PRODUCTION & EMISSIONS ANALYSIS

03 SULFURIC ACID PLANT

IMC FERTILIZER, INC.

NEW WALES OPERATIONS

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DECEMBER 12, 1991

The following analysis of the production and emissions from the
IMCF 03 Sulfuric Acid Plant was prepared in response to questions
contained in a letter from J. H. Kerns of the Florida Department
of Environmental Regulation to J. M. Baretincic of IMCF, dated
November 19, 1991. If it is necessary, the analysis can be
expanded further. The questions and responses are as follows:

(1) Were the 1989 and 1990 tests representative of the normal
     operation of the 03 Sulfuric Acid Plant?

     Three graphs of the emissions and production for the three
sulfuric plants, 01, 02 and 03 have been prepared. These are
sister plants were constructed at the same time and are operated
in the same manner. The graphs contain daily production of
greater than 2000 tpd where the tpd has been adjusted based on
the inventory of sulfur used. Emission data based on the average
of the three instantaneous readings of ppm and furnace
temperature done daily pursuant to 40 CFR 60.84(b). Manual OSO
results from the annual compliance testing are also shown on the
graphs.
     These graphs illustrate that there is much daily fluctuation
in both the production rates and emissions from these plants.
From general survey of the graphs, 02 and 03 seem to more closely
parallel each other in operation than either does with 01. Since
November, 1990, the three appear to have become more similar than
before that time. The major repairs to these units are also
represented on the production curves. There is no dramatic
impact apparent from these activities. This is true of the
installation of the HRS unit on 03.
     Appendix A contains the comparisons of the continuous monitor
chart readings to the manual test results for the days tested.
They indicate that the continuous monitor will reflect the plant
emissions. There is, however, a variability in the comparison of
the two. There is no consistent bias in the comparisons.
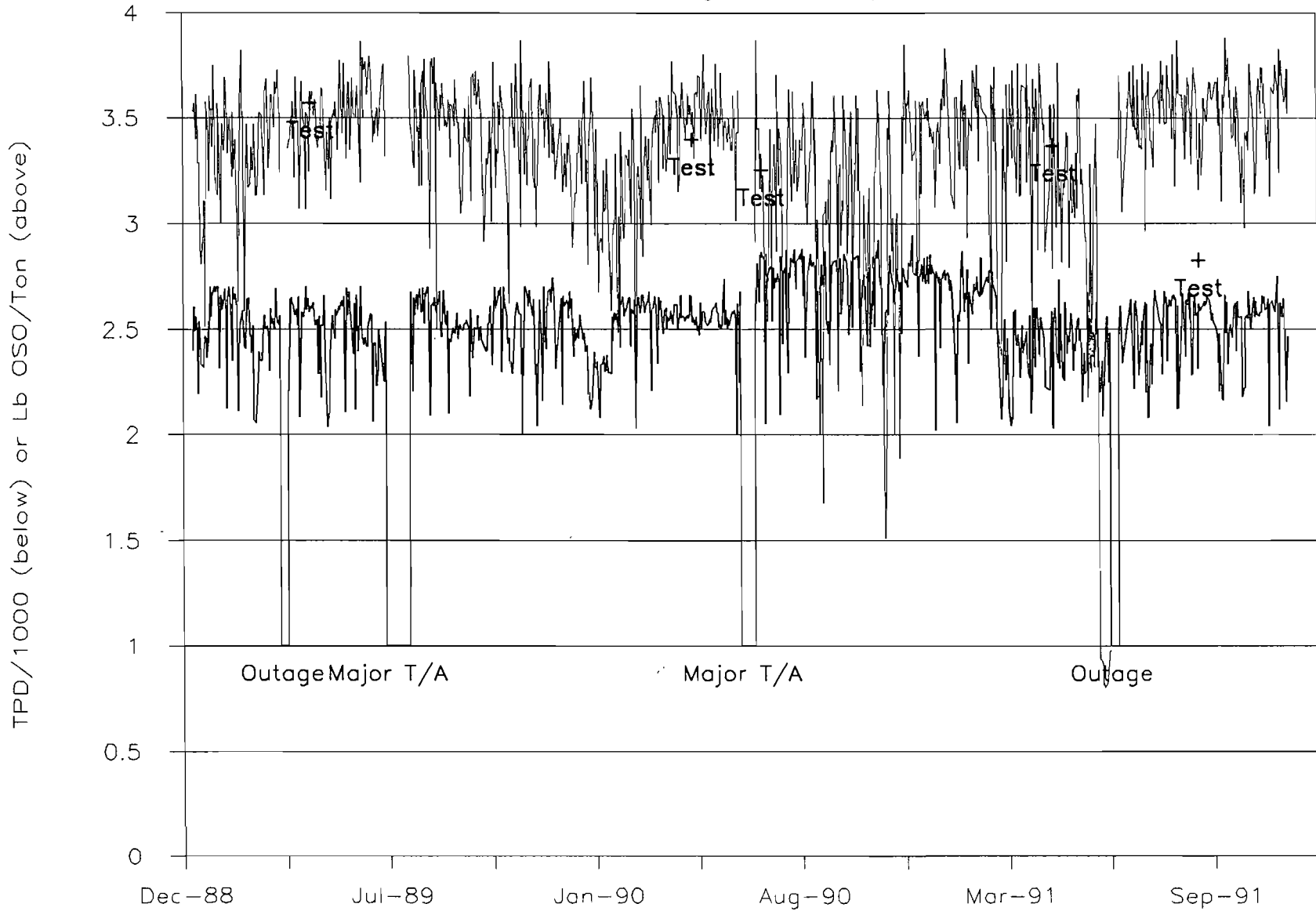   Plant operation for 1989 through November 1991 has been
analyzed using the t-test to compare averages, see Table 1.
Several general statements can be made:

01 average TPD greater than 02 and 03 average TPD
02 average TPD not different from 03 average TPD
01 average Emissions greater than 02 and 03 average Emissions
02 average Emissions not different from 03 average Emissions

     The production of the plants for the whole period of 1989 to
November, 1991 could be considered to be "representative" of
normal operation. There is very little overall change when the
day to day fluctuations are ignored. This poses a problem in
using a particular day as an indication of normal operation
because it was the day on which an emission test was conducted.

