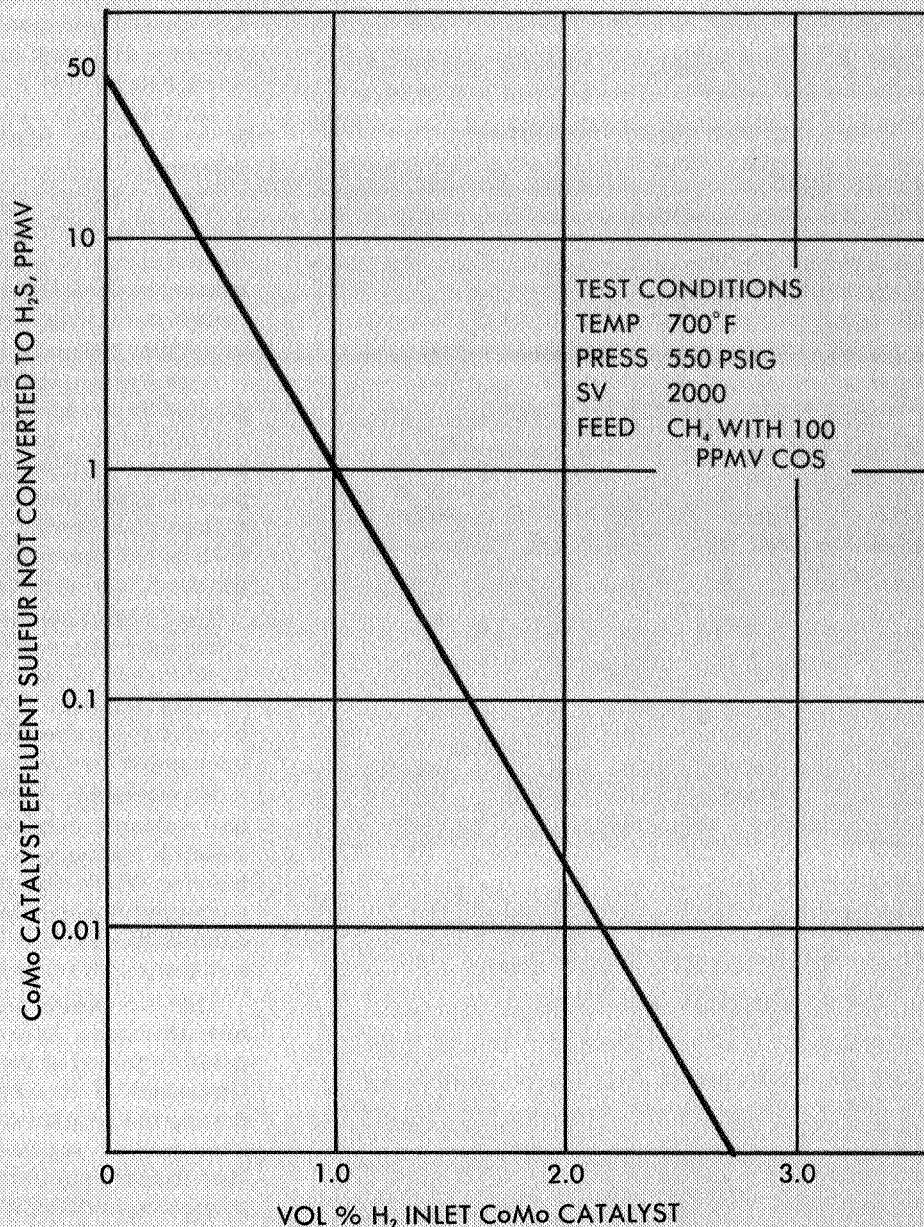


**Figure 1. Effect of hydrogen concentration on CoMo catalyst performance.**



**COAL PROCESSING:**

# Developments in Natural Gas Desulfurization

Improved analytical equipment is beginning to help in monitoring the performance of systems that use cobalt molybdenum catalyst-zinc oxide.

