushed vs Whole Catalyst Xylenes-Washed