O1 Plant
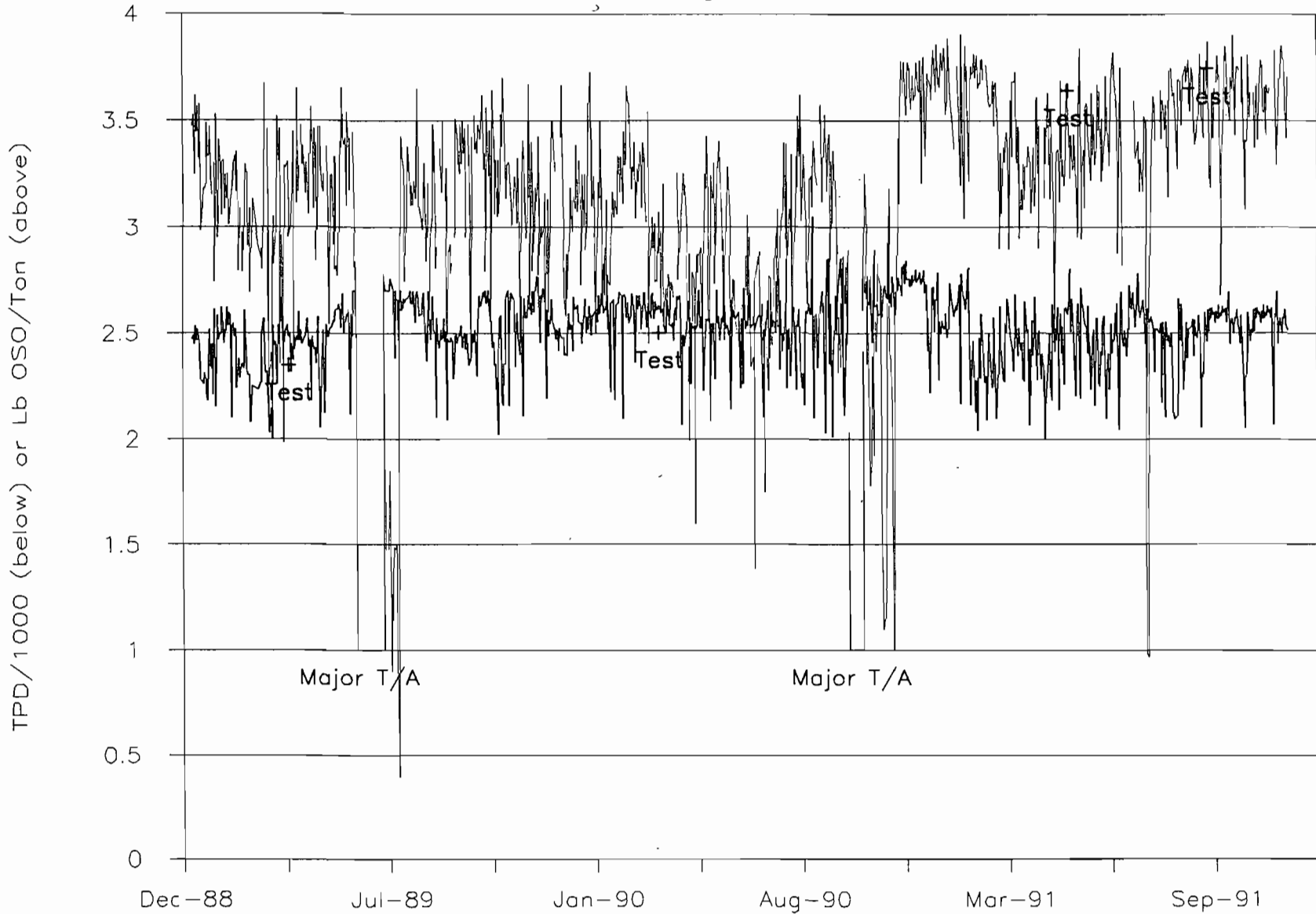
1989 through November 1991

O2 Plant

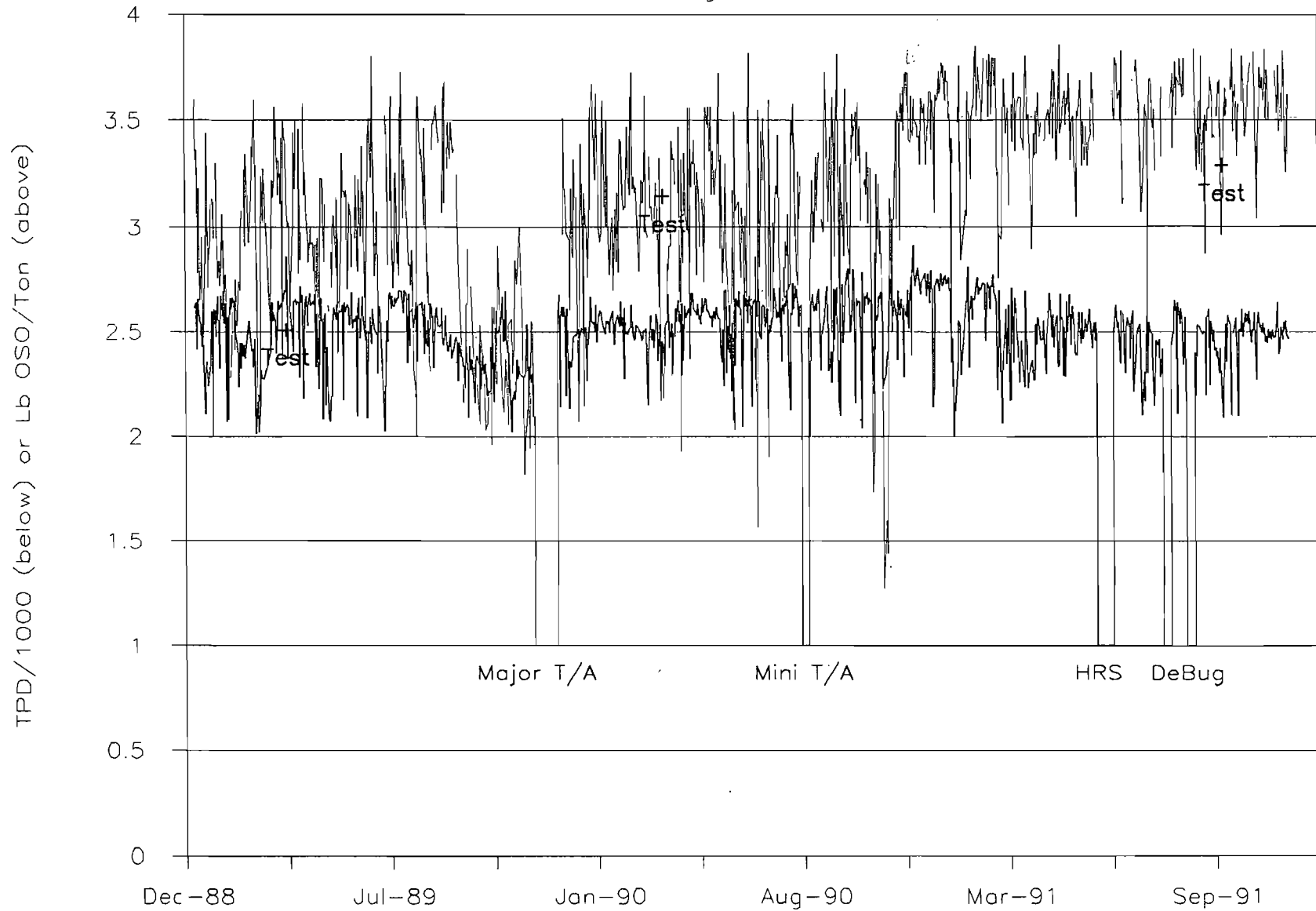## 1989 through November 1991

O3 Plant

1989 through November 1991

TPD/1000 (below) or Lb OSO/Ton (above)

Major T/A   Mini T/A   HRS DeBug

Dec-88   Jul-89   Jan-90   Aug-90   Mar-91   Sep-91

TABLE 1

Production and Emission Comparisons
Based on Student t-test

t<1.64 means no significant difference for large no

	tpd	std	no	Sv	t	lb/tonstd	std	no	Sv	t
01	2544	181.6	946			3.328	0.412	897		
02	2516	162.1	950	172.1	3.507	3.172	0.488	904	0.45	7.32
02	2516	162.1	950			3.172	0.488	904		
03	2505	163.3	919	162.7	1.470	3.149	0.453	866	0.47	1.02
03	2505	163.3	919			3.149	0.453	866		
01	2544	181.6	946	172.8	4.846	3.328	0.412	897	0.43	8.69
03<6/10	2540	172.4	146			3.504	0.222	164		
03>6/10	2456	133.2	146	154.1	4.616	3.545	0.215	126	0.21	1.57
may 90	2571	92.58	31			3.212	0.270	30		
sep 91	2425	131.2	29	91.23	6.187	3.455	0.225	28	0.24	3.70
03<12/3/89	2356	135.2	74			2.531	0.430	70		
03>12/16/89	2509	105.3	74	74.52	12.50	3.104	0.318	70	0.37	8.95
03<8/13/90	2555	151.8	71			2.930	0.419	71		
03>8/17/90	2535	196.8	71	139.2	0.863	3.149	0.345	69	0.38	3.36
03<7/30/91	2370	164.6	14			3.407	0.307	14		
03>8/4/91	2481	168.5	14	119.2	2.480	3.646	0.120	13	0.23	2.61
03>8/4/91	2481	168.5	14			3.646	0.120	13		
03>8/27/91	2454	139.4	14	98.67	0.745	3.460	0.246	14	0.19	2.45
03>11/90	2511	163.9	317			3.522	0.220	290		
02>11/90	2512	174.9	350	126.7	0.102	3.498	0.315	327	0.27	1.08
02>11/90	2512	174.9	350			3.498	0.315	327		
01>11/90	2530	193.2	317	133.2	1.673	3.332	0.520	317	0.42	4.89
03>11/90	2511	163.9	317			3.522	0.220	290		
01>11/90	2530	193.2	317	136.6	1.685	3.332	0.520	317	0.40	5.75

(2) Would a different time period be more representative of normal operation? If so, what time period would IMC suggest and why?

Based on the previous discussion, the complete time period is representative of the production. If production and emissions are considered, then November, 1990 through present represents the current status of the plants on an average basis.

Based on comparison using the t-test, the following statements are made for the period since November, 1990, see Table 1:

01 TPD slightly greater than 03 and 02 TPD (<1%)
02 TPD not different from 03 TPD
02 and 03 Emissions are not different
02 and 03 emissions greater than 01 emissions (<6% diff)

(3) Please submit calculations and results as described in 40 CFR 60, Appendix C. --"Determination of Emission Rate Change"

1. There is no significant change in emission rate for 5/90 and 10/91 per based on the Student's t test since $t = 1.065 < t' = 2.132$.

9/26/91	%OO	mg	dscf	PPTon		
Run 1	5.13	1121	42.59	3.417		
Run 2	5.13	1107	42.04	3.419	avg	s
Run 3	5.28	969	42.03	3.022	3.286	0.229

5/31/90	%OO	mg	dscf	PPTon		
Run 1	5.63	933	40.13	3.117		
Run 2	5.67	946	39.81	3.194		
Run 3	5.53	962	41.09	3.118	3.143	(0.044)

Sv = 0.165
t = 1.065

(4) Please describe all changes between May 1990 and October 1991 which might affect emissions (other than the installation of the HRS and elimination of the IPA tower). The response should include, but not be limited to, items such as catalyst changes, equipment upgrades, cleaning, maintenance, etc.

Typically the major overhaul or turn around will include:
All instrumentation is checked, repaired, and calibrated.
Electric motors removed and rebuilt.
Boiler repairs made.
Refractory repairs made.
Catalyst is removed and screened, from 2 to 4 passes, whole pass or only top 10 inches.
The duct work for the drying and IPA towers is being upgraded from mild to stainless steel during certain turn

arounds.
The mesh pads on the drying towers are being upgraded from
6 inch to 8 inch thickness.

Major down times occurred at:
        8/13/90 to 8/17/90   The first pass and a bad grid area were
                             screened.
        5/27/91 to 6/10/91   The HRS was installed and all 4 passes
                             were screened in the converter. In the
                             drying tower, the mesh pad was
                             increased to 8 inches and the baffle
                             dome removed.
        7/30/91 to 8/4/91   Inspection and repairs to HRS system
        8/22/91 to 8/27/91   Inspection and repairs to HRS system
The previous major down time was 12/3/89 to 12/15/89 for major
overhaul.

    Based on the use of the t-test for comparisons, the affects
on production were, see Table 1:

TPD after 12/3/89 T/A greater than before.
TPD after 8/12/90 T/A not different than before.
TPD after 5/27/91 HRS T/A less than before.
TPD after 7/30/91 HRS inspection greater than before.
TPD after 8/4/91 HRS inspection not different than before.

(5) For each change listed in the response to question (4), what
     affect might the change have on emissions?

    In general, maintenance either restores conversion or
increases absorption and collection of the acid which means that
the plants can be operated at a higher rate and be in compliance.
As emissions increase, production is reduced so that operation
will remain in compliance.
    Based on the graph of this period, there was no clearly
predictable impact on emissions beyond the normal fluctuation.
The periods of work are indicated on the graph of O3. Similar
periods are shown on the O1 and O2 graphs also.

    The t-test comparisons are, see Table 1:

Emissions after 12/3/89 T/A greater than before.
Emissions after 8/12/90 T/A greater than before.
Emissions after 5/27/91 HRS T/A no different than before.
Emissions after 7/30/91 HRS inspection greater than before (7%).
Emissions after 8/4/91 HRS inspection less than before (5%).

    Three graphs were prepared showing the measured emission
points verses the production for the three plants. A simple
regression analysis was done for each to illustrate the lack of
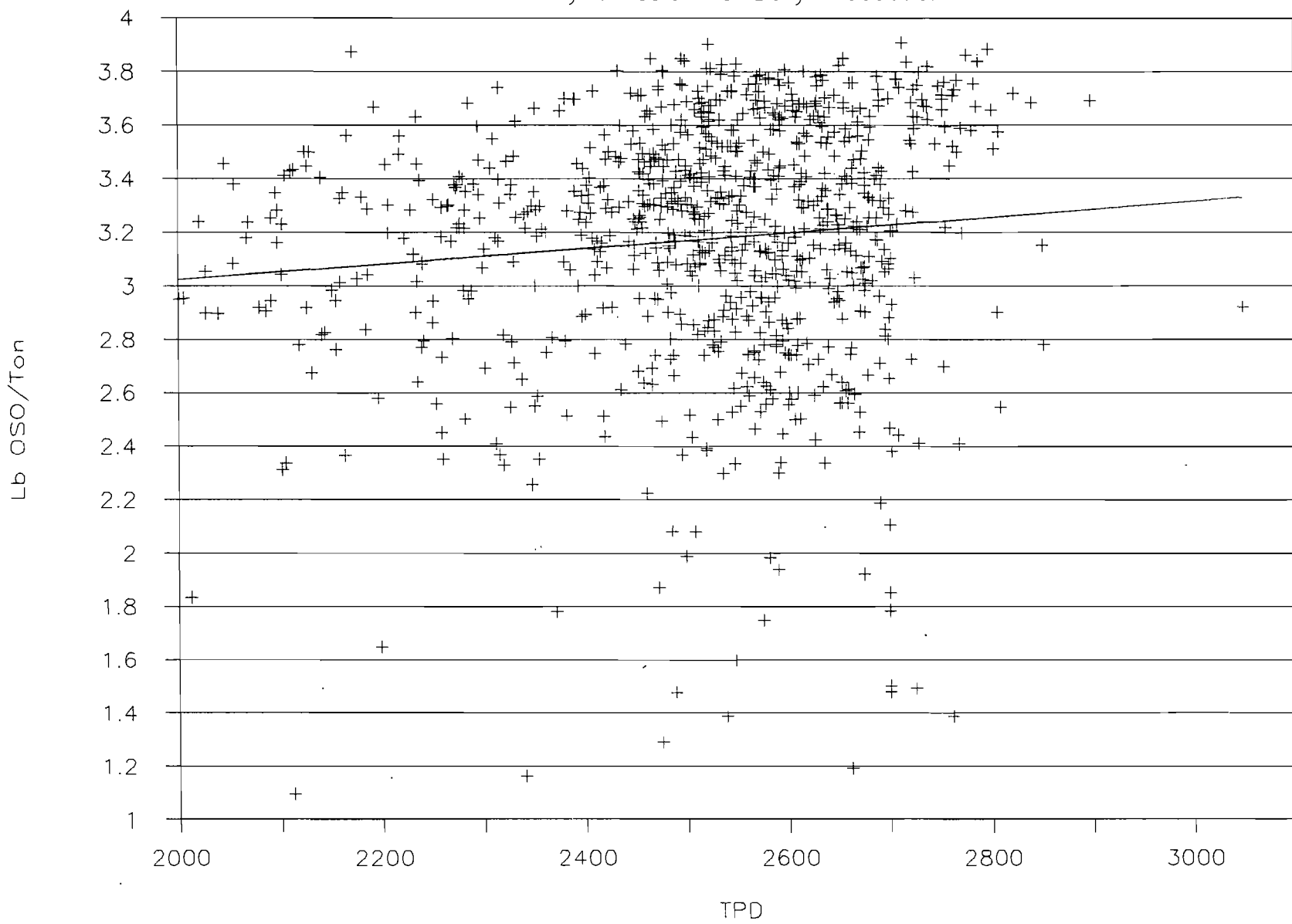dependency between production and emissions. The regression line
is shown on each graph.