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Desulfurization of natural gas feedstocks for ammonia, methanol, and hydrogen production units has been accomplished by adsorption of sulfur compounds on metal impregnated activated carbon (treated carbon) for many years.

The technique works quite well as long as the sulfur compounds being removed are H<sub>2</sub>S and/or light mer-

captans and the natural gas does not contain an appreciable quantity of heavier hydrocarbons. Heavier hydrocarbons are preferentially absorbed by the carbon and greatly reduce its ability to adsorb sulfur compounds, while sulfur compounds other than H<sub>2</sub>S and mercaptans tend to either cause extremely short operating cycles or pass through the treated carbon. Carbonyl sulfide (COS) is the most often

**Table 1. Tests to measure effect of hydrogen concentration on CoMo catalyst performance.**

Test Conditions:  
 Pressure, lb./sq. in. gauge ..... 550  
 Temperature, °F ..... 700  
 Space velocity, hr<sup>-1</sup> ..... 2,000 to 10,000  
 Feed Stream Components:  
 CH<sub>4</sub> with 100 parts/million by vol. COS.  
 H<sub>2</sub> varied as necessary to attain sulfur conversion.  
 Results:

Vol. % H <sub>2</sub> Inlet	Space Velocity, hr <sup>-1</sup>	Outlet, parts/million by vol.		
		H <sub>2</sub> S	COS	Unidentified Sulfur Compounds
0	2,000	50	nil	50
0.2	2,000	87	nil	10
1.4	2,000	92	nil	1
2.2	2,000	100	nil	nil
2.2	4,000	100	nil	nil
2.2	6,000	100	nil	nil
2.2	8,000	100	nil	nil
2.2	10,000	100	nil	nil

**Table 2. Tests to measure low-temperature activity of CoMo catalyst.**

Test Conditions:  
 Pressure, lb./sq. in. gauge ..... 250  
 Temperature, °F ..... 400-450-500  
 Space Velocity, hr<sup>-1</sup> ..... 3,000-6,000-10,000  
 Feed Stream Components:  
 H<sub>2</sub> vol. % ..... 2  
 CO<sub>2</sub> vol. % ..... 1  
 CH<sub>4</sub> vol. % ..... Balance  
 COS, parts/million by vol. .... 10-20  
 CH<sub>3</sub>SH, parts/million by vol. .... 8-10  
 Results:

Temp., °F	Space Velocity Exit	Percent parts/million by vol.						
		H <sub>2</sub>	CO <sub>2</sub>	CO	H <sub>2</sub> S	COS	CH <sub>3</sub> SH	S <sub>x</sub>
Inlet	—	2.0	0.82	—	3	10.4	8.5	—
(a)	400 .. 3,000	2.0	0.81	—	22.6	<0.1	<0.05	—
(b)	450 .. 3,000	1.9	0.75	—	27.9	<0.1	<0.05	—
(c)	500 .. 3,000	1.8	0.77	—	22.5	<0.1	<0.05	—
(d)	450 .. 6,000	1.86	0.80	—	16.4	<0.1	<0.05	1.0
(e)	450 .. 10,000	1.90	0.87	—	12.6	<0.1	<0.05	1.0

\*S<sub>x</sub> = Unidentified higher molecular weight sulfur.

the most common desulfurization system for these streams. Hot zinc oxide by itself has been employed on some natural gas streams containing significant amounts of heavier hydrocarbons and by some plants that preferred a long cycle length non-regenerative desulfurization system.

Until recently, treated carbon has been an excellent means of desulfurizing North American natural gases with the exception of some gas fields in western Canada which contained COS. Of late, however, many gas suppliers have installed facilities on the raw natural gas that employ molecular sieves for a portion of the processing.

Regeneration of the molecular sieves is often accomplished by stripping with hot product natural gas. During the molecular sieve stripping process, a portion of the sulfur compounds are converted to COS; consequently natural gases that were formerly desulfurized by treated carbon now contain significant quantities of COS. This COS is not removed by the treated carbon, necessitating the modification of existing sulfur removal systems.