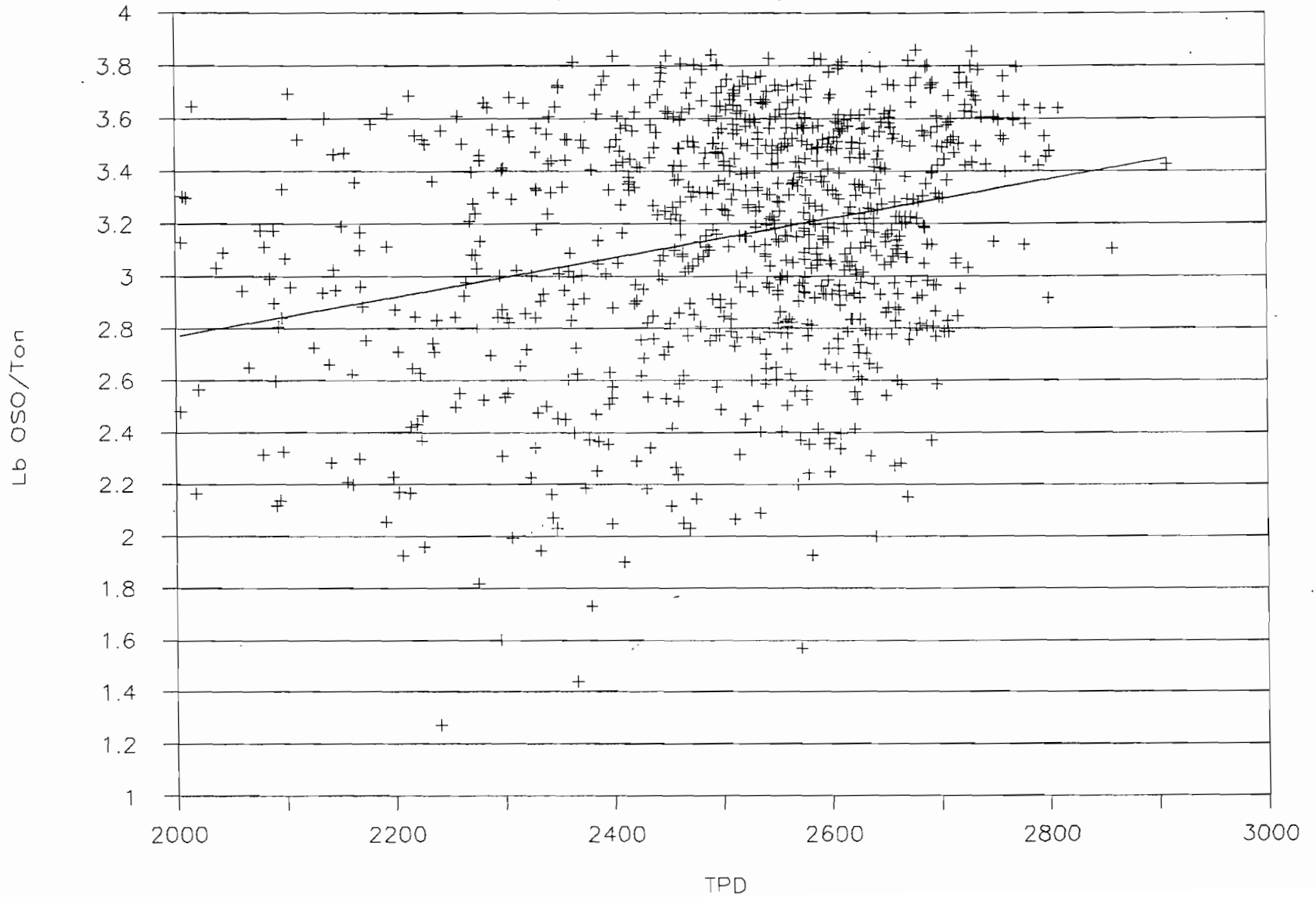## 01 Plant

Daily Emission vs. Daily Production
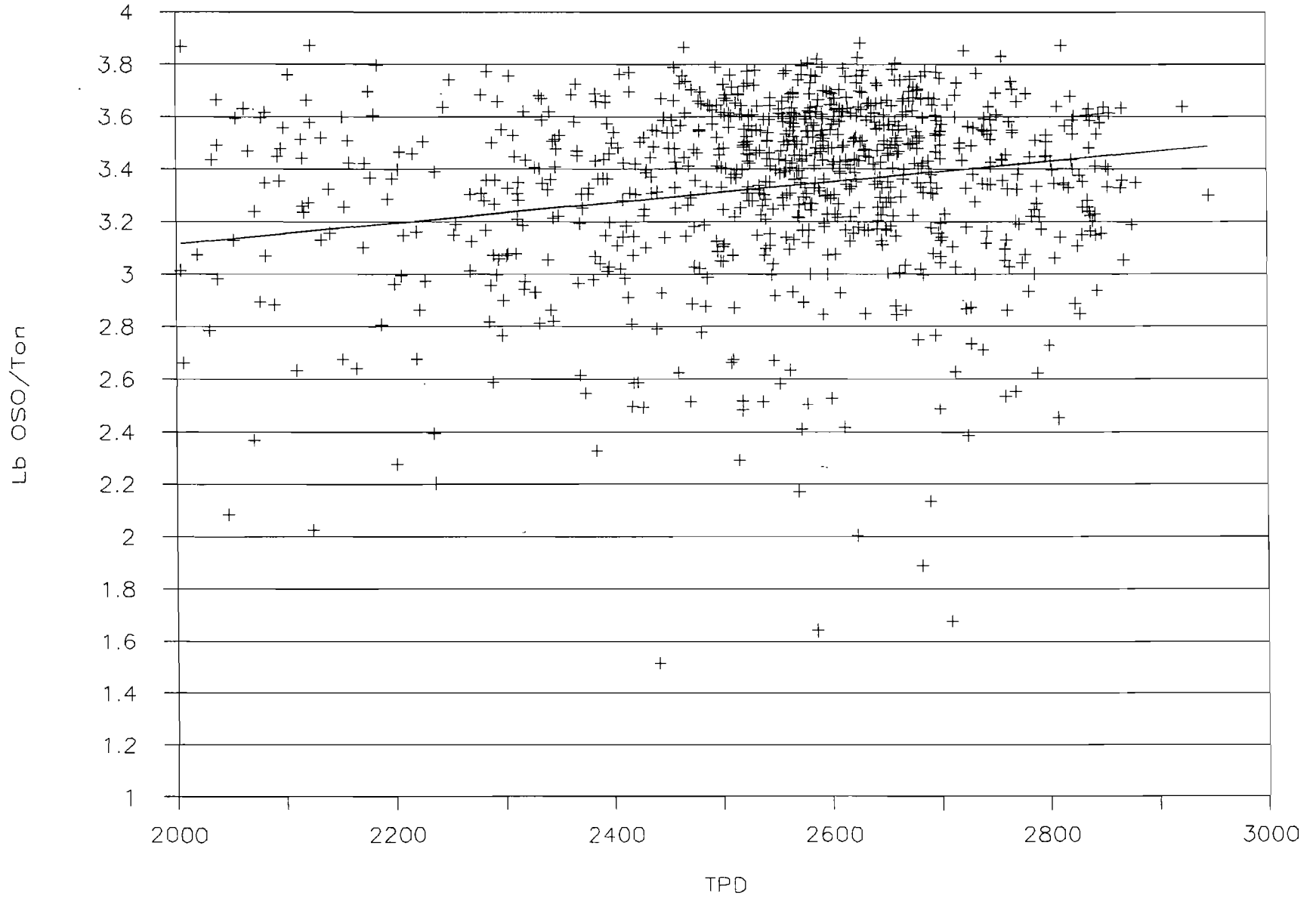
O2
~~O3~~ Plant

Daily Emission vs. Daily Production

O3 Plant

Daily Emission vs. Daily Production

Lb OSO/Ton vs. TPD

(6)   The May 1990 test was conducted at a process rate which was
      approximately 10% greater than the recent conducted in
      September 1991. What affect, if any, might this difference
      in process rate have on the emissions?

      As discussed previously "normal operation" has fluctuations
in both emission rates and production rates. The 10% difference
in rate does not indicate a change in operation other than a
normal fluctuation. Since there is no strong relationship
between emissions and production, the 10% change will have little
impact on emissions. Under normal operation, the production rate
is constrained by compliance, the maximum production of this unit
will be dependent on emissions rather than the reverse. The
units will not be operated above the permitted emission limit.
      The specific comparisons of those month's production and
emissions are as follows, see Table 1:

TPD for Sept 1991 are less than May 1990 TPD (6%).
Emissions for Sept 1991 are greater than May 1990 Emissions (7%).

(7)   Please describe all maintenance or operational problems, or
      equipment or process failures, which might have affected
      emissions, since starting up the HRS. This response should
      address, but not be limited to, corrosion problems.

      The problems generally have been related to the liquid acid
phases of the project. Monsanto paper describes generally the
problems of the HRS unit. The portion dealing with IMCF is
attached.

HEAT RECOVERY SYSTEM UPDATE

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PRESENTED AT

FERTILIZER INDUSTRY ROUND TABLE

TAMPA, FLORIDA

OCTOBER, 1991

ABSTRACT

Over five years ago, K. P. Chae, General Manager of Namhae Yeosu site, had the courage to install HRS on his two 1350 MTPD sulfuric plants. HRS was installed as the IPA tower as part of conversion to IPA.

At the time, competitors said HRS was unsafe. Consultants did not recommend it. Why was K. P. Chae willing to bet his reputation on HRS? Why was Namhae willing to put their fertilizer production at risk? B.J. Lee, Namhae's managing director, told us, "We are committed to use the best technology to give us the lowest costs."

HRS has been a success at Namhae. It has made them money. They are happy.

The first Heat Recovery System in the USA was installed to replace the original interpass absorption tower on IMCF's 2500 STPD plant at New Wales, Florida. It was put in service in June 1991. The start-up went well with only minor problems such as excessive vibration of the diluter. This was cured by modifying the water sparger. There were too many flow measurement instrument problems and Enviro-Chem is determined to have instrumentation in better shape on future start-ups. The plant was demonstrated seven days after start-up and all guarantees were met. Testing at the outlet of the Heat Recovery tower showed mist was .24 mg/ACF and SO_3 and vapor was .27 mg/ACF which is as good or better than a typical interpass absorber.
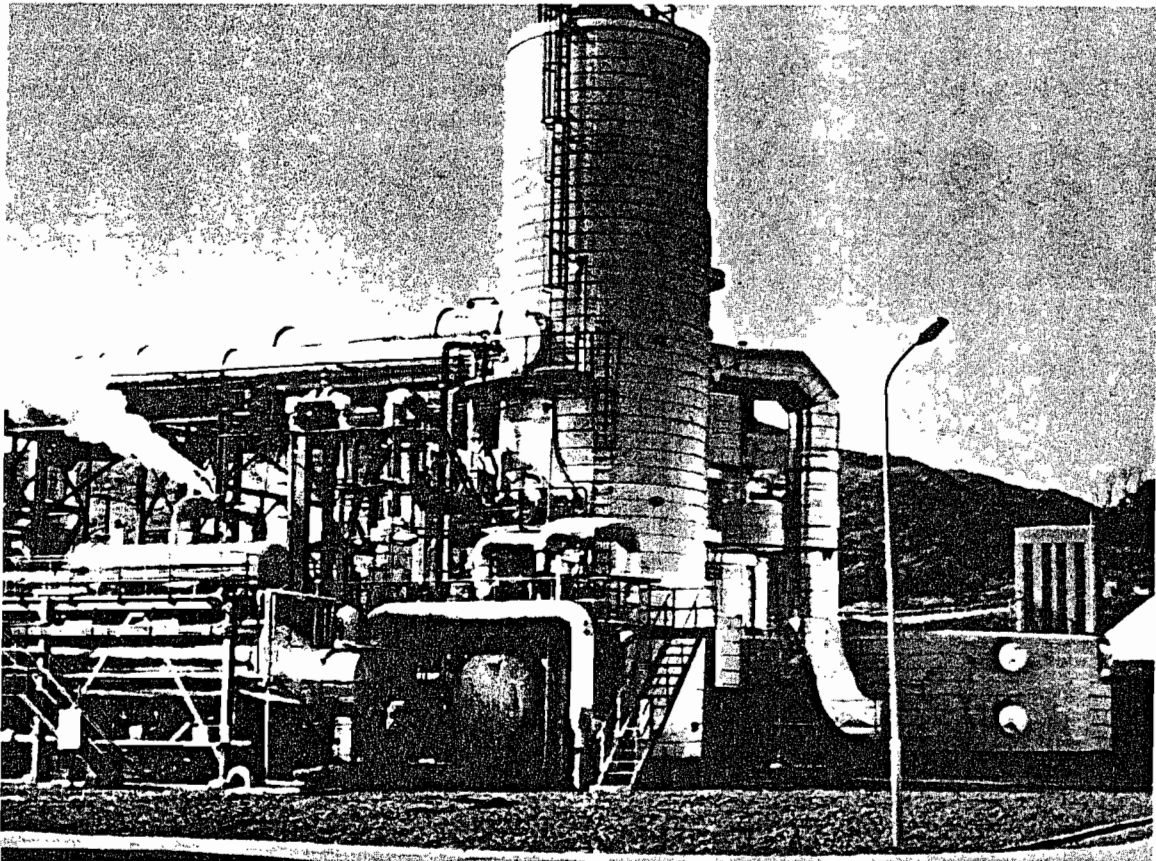

Photo of Namhae Heat Recovery System

About one month after start-up, IMCF detected some drip acid in the duct exiting the HRS. Internal inspection showed poor irrigation in the lower stage from a pipe distributor. Some improvement was made by moving some of the orifices in the piping header farther away from the distributor.

A second inspection in late August showed that lower stage acid distribution had deteriorated even more. Further inspection showed corrosion on the orifices in the acid headers and on the acid feed holes in the pipe distributor. The excessive corrosion was found only in the high velocity areas.

A secondary problem found was pluggage of the upper stage acid distributor with a black organic material. IMCF engineers identified it as being cation resin which had been charred by the acid. IMCF uses the cation backflush water for dilution. Therefore, IMCF will install a filter to be sure that the resin does not get into the acid system.

With temporary repairs made, the plant was re-started. Mist testing after start-up showed excessive sulfuric vapor and SO_3 leaving the tower. Lowering the strength of the acid being circulated over both the lower and upper stage resulted in quite good operation. The lower acid strengths compensate for the poor acid distribution over the lower stage. IMCF is now running with a good stick test at the exit of the absorber and no drip acid in the duct after the tower or in the economizers.

Enviro-Chem is fabricating a new trough distributor for the lower stage. This new trough design eliminates high velocity acid feed points. At the same time, we will also replace the one and one half inch Intalox in the upper stage with one inch Super Intalox saddles. The increased packing effectiveness will help compensate for acid distribution problems. These design changes will be part of all future HRS plants including the seven currently in various project stages.

Extensive testing, including mist and SO_3 sampling, is planned at IMCF. More tests are being made to determine if any other improvements are needed. Tests will be made after the modifications to assure us that the mist and vapor leaving the Heat Recovery tower is no greater than that found in the standard double absorption plant.

For IMCF and all of the current HRS plants that are being designed, a lot of thought has been put into dealing with an HRS boiler leak when and if one ever occurs. The basic concept is to get the acid, water, and steam out of the boiler very quickly. We have designed these plants so that if an acid leak occurs, the plant is shut down and within a few minutes, the boiler water is blowed down until the boiler is dry, the steam pressure is vented to zero atmosphere which quickly cools the boiler from 400 ° F operating temperature to about 212 ° F and the acid is allowed to run back into the pump tank. More instrumentation has also been provided. Printed information for operators is available that will make it much easier for them to detect boiler leaks. The new Heat Recovery units are even safer than the ones that have run very well for the last four years in Korea. In fact, we now have over 15 years combined experience with full-scale HRS with no injuries or catastrophic failures.
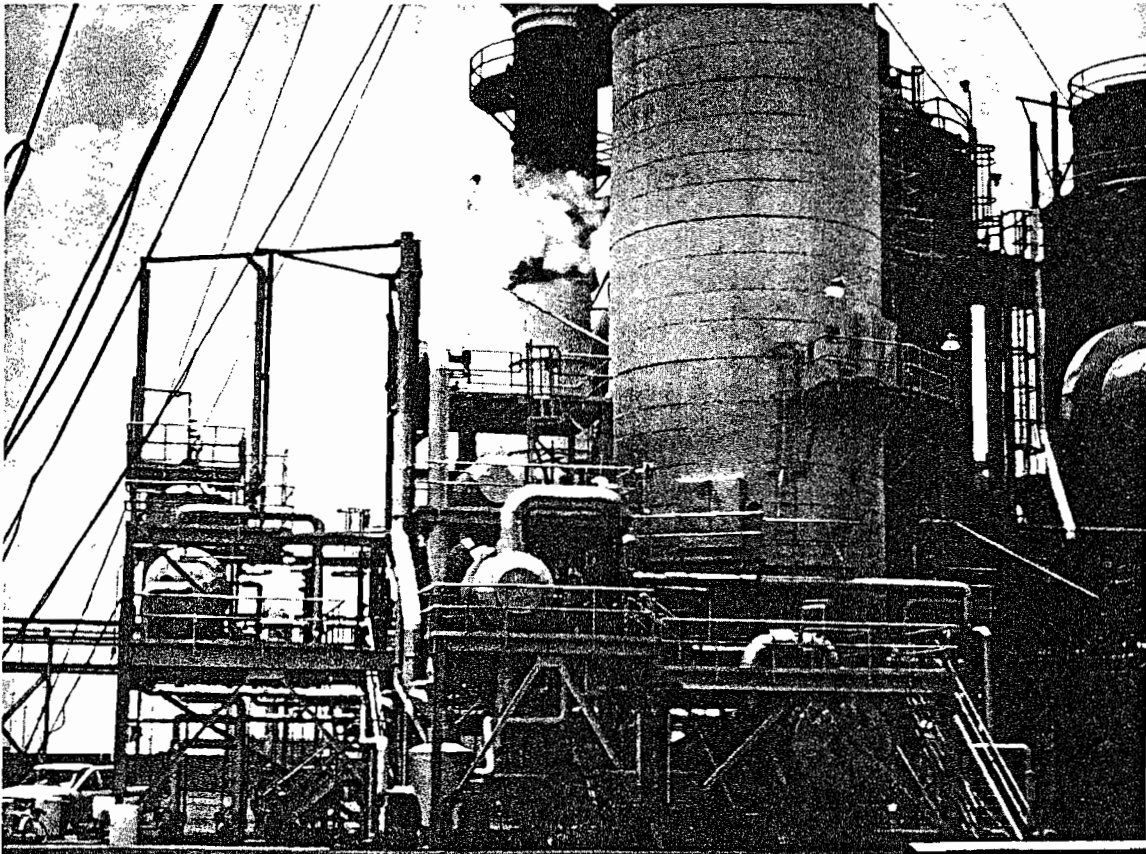

Photo of IMCF Heat Recovery System

(8) For each item described in (7), what was the affect on emissions?

Conversion reduction means higher final loading of OSO or absorption reduction means higher final loading of OSO. If either of these conditions occur, production is curtailed such that emissions remain in compliance.

(9) For each item described in (7), does IMC have a plan to reduce the frequency of occurrence? If so, please describe the plan.

IMC plans to improve the operation of the HRS at every opportunity. Because of the continuous operation of an acid plant, it is difficult to exactly identify problems until such time as the plant is down and can be inspected. Current plans are for the replacement of the acid distribution system in the HRS tower as described in the attached paper.

(10) Please describe all instances where emissions, resulting from a malfunction, may have exceeded the emission limits in Permit AC53-192221.

No excess emission have occurred for this plant due to any circumstance. If there had been excess emissions, they would have been reported to the FDER in the Excess Emission and Monitoring System Performance Reports which are submitted quarterly to the district office.

APPENDIX A

Comparison of Monitor Strip Chart,
Emission Test Run Results,
and
Daily Monitor Conversion Factor Records
Using Student's t-test.
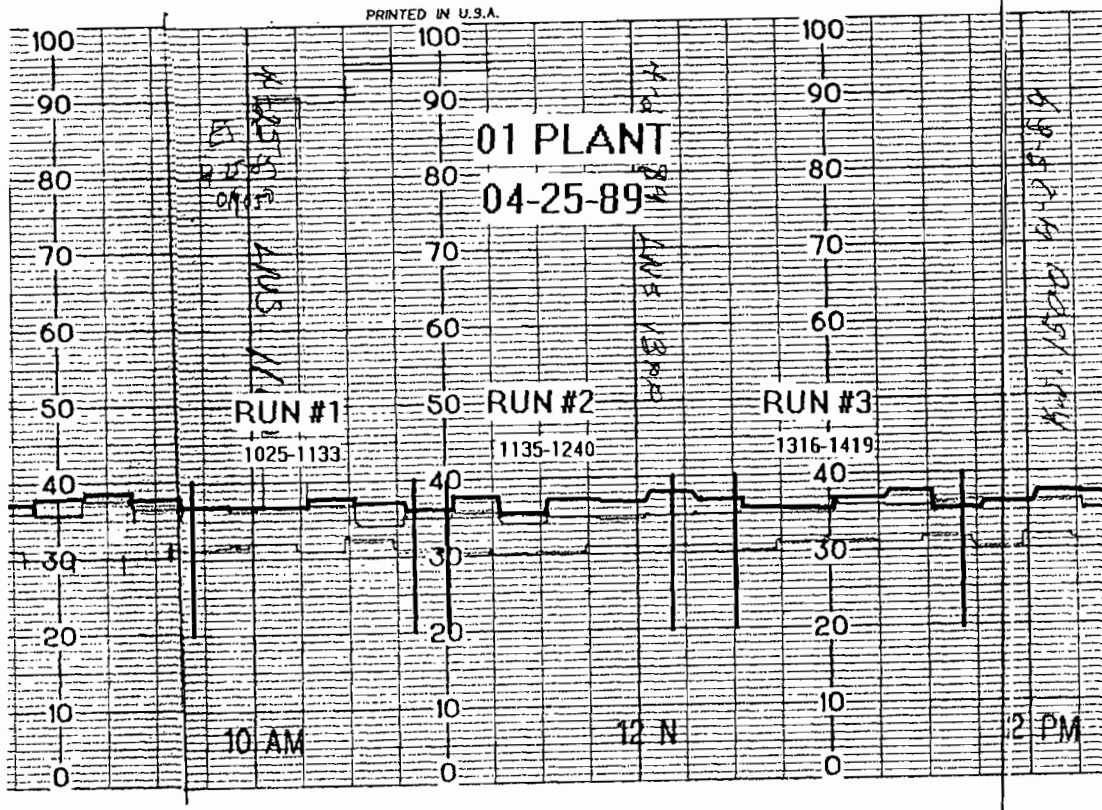
Strip Chart During Test
01 Sulfuric Plant
4/25/89