The CoMo-ZnO desulfurization system has been the most often used alternative because of its ability to handle a wide range of sulfur compounds. Catalytic hydrolysis of COS followed by zinc oxide has been used in some plants having specific COS problems, but most designers have opted for the more flexible CoMo-ZnO system.

Historically, hydrotreating technology for cobalt-molybdenum catalysts was developed for the petroleum refining industry to use on feedstocks of naphtha and heavier. When situations infrequently arose where lighter-than-naphtha streams were to be desulfurized, the design conditions specified were based on extrapolations of data and designs developed for refinery applications.

This has caused no particular problem when designing new ammonia, hydrogen, or methanol plants other than possibly to introduce an excessive degree of conservatism. One effect of this conservatism has been to specify operating temperatures and hydrogen partial pressures that have proved successful in naphtha applications rather than to carry out development work to better define milder process conditions, which might be applicable for the relatively low-sulfur, light hydrocarbon streams.

### Major variables

The aforementioned trend of changing natural gas feedstocks and increasing use of CoMo-ZnO desulfurization systems created a need to better define the basic performance of the CoMo-ZnO desulfurization system with relation to natural gas feedstocks. Catalysts and Chemicals, Inc., initiated a laboratory test program during late 1974 to evaluate the effect of major variables specific to natural gas feedstocks. This is an ongoing program with additional work being done from time to time as the needs for additional information are defined.

The variables studied to date and the purpose of the studies are outlined below.

*Variable:* Hydrogen partial pressure in hydrocarbon stream to CoMo catalyst. *Purpose:* To define minimum hydrogen recycle required for the desulfurization system as not to unnecessarily reduce plant throughput or add additional compression capacity or costs.

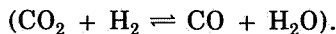
*Variable:* Low temperature performance of CoMo catalyst. *Purpose:* To define performance of CoMo in the temperature range of 400 to 500°F. Normal CoMo-ZnO systems are designed to operate at 650-750°F, and the major part of commercial experience is at these higher temperatures.

*Variable:* CO<sub>2</sub> concentration in natural gas. *Purpose:* previous work had indicated that CO<sub>2</sub> in dry gases treated

encountered sulfur compound that treated carbon does not remove.

Concurrent with the use of treated carbon for plants having normal natural gas feedstocks, other desulfurization systems were developed for use in refinery off-gas streams and for naphtha feedstocks. Cobalt molybdenum catalyst (CoMo) for hydrogenation of sulfur compounds to H<sub>2</sub>S, followed by zinc oxide (ZnO) for sulfur removal, evolved as

over CoMo catalyst tended to reverse shift



This work was needed to confirm this phenomenon and measure the effect of any CO formed on COS equilibrium exit the CoMo catalyst.

*Variable:* Zinc oxide capacity for COS removal. *Purpose:* To adequately define the ability of ZnO to remove COS so as to have sufficient data to make a valid economic comparison between a CoMo-ZnO system and ZnO by itself. Also, streams containing CO<sub>2</sub> present the possibility of an equilibrium COS level reaching the ZnO in the CoMo-ZnO system.

The test work reported was carried out in bench-scale isothermal reactors using synthesized feed gas preparations. The reactors consist of a single tube of Hastalloy C, 8 in. long and 3/8 in. I.D., containing a catalyst volume of 10 cu. cm. Temperature was maintained by an electrical resistance heater surrounding the reactor.

Feed gases were prepared by mixing pure component gases into a common cylinder from which the test units received the synthesized feedstock. Catalysts & Chemicals' C49-1-01 CoMo catalyst and C7-2-01 ZnO were used in the test work. Both were sized to a range of 10 to 12-mesh for use in the small, bench-scale reactors.