	Emission test result				Chart result	
	%OO	mg	dscf	lb/ton	ppm	lb/ton
Run 1	6.31	1066	39.97	3.740	370	3.896
Run 2	5.98	1033	39.12	3.610	370	3.798
Run 3	5.88	974	39.47	3.363	366	3.744
			avg:	3.571	avg:	3.812
			std:	0.192	std:	0.077
					Sv:	0.146
					t:	2.024

Daily Readings				Production	
Time	Temp	ppm	lb/ton	tpd	
1100	1941	378	3.656	2651	test
1900				2609	adj 24hrs
1935	1933	370	3.599		
		avg:	3.628		
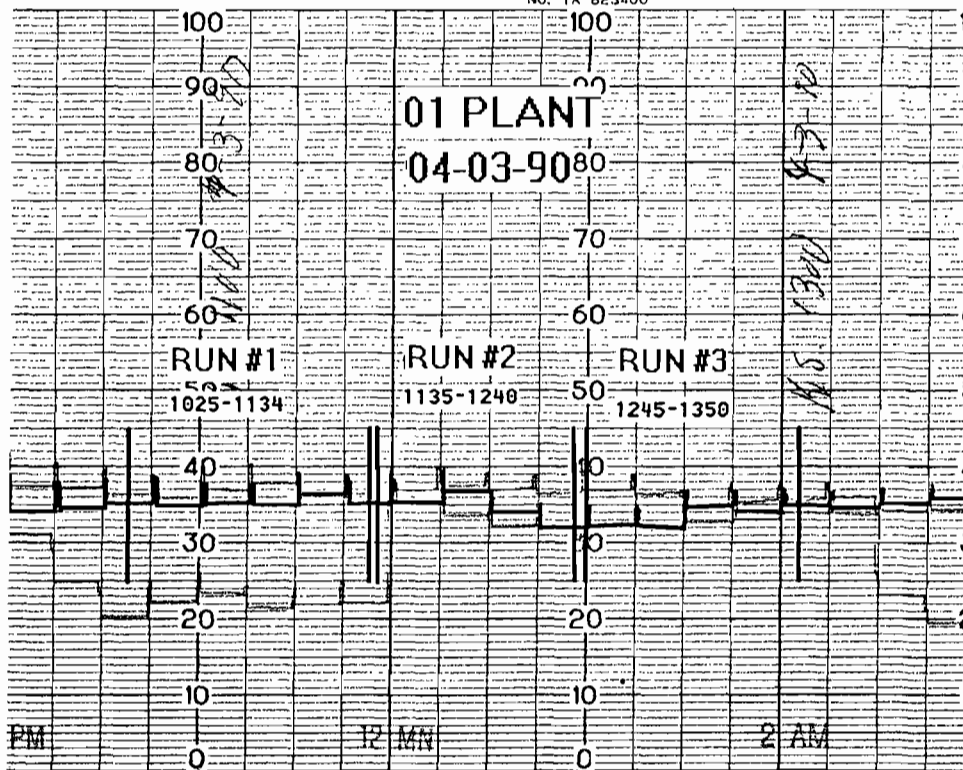
Strip Chart During Test
01 Sulfuric Plant
4/3/90

	Emission test result				Chart result	
	%OO	mg	dscf	lb/ton	ppm	lb/ton
Run 1	5.83	1291	48.81	3.592	352	3.589
Run 2	5.92	1127	47.80	3.221	345	3.539
Run 3	6.04	1141	46.55	3.376	333	3.443

avg: 3.396   avg: 3.524
std: 0.186   std: 0.074

Sv: 0.142
t: 1.098

Daily Readings				Production	
Time	Temp	ppm	lb/ton	tpd	
1100	1895	350	3.502	2612	test
1900	1895	367	3.673	2594	adj 24hrs
1935	1876	332	3.370		

avg: 3.515
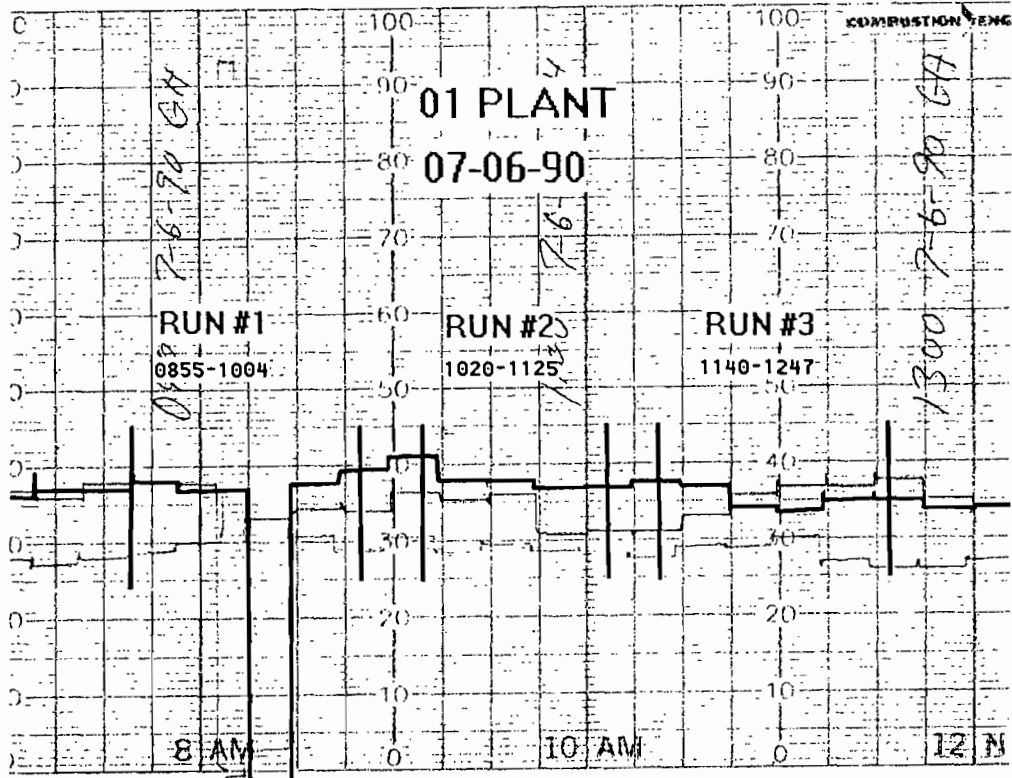
Strip Chart During Test
01 Sulfuric Plant
7/6/90

	Emission test result				Chart result	
	%OO	mg	dscf	lb/ton	ppm	lb/ton
Run 1	4.32	1142	41.52	3.398	378	3.506
Run 2	4.36	1142	41.58	3.401	380	3.533
Run 3	4.35	983	41.25	2.949	352	3.271
			avg:	3.250	avg:	3.436
			std:	0.260	std:	0.144
					Sv:	0.210
					t:	1.089

Daily Readings				Production	
Time	Temp	ppm	lb/ton	tpd	
1100	1963	371	3.479	2863	test
1900	2001	382	3.536	2866	adj 24hrs
1935	1985	317	2.967		
		avg:	3.328		
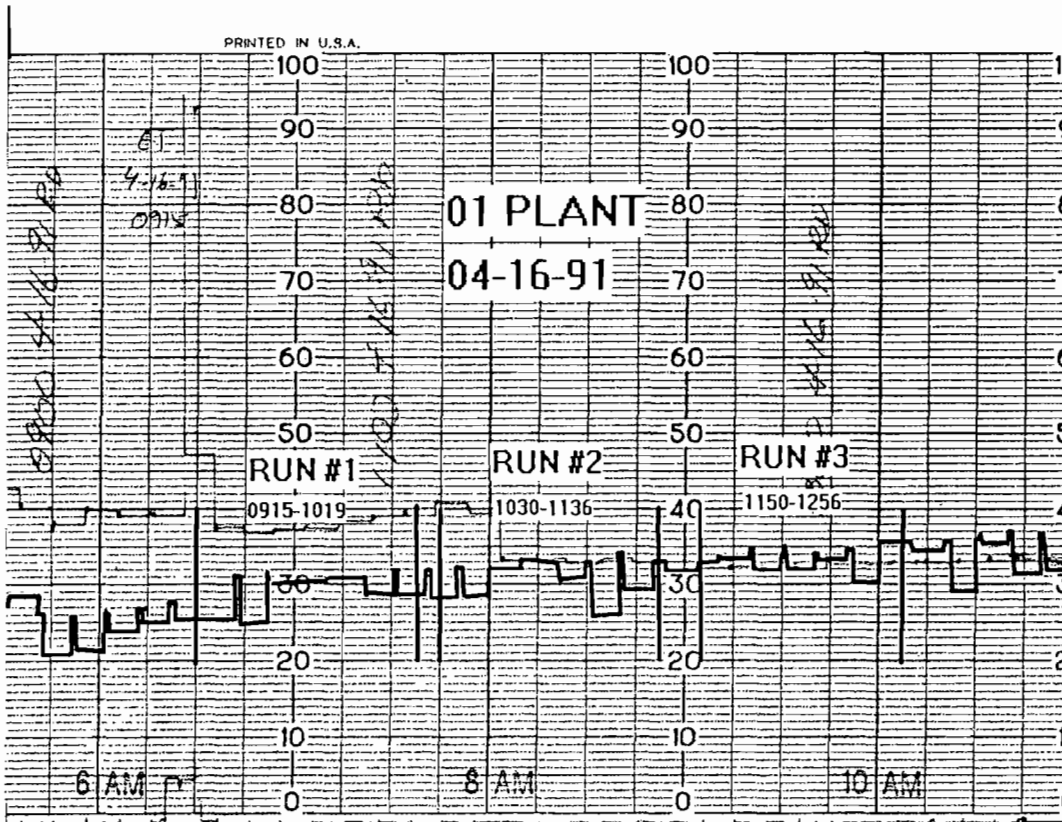
Strip Chart During Test
01 Sulfuric Plant
4/16/91

Emission test result

	%OO	mg	dscf	lb/ton
Run 1	4.91	1010	39.45	3.279
Run 2	4.94	1030	39.79	3.321
Run 3	4.93	1080	39.58	3.499
			avg:	3.366
			std:	0.117

Chart result

ppm	lb/ton
276	2.654
309	2.976
327	3.148
avg:	2.926
std:	0.251
Sv:	0.196
t:	2.756

Daily Readings

Time	Temp	ppm	lb/ton
1100	1985	343	3.211
1900	1975	339	3.197
1935	1990	377	3.518
		avg:	3.308

Production

tpd	
2647	test
2535	adj 24hrs
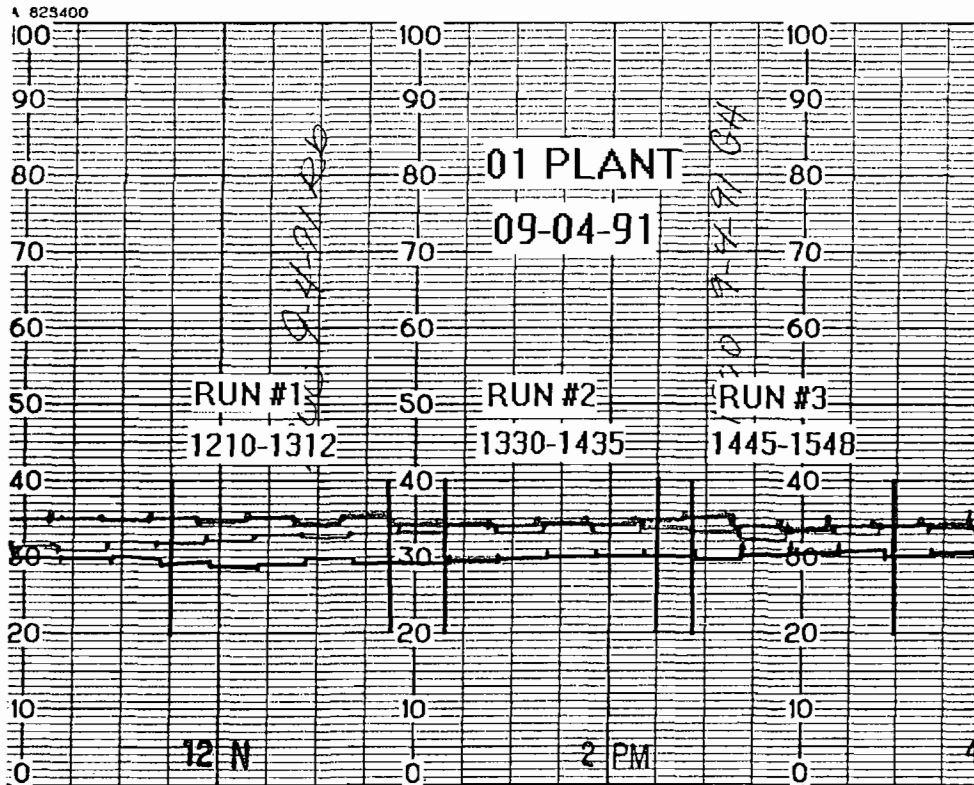
Strip Chart During Test
01 Sulfuric Plant
9/4/91