Sulfur analyses were carried out on a Tracor 560 gas chromatograph with flame photometric detector using Tracor's special 1/8 in. sulfur column. Sulfur detection limit with this system is nominally 0.05 parts/million by vol. Gas analyses for other compounds were carried out on a Beckman gas chromatograph with thermal conductivity detectors.

## Effects of the variable

*Hydrogen partial pressure.* At the time this work was done, it was of primary interest to establish a realistic minimum hydrogen concentration for many new plants being designed. Operating conditions were therefore established based on modern high pressure reforming plants.

In this series of tests, a methane stream containing 100 parts/million by vol. COS was used as the feedstock to CoMo catalyst. Inlet temperature and pressure were held constant, with hydrogen being adjusted as required to give complete conversion of COS to H<sub>2</sub>S. After the minimum hydrogen level was established, additional tests were conducted at higher space velocities to determine if reaction kinetics would require adjustment of the hydrogen level. The test conditions and test results are given in Table 1.

With no hydrogen present, 50% of the inlet COS was converted to H<sub>2</sub>S and the remainder of the COS was converted to higher molecular weight sulfur compounds. Four distinct higher molecular weight compounds were noted but not identified. No COS was found in the reactor effluent.

The addition of hydrogen increased the conversion of COS to H<sub>2</sub>S and reduced the amount of higher molecular weight sulfur compounds. At an inlet hydrogen level of 2.2 vol. %, conversion of COS to H<sub>2</sub>S was complete, with no higher molecular weight sulfur compounds remaining in the reactor effluent. Space velocity was varied over a wide range and showed no effect on hydrogen requirements.

Figure 1 illustrates the relationship between hydrogen concentration and sulfur not converted to H<sub>2</sub>S. From evaluation of these test results it was concluded that a level of 2 vol. % hydrogen inlet, the CoMo catalyst should provide sufficient excess hydrogen to assure complete conversion of COS to H<sub>2</sub>S for natural gas feedstocks treated at or near the given operating conditions.

*Low temperature performance of CoMo catalyst.* For the CoMo-ZnO desulfurization system to be effective, it must be used on a dry gas stream. Many plants preheat natural

**Table 3. Tests to evaluate effect of CO<sub>2</sub> in feedstock to CoMo catalyst.**

Test conditions:

Pressure, lb./sq. in. gauge .....	500
Temperature, °F .....	700
Space velocity, hr <sup>-1</sup> .....	2,000

Results:

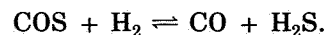
	Low CO <sub>2</sub> Case			High CO <sub>2</sub> Case		
	Feed	Outlet		Feed	Outlet	
		Theo.	Act.		Theo.	Act.
CH <sub>4</sub> , vol. % .....	.97.5	.97.62	.97.59	.89.40	.90.20	.89.53
H <sub>2</sub> , vol. % .....	2.0	1.89	1.95	2.65	1.76	1.93
CO <sub>2</sub> , vol. % .....	0.5	0.38	0.36	7.95	7.10	7.84
CO, vol. % .....	nil	0.10	0.10	nil	0.91	0.70
COS, parts/million						
by vol. ....	.50	0.26	0.57	.50	2.46	2.61
H <sub>2</sub> S, parts/million						
by vol. ....	nil	49.74	50.8	nil	47.54	42.60

gas to only 400 to 450°F prior to mixing with steam while temperatures of 650 to 700°F are normally specified for CoMo catalyst. The work described in this section was performed to define CoMo catalyst performance in the temperature range of 400 to 500°F. A pressure of 250 lb./sq. in. gauge was used so that the data collected would be at conditions existing in many older plants.

In these tests, a methane stream containing 2 mol. % hydrogen, 1 mol. % carbon dioxide, 10 to 20 parts/million by vol. COS and 8 to 10 parts/million by vol. CH<sub>3</sub>SH were passed over CoMo catalyst at various space velocities. The temperature level of operation was varied from 400 to 500°F. Pressure was controlled at 250 lb./sq. in. gauge. The concentrations of unreacted hydrogen, carbon dioxide and sulfur in the reactor exit gas were monitored.