	Emission test result				Chart result	
	%OO	mg	dscf	lb/ton	ppm	lb/ton
Run 1	4.98	885	40.64	2.801	291	2.810
Run 2	4.99	910	40.08	2.922	298	2.879
Run 3	4.93	868	40.39	2.756	299	2.878
			avg:	2.826	avg:	2.856
			std:	0.086	std:	0.040
					Sv:	0.067
					t:	0.541

Daily Readings				Production	
Time	Temp	ppm	lb/ton	tpd	
1100	1949	339	3.258	2606	test
1900	1959	321	3.062	2620	adj 24hrs
1935	1960	330	3.146		
		avg:	3.155		
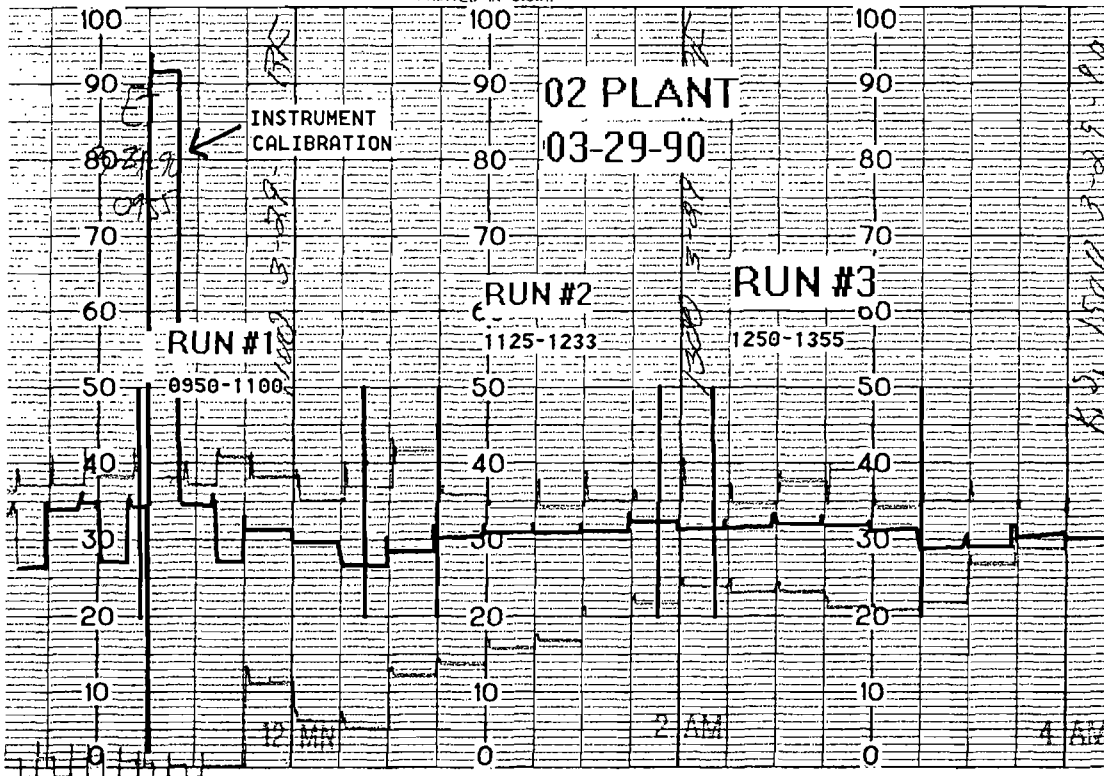
Strip Chart During Test
02 Sulfuric Plant
3/29/90

		Emission test result				Chart result	
	%OO	mg	dscf	lb/ton		ppm	lb/ton
Run 1	4.70	764.5	43.19	2.238		305	2.895
Run 2	4.60	851.2	43.35	2.467		306	2.886
Run 3	4.58	961.5	43.08	2.801		313	2.949
			avg:	2.502		avg:	2.910
			std:	0.283		std:	0.034
						Sv:	0.202
						t:	2.478

	Daily Readings				Production	
Time	Temp	ppm	lb/ton		tpd	
1100					2625	test
1900	1978	285	2.680		2612	adj 24hrs
1935	1938	328	3.055			
		avg:	2.877			
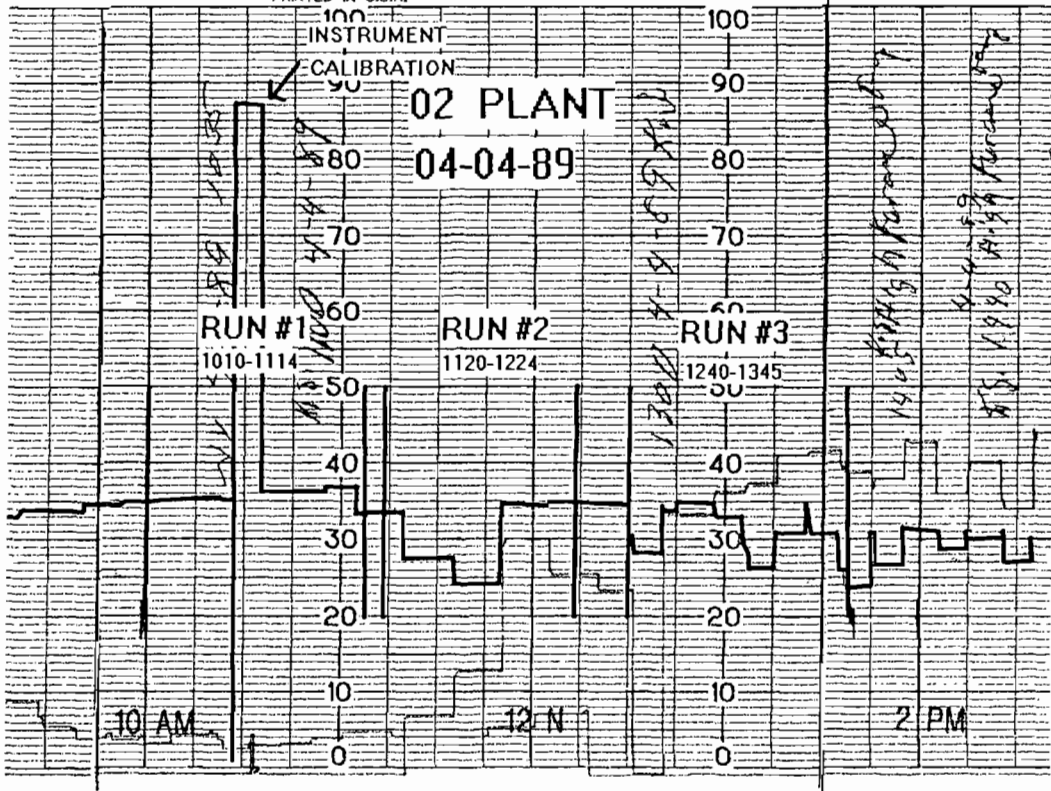
Strip Chart During Test
02 Sulfuric Plant
4/4/89

	Emission test result				Chart result	
	%OO	mg	dscf	lb/ton	ppm	lb/ton
Run 1	4.63	954	45.74	2.625	354	3.345
Run 2	4.90	723	45.91	2.016	298	2.863
Run 3	4.62	871	45.58	2.404	296	2.796
			avg:	2.348	avg:	3.001
			std:	0.309	std:	0.300
					Sv:	0.304
					t:	2.629

Daily Readings				Production	
Time	Temp	ppm	lb/ton	tpd	
1100				2523	test
1900				2454	adj 24hrs
1935	1965	311	2.953		
			avg: 2.953		

NO. TA 829400

02 PLANT

04-30-91

RUN #1   RUN #2   RUN #3

1123-1230   1240-1345   1355-1500

12 N   2 PM   4
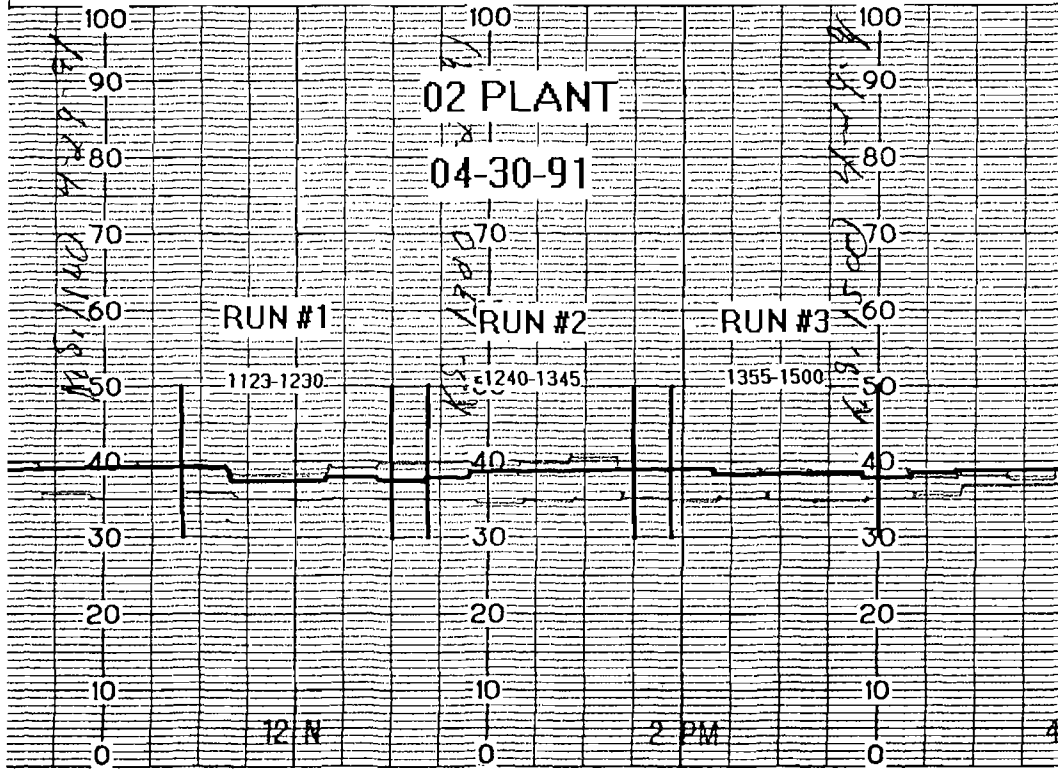
Strip Chart During Test
02 Sulfuric Plant
4/30/91

	Emission test result				Chart result	
	%OO	mg	dscf	lb/ton	ppm	lb/ton
Run 1	4.68	1280	45.02	3.590	380	3.602
Run 2	4.62	1360	44.95	3.806	386	3.646
Run 3	4.69	1250	44.73	3.531	384	3.642
			avg:	3.642	avg:	3.630
			std:	0.145	std:	0.024
					Sv:	0.104
					t:	0.145