Results of these tests are given in Table 2. Review of the results shows satisfactory sulfur conversion to H<sub>2</sub>S at a space velocity of 3,000 hr<sup>-1</sup> which is at the high end of the normal design range. At the two higher space velocities tested, some unidentified higher molecular weight sulfur compound appeared in the effluent gas. This work demonstrates that satisfactory sulfur conversion to H<sub>2</sub>S by CoMo catalyst can be obtained at temperatures as low as 400°F.

*Effect of CO<sub>2</sub> in feedstock.* As previously stated, earlier test work had shown a tendency for CO<sub>2</sub> containing feedstreams to reach an equilibrium condition for the reverse water gas shift reaction: CO<sub>2</sub> + H<sub>2</sub> ⇌ CO + H<sub>2</sub>O. For dry, CO-free gas streams containing CO<sub>2</sub> and H<sub>2</sub>, this reverse shift reaction produces CO and H<sub>2</sub>O. The CO produced could in turn influence the equilibrium COS concentration in the effluent by the reaction:



To evaluate whether or not both the CO shift reaction and COS hydrogenation reaction would reach equilibrium over the CoMo catalyst, test conditions were chosen for a low CO<sub>2</sub> case and a high CO<sub>2</sub> case to be tested. Calculations were made to satisfy the equilibrium conditions for the two tests and theoretical outlet gas compositions were compared to measured values. The results of these tests, Table 3, show a close agreement between theoretical and actual outlet gas compositions. It therefore appears that the "reverse shift" reaction does occur and approaches equilibrium conditions. The CO thereby produced causes an equilibrium limiting effect on the COS hydrogenation reaction.

This work indicates the "reverse shift" reaction must be considered when designing CoMo desulfurization systems in order to properly predict the level of unconverted COS.

**Removal of COS by ZnO.** As demonstrated above, it is quite probable that many CoMo-ZnO systems will pass unconverted COS on to the ZnO portion of the system. It therefore becomes necessary to better define the anticipated performance of ZnO for COS removal. Since the ZnO will have to remove COS to be effective, one must ask if the CoMo catalyst is really necessary.

Work to fully characterize the ability of ZnO to remove COS at lower temperatures is still in progress. Tests at 650 to 700°F for a somewhat unusual high CO<sub>2</sub> content natural gas have been carried out. These results are given in Table 4.

The test results show a calculated sulfur pickup of 4.6 wt. % on the zinc oxide before sulfur breakthrough of greater than 0.2 parts/million by vol. Analysis of the zinc oxide after removal from the test unit indicated an average sulfur pickup of 7.93 wt. %. This discrepancy between the calculated and analyzed sulfur values was caused by difficulties encountered in maintaining consistent sulfur concentrations at the high levels used for the accelerated aging test. These difficulties appeared to be caused by reaction of the sulfur compounds with feed gas cylinders and/or metal tubing connecting the system.

When sulfur breakthrough from the ZnO did occur, the sulfur compound that first appeared was identified as dimethyl sulfide (CH<sub>3</sub>S CH<sub>3</sub>) rather than any of the sulfur compounds contained in the feed gas. Hydrogen was added to the feed gas after sulfur breakthrough occurred to determine if the hydrogen would enhance the ZnO ability to remove sulfur. The effect of hydrogen addition was not significant.

The test results are not conclusive as to the exact ZnO capacity for COS removal from this gas stream, but it appears reasonably conservative to use a level of 5 wt. % sulfur pickup for this application. Normal capacity for a single bed of zinc oxide operating at 650 to 700°F removing H<sub>2</sub>S is 15+ wt. % sulfur pickup before breakthrough. Consequently, it appears that the CoMo-ZnO system will allow significantly greater utilization of ZnO for COS removal than if ZnO is used by itself.

## In conclusion

1. Two vol. % hydrogen in the inlet gas to CoMo-ZnO systems treating natural gas feedstocks should normally be sufficient to assure proper sulfur conversion.

2. Co-Mo catalyst can be expected to convert COS in natural gas streams at temperature as low as 400°F.

3. When CO<sub>2</sub> is present in the feed stream to CoMo catalyst, it is important to consider the effect of the reverse shift reaction on COS equilibrium to properly predict the level of unconverted COS.

4. ZnO by itself will remove COS at 650-700°F, but at a considerable sacrifice in ZnO capacity as compared to that attainable with a combined CoMo-ZnO system.

Of the various catalytic steps used in the industrial processes for the production of ammonia, hydrogen and methanol, natural gas desulfurization systems are in general the least effectively monitored. If the system works well, the user normally gathers little meaningful data. If some variable changes with time causing the system to no longer attain satisfactory desulfurization, trouble-shooting the system is hampered by this lack of data. Characterization of the amount and type of inlet and outlet sulfur compounds is the data most often neglected by the user because of the difficulty in obtaining it on a routine basis.

During the last few years considerable progress has been made in the available analytical equipment for sulfur

**Table 4. Tests to measure ZnO ability to remove COS.**

Test Conditions:	
Pressure, lb./sq. in. gauge	325
Temperature, °F	650-700
Space Velocity, hr <sup>-1</sup>	750
Feed Gas Components:	
CO <sub>2</sub> , vol. %	10.0
CH <sub>4</sub> , vol. %	80.0
C <sub>2</sub> H <sub>6</sub> , vol. %	7.0
C <sub>3</sub> H <sub>8</sub> , vol. %	2.5
C <sub>4</sub> H <sub>10</sub> , vol. %	0.5
H <sub>2</sub> S, parts/million by vol., normal	7-10
H <sub>2</sub> S, parts/million by vol., max. during accelerated capacity test	170
COS, parts/million by vol. normal	120
COS, parts/million by vol. max. during accelerated capacity test	7-10
CH <sub>3</sub> SH, parts/million by vol. normal	1
CH <sub>3</sub> SH, parts/million by vol. max. during accelerated capacity test	5

## Results:

Time Onstream, hr.	Parts/million by vol.			Total Outlet Sulfur	Calculated Sulfur Pickup, wt. %
	COS	H <sub>2</sub> S	CH <sub>3</sub> SH		
0-44	2.9	3.7	0.1	Nil	0.026
44-306	7.4	13.8	0.65	Nil	0.54
Raised sulfur levels to accelerate the test					
306-446	120	170	2.5	Nil	4.2
446	Sulfur breakthrough			0.2	4.2
446-452	69	79	1.7	Nil	—
452	Sulfur breakthrough			0.2	—
Lowered inlet sulfur to normal levels					
452-476	1.5	14	1.2	Nil	4.6
476	Sulfur breakthrough			0.2	—

analysis. It is hoped that as this improved analytical equipment comes into wider use, more accurate and more frequent sulfur analyses will be taken across desulfurization systems. Improved feedback of this type information from industry will be a welcome tool in the optimization of desulfurization system design. #



**B. W. Burklow**, manager, technical services, for CCI, previously served as a technical representative in the Marketing Div. and as manager of engineering services and technical service engineering. He earned his B.S.Ch.E. from Purdue Univ. and has served in engineering and manufacturing capacities in the fertilizer, vegetable oil and polymer industries.



**R. L. Coleman**, currently a research chemist in the Research Dept. of CCI, has served as a research chemist for both industry and private research groups. He has expertise in the areas of synthetic organic chemistry related to the manufacture of tobacco products.

## DISCUSSION

**BOB OSMAN**, Exxon Chemical Co.: Your first graph shows the amount of COS that was not converted to H<sub>2</sub>S as a function of hydrogen content. Now can you say that this graph was a result of an equilibrium limitation, or could it have been a kinetic limitation as well? Could we compensate for a lower hydrogen content by a longer residence time?