Daily Readings				Production	
Time	Temp	ppm	lb/ton	tpd	
1100	1994	370	3.442	2647	test
1900	2003	375	3.466	2670	adj 24hrs
1935	1990	404	3.771		
		avg:	3.560		

02 PLANT
09-12-91

RUN #1 1010-1115 RUN #2 1130-1235 RUN #3 1243-1350

10 AM 12 N 2 PM
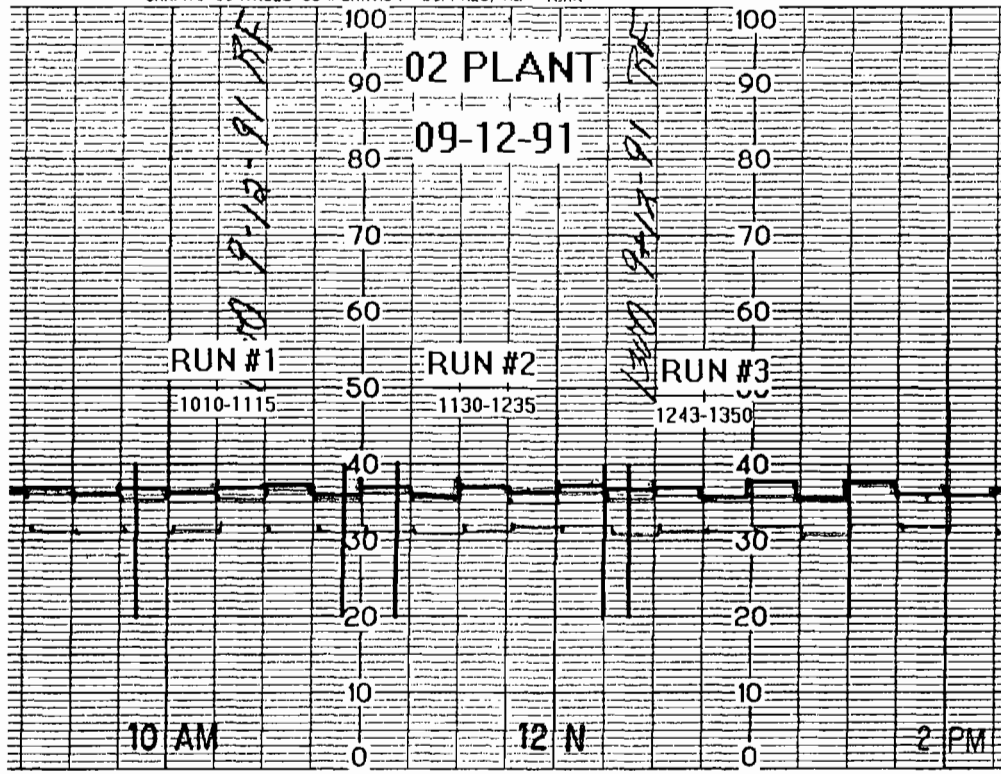
Strip Chart During Test
02 Sulfuric Plant
9/12/91

	%OO	mg	dscf	lb/ton	ppm	lb/ton
	Emission test result				**Chart result**	
Run 1	5.48	1135	40.04	3.763	366	3.648
Run 2	5.30	1135	40.08	3.716	366	3.606
Run 3	5.35	1155	40.53	3.752	368	3.637

avg: 3.744 avg: 3.630
std: 0.024 std: 0.022

Sv: 0.023
t: 6.017

Time	Temp	ppm	lb/ton	tpd	
	Daily Readings			**Production**	
1100	1918	384	3.778	2496	test
1900	1910	368	3.642	2545	adj 24hrs
1935	1910	381	3.774		

avg: 3.730
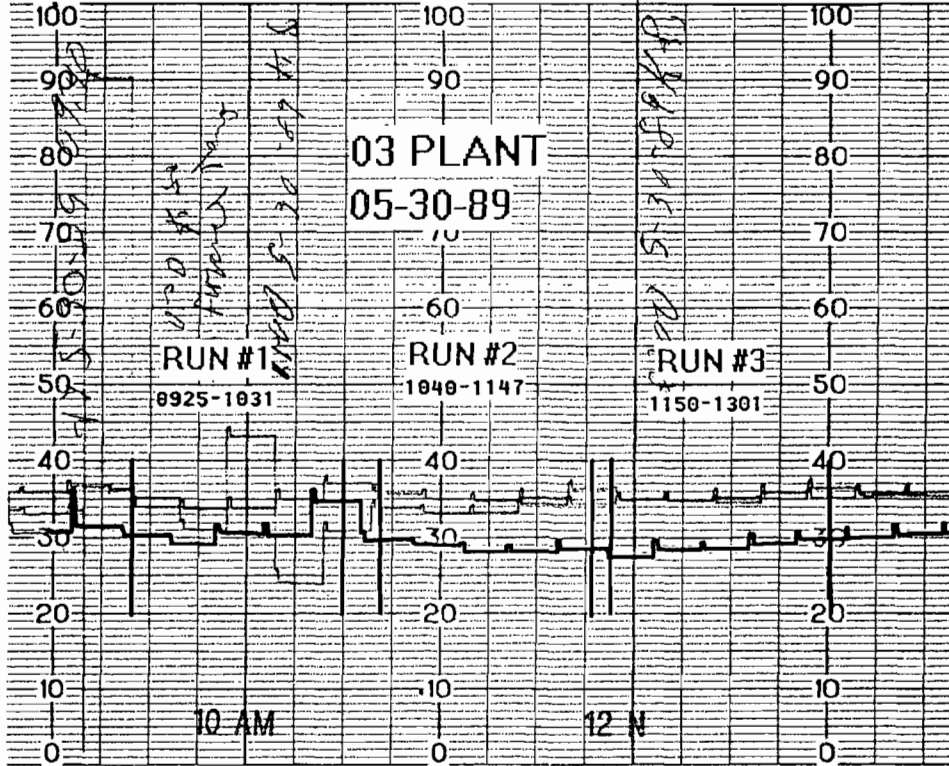
Strip Chart During Test
03 Sulfuric Plant
5/30/89

Emission test result					Chart result	
	%OO	mg	dscf	lb/ton	ppm	lb/ton
Run 1	4.62	1013	56.45	2.258	310	2.928
Run 2	5.93	1181	56.25	2.870	285	2.925
Run 3	4.75	1056	55.98	2.392	287	2.732

avg: 2.507   avg: 2.862
std: 0.322   std: 0.112

Sv: 0.241
t: 1.803

Daily Readings				Production	
Time	Temp	ppm	lb/ton	tpd	
1100	1985	300	2.807	2641	test
1900	1991	320	2.982	2619	adj 24hrs
1935	1971	287	2.713		

avg: 2.834
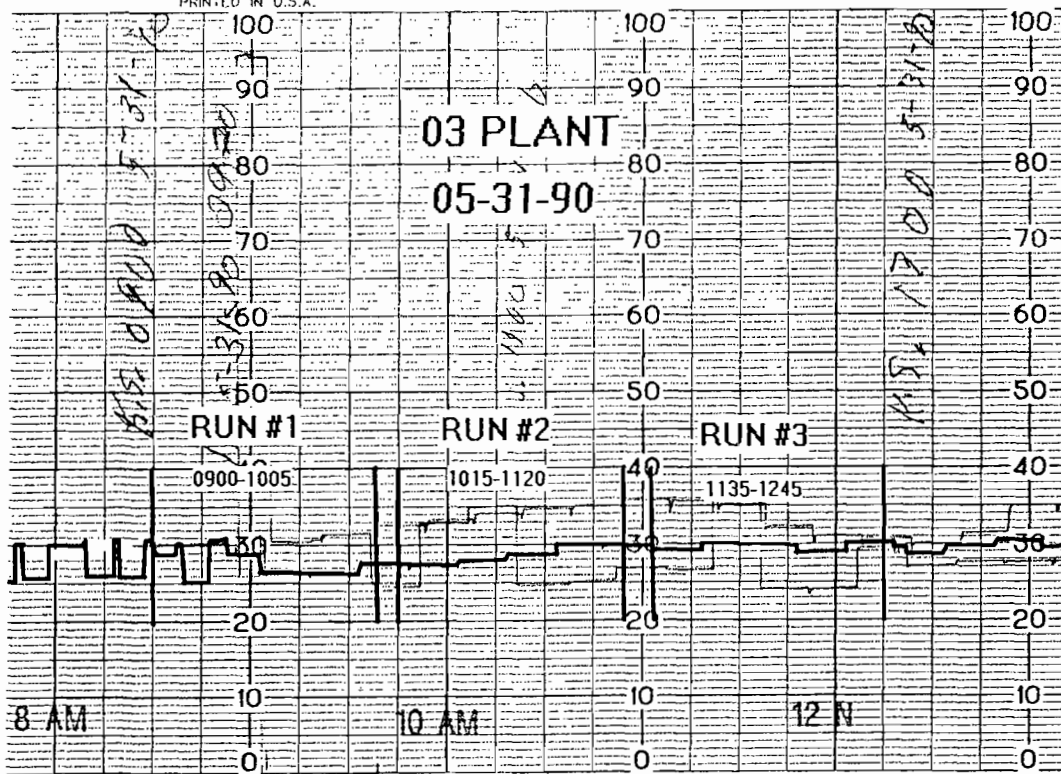
Strip Chart During Test
03 Sulfuric Plant
5/31/90

	Emission test result				Chart result	
	%OO	mg	dscf	lb/ton	ppm	lb/ton
Run 1	5.63	933	40.13	3.117	268	2.697
Run 2	5.67	946	39.81	3.194	288	2.906
Run 3	5.53	962	41.09	3.118	295	2.950
			avg:	3.143	avg:	2.851
			std:	0.044	std:	0.135
					Sv:	0.100
					t:	3.561

Daily Readings				Production	
Time	Temp	ppm	lb/ton	tpd	
1100	1960	314	2.993	2696	test
1900	1953	380	3.643	2700	adj 24hrs
1935	1967	344	3.263		
		avg:	3.299		

03 PLANT
09-26-91

RUN #1   RUN #2   RUN #3
0940-1045   1050-1156   1230-1345

10 AM   12 N
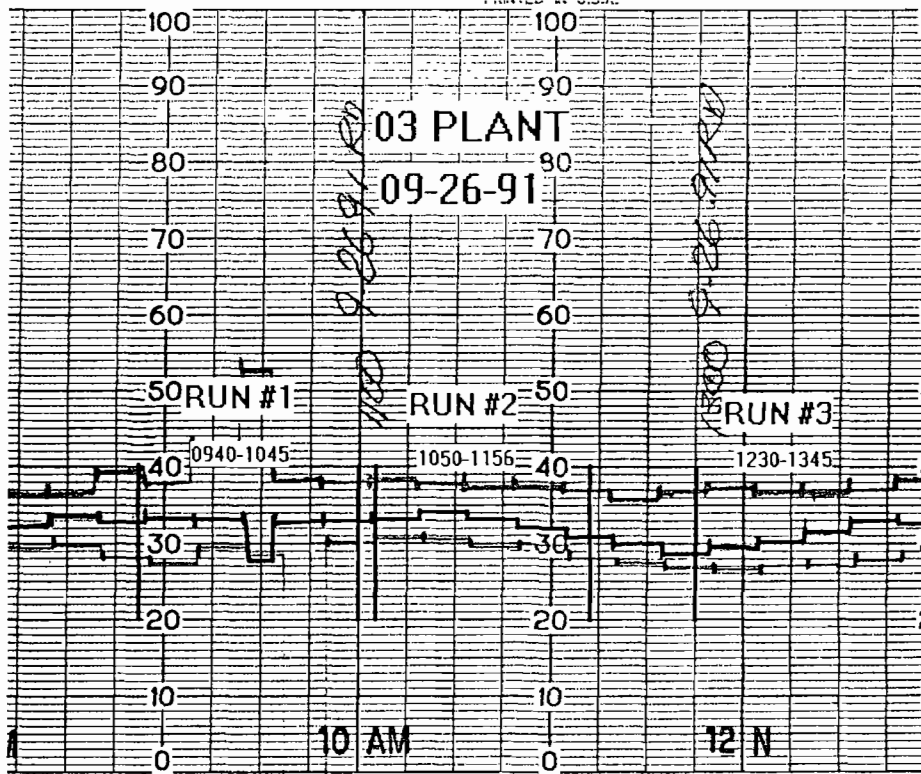
Strip Chart During Test
03 Sulfuric Plant
9/26/91

	Emission test result				Chart result	
	%OO	mg	dscf	lb/ton	ppm	lb/ton
Run 1	5.13	1121	42.59	3.417	322	3.139
Run 2	5.13	1107	42.04	3.419	326	3.178
Run 3	5.28	969	42.03	3.022	309	3.041
			avg:	3.286	avg:	3.119
			std:	0.229	std:	0.071
					Sv:	0.169
					t:	1.209

	Daily Readings			Production	
Time	Temp	ppm	lb/ton	tpd	
1100	1921	341	3.346	2442	test
1900	1935	321	3.117	2090	adj 24hrs
1935	1935	315	3.058		
		avg:	3.174		

SO_2 EMISSIONS REDUCTIONS IN SULFURIC ACID PLANTS

by

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ABSTRACT

The current trend in the sulfuric acid industry is to reduce the emission of sulfur dioxide (SO_2) to the atmosphere while maintaining or increasing acid production.   Utilizing Monsanto cesium-modified catalysts, a number of sulfuric acid producers have effectively reduced their SO_2 emissions in both single absorption and double absorption cases. This paper will present the realized possibilities for the reduction in emissions using Monsanto Cesium Catalyst and the optimization of plant operations utilizing the Monsanto Portable Gas Analysis System (PeGASyS). The portable gas analyzer has served as an invaluable tool to optimize plant operations and demonstrate the advantages of the cesium catalyst in reducing emissions. The utilization of both the Monsanto Cesium Catalyst and the Portable Gas Analysis System in many plant applications will set the new standard for sulfuric converter performance.

INTRODUCTION

The trends in sulfuric acid plant design have changed dramatically over the last several decades. The demand for operations with minimal SO_2 emissions has required the development of the double absorption contact process for SO_2 oxidation which is capable of generating greater than 99.7 % conversion of the sulfur dioxide fed to the plant. Pollution reduction commitments by many major corporations as well as government regulatory requirements are responsible for the continuing trend to develop new and cost effective technologies to further reduce the SO_2 emission levels from sulfuric acid plants.

There are still a large number of sulfuric acid plants in the world which operate in the single absorption mode with SO_2 conversion levels near 98 %. Although these plants are operating within authorized conversion limits, many companies are striving to reduce the SO_2 emissions as much as is technically and economically feasible. Until recently, the technologies to accomplish this goal were limited. Plant operations were "optimized" using crude chemical techniques and often inaccurate temperature measurements, resulting in less than ideal performance in the plants. Over the years, conventional sulfuric acid catalyst improvements have enhanced the plant performance significantly, but further advances were limited by thermodynamic and kinetic barriers.

This paper presents the results of implementing two new technologies in the sulfuric acid industry. Monsanto Enviro-Chem has developed a low temperature cesium-promoted catalyst which eases some of the aforementioned limitations and improves the overall conversion in both single and double absorption plants, resulting in significantly less SO_2 emissions to the stack. A discussion of some case histories of cesium (Cs) catalyst installations and the potential applications of the technology are presented. The second technology developed by Monsanto Enviro-Chem is the Portable Gas Analysis System (PeGASyS) which is used to measure and optimize sulfuric acid plant converter/heat exchanger performance. Using this state-of-the-art instrumentation, plant problems are quickly and easily identified and resolved. Catalyst performance can be quickly determined and optimum operation conditions can be determined based on the catalyst quality and desired conversion results. Examples of the applications of the PeGASyS technology are presented in this paper. When utilized together, the cesium catalyst technology and the PeGASyS system can generate the optimum performance from any sulfuric acid plant and lead to lower SO_2 emissions.

CATALYST DEVELOPMENT AND APPLICATIONS

In the contact sulfuric acid process, there is often an interest in lowering the inlet temperatures to the various adiabatic catalyst beds in order to provide more favorable equilibrium conditions. The addition of cesium (Cs) to the conventional alkali-vanadium sulfuric acid catalyst has long been known to enhance the low temperature properties of the catalyst (1). The cesium salt promoter stabilizes the vanadium +5 oxidation state at temperatures below $420^{O}C$ ($790^{O}F$) and keeps the vanadium species solubilized in the melt and available for reaction. In the conventional K-V catalyst, vanadium compounds precipitate out of the molten salt at lower temperatures, causing loss of catalyst

activity (2,3). The stabilizing effects of the cesium appear at relatively low Cs concentrations. A qualitative display of this effect is shown in Figure 1. At high temperatures (> 430°C/806°F), the activity of the conventional catalyst and the cesium-promoted catalysts are fairly similar. However, near 410°C (770°F), the reaction rate of the conventional catalyst drops off dramatically due to the precipitation of vanadium compounds (curve breakpoint # 1). As the temperature is further lowered (moving to the right on the graph), the cesium-promoted catalyst maintains a higher reaction rate until the temperature drops well below 400°C (750°F) when its activity finally begins to decline due to vanadium salt precipitation (curve breakpoint # 2). Although the reaction rate of the cesium-promoted catalyst drops off at relatively low temperatures, it is still sufficiently high to generate good conversion at acceptable catalyst loadings. Over the last several years, Monsanto Enviro-Chem has utilized its strong base in cesium catalyst studies (4-7) to develop an optimized and affordable cesium promoted catalyst (Cs-120 and Cs-110). These products contain the optimum levels of alkali metal salts (potassium and cesium) to provide excellent *low* and *high* temperature performance in the converter. Following extensive lab development and field testing, the products were commercialized in 1989 and have been installed in over 20 sulfuric acid plants worldwide.

There are many applications for the cesium-promoted catalyst in sulfuric acid plants. The smaller 9.5 mm (3/8 in.) Cs-110 rings can be loaded into the lower beds and allow for lower bed inlet temperatures and higher overall conversion. Figure 2 shows a graphical display of the advantage of using the Cs-110 catalyst in the 4th pass of a single absorption plant. The lower inlet temperature with Cs-110 catalyst opens a larger thermodynamic "window" which permits greater overall conversion. This higher level of conversion is not possible with the conventional catalyst at the lower inlet temperature as the catalyst loadings would have to be extremely high, creating excessive pressure drop. A similar scenario can be devised for the lower beds of double absorption plants, resulting in lower stack emissions.

Another cesium-promoted catalyst application involves installing a 33-50 % cap of Cs-120 rings in the first pass of a sulfuric acid plant. This catalyst configuration will dramatically lower the required inlet temperature for good conversion in this bed. Figure 3 shows that the conversion versus bed depth profile for a capped Cs-120 bed with an inlet temperature of 380°C (715°F). A full bed of conventional catalyst will produce very little conversion with this low inlet temperature at any reasonable catalyst

loading. A full first bed of Cs-120 rings is not required in this application as the outlet temperature from the cesium catalyst portion of the bed is high enough to ignite the remaining conventional catalyst layer. The lower first pass inlet temperature is advantageous for plants with very high inlet SO_2 strength. In this case, the lower inlet temperature will lead to a lower outlet temperature, therefore extending the life of the first pass exit posts and grids. Furthermore, the overall conversion in the first pass will also be increased over that possible with conventional catalyst. The use of the Cs-120 rings in Pass 1 will also reduce or eliminate the need for startup gas pre-heating in spent acid and metallurgical plants following short shutdowns.

The cesium-promoted catalyst can also be utilized in situations where heat exchanger deficiencies (undersized or plugged) limit the inlet temperatures to lower passes. The Cs-110 rings can effectively operate at the reduced temperatures and hence maintain the needed conversion in the lower beds. Also, the Cs-120 first pass caps and the full beds of Cs-110 in the lower passes can greatly reduce the time required to startup the sulfuric acid plant. The cesium catalyst beds will ignite at much lower temperatures than conventional catalyst beds and hence require less pre-heating. Also, due to the high activity at low temperatures, the cesium catalyst beds help to minimize the stack SO_2 emissions during plant startup operations. Examples of many of these cesium catalyst applications are presented in subsequent sections.

Cs-110/Cs-120 CATALYST APPLICATIONS

The applications of the Cs-110 and Cs-120 catalysts in reducing SO_2 emissions will be presented as a series of case histories. Although the applications vary from plant to plant, the common threads in each case are lower stack emissions and improved operating versatility. The following are five examples of Monsanto cesium promoted catalyst performance: (Note: STPD = Short Tons acid produced Per Day)

Case 1: *Single Absorption Spent Acid Plant*

Pre-Cs Data:

(1) Conventional catalyst in Pass 4.
(2) Pass 4 operating at 430°C (806°F) inlet temperature.
(3) Conversion at 98.0 % with 9 % SO_2 feed gas.
(4) Stack SO_2 emissions were over 25 lbs./STPD.

Post-Cs Information:

(1) Installed full bed of Cs-110 ring in Pass 4.
(2) Pass 4 inlet temperature optimized at 410°C (770°F).
(3) Conversion measured at 98.5 % with 9 % SO_2 fed.
(4) Stack SO_2 emissions at 19 lbs./STPD (24 % reduction).

Case 2: *Single Absorption Sulfur Burning Plant*

Pre-Cs Data:

(1) Aging, conventional catalyst in all beds.
(2) Pass 4 operating at 427°C (800°F) inlet temperature.
(3) Conversion at 97.5 % with 8 % SO_2 feed gas.
(4) Stack SO_2 emissions at 33 lbs./STPD.

Post-Cs Information:

(1) Screened all beds; full fourth pass of Cs-110.
(2) Pass 4 operating at 395-405°C (743-760°F).
(3) Conversion measured at 98.4 % with 8 % SO_2 fed.
(4) Stack SO_2 emissions at 21 lbs./STPD (36 % reduction).

Case 3: *Single Absorption Sulfur Burning Plant*

Pre-Cs Data:

(1) Used conventional catalyst in all five passes.
(2) Pass 5 operating near 430°C (806°F) inlet temp.
(3) Conversion at 98 % (air dilution plant).
(4) Stack SO_2 emissions at 26 lbs./STPD.

Post-Cs Information:

(1) Fresh catalyst in all beds; Cs-110 in Passes 4 and 5.
(2) Passes 4 and 5 operating at 410°C (770°F) inlet temp.
(3) Conversion reaches *99.1* % with 8 % SO_2 fed.
(4) Stack SO_2 emissions at 12 lbs./STPD *(50 % reduction)*.

Case 4: *Double Absorption Spent Acid Plant*

Pre-Cs Data:

(1) Standard catalyst in all beds; 12 % SO_2 gas strength.
(2) Pass 1 at 405°C (760°F); Pass 3 at 400°C (750°F).
(3) Heat exchanger pluggage limited Pass 3 inlet temp.
(4) Pre-heater required, especially after short shutdowns.
(5) Rate reduced to stay with SO_2 stack requirements.

Post-Cs Information:

(1) Cs-120 cap in Pass 1; full 3rd bed of Cs-110 rings.
(2) Pass 1 inlet at 360°C (680°F); outlet at 600°C (1110°F).
(3) Pass 3 operating well at 400°C (750°F).
(4) Need for