**BURKLOW**: We didn't feel it was a kinetic limitation because we ran up to 10,000 space velocity and saw no difference from 2,000 to 10,000, so I don't believe it was kinetic.

**OSMAN**: Do you actually have an equilibrium model for this system?

**BURKLOW**: Yes, depending on the feed stock.

**OSMAN**: Did you ever actually check the results that you got as a function of percent hydrogen to see if they represented equilibrium compositions?

**BURKLOW**: Yes, we've done that. One reason that we're confident that wasn't the major factor is that portion of the data.

**JAN BLANKEN**, UKF-Holland: I would like to make one comment and ask one question. From 1960 to 1970 we operated a partial oxidation unit for heavy fuel oil. We had a sulphur removal unit, which consisted of an alkazid wash in two stages. The bottom stage removed the bulk of the hydrogen sulfide — in between the stages we converted carbon oxy sulfide over a cobalt molybdenum catalyst to hydrogen sulfide and in the second stage we removed the additional hydrogen sulfide.

The catalyst converted the carbon oxy sulfide with water vapor added into carbon dioxide and hydrogen sulfide. We heated the gas up with steam to about 180°C and the conversion took place at that temperature. The catalyst was bought from a company producing catalysts for refineries in Holland. We operated the unit for 10 yr. without problems.

**BURKLOW**: Is that the so-called purple sandwich arrangement where you had zinc oxide, cobalt-moly, followed by a second layer of zinc oxide?

**BLANKEN**: We converted the carbon oxide sulfide to hydrogen sulfide and removed the hydrogen sulfide in the top stage of the alkazid was unit.

**BURKLOW**: Oh, I see, that is very interesting.

**BLANKEN**: I do not know the lifetime of the catalyst but it worked all right. One of the minor problems we had,

was that the catalyst also converted organic chlorides we had in the gas into hydrogen chloride, which corroded our cooler.

I would like to ask the following question: Some years ago a hydro-desulphurization reactor failed in Finland because of the strong exothermic methanation reaction which was induced by the hydro desulphurization catalyst and the carbon monoxide and carbon dioxide content of the recycle gas. In one of our ammonia plants using the cobalt molybdenum-zinc oxide desulphurization system we will perhaps get natural gas with a high CO<sub>2</sub> content in future and the Finland incident makes us worry about possible methanation of the CO<sub>2</sub> with recycle hydrogen. Could I have your opinion?

**BURKLOW**: Concern about the possibility of methanation of carbon oxides over cobalt molybdenum catalysts is quite common. This has not been a significant commercial problem to the best of my knowledge. We have done lab work to define this methanation potential. Mr. Karl Russ of our laboratory is in attendance today and can add to my comments on this subject if I miss any of the points we evaluated.

My impression is that we found that with carbon oxides, both CO and CO<sub>2</sub>, in the feed gas to cobalt moly catalysts, as a rule of thumb about 50% of the CO that's present can, and may methanate and then the water gas shift reaction will tend to seek equilibrium.

We normally find that a portion of the CO will hydrogenate and then the water-gas shift reaction will tend to try to seek equilibrium, and so unless you have a very high concentration, we have noted no CO<sub>2</sub> by itself methanating. We think that rather than being a methanation of CO<sub>2</sub>, we are satisfying these other two parameters, one that CO partially will methanate, and the water-gas shift reaction will seek equilibrium.

To get in trouble with that type of reaction from a temperature rise, you would have to have a very significant quantity of carbon oxides in the feed. I would think this level would be well above what most plants would have. I'm sure, however, that a set of conditions does exist where that would cause you problems.

**BLANKEN**: At the moment we have about 0.8% CO<sub>2</sub> in the natural gas and never found any methanation, but with feed possibly going up to 5-6% of CO<sub>2</sub> we started worrying.

I understand from you that you would not worry too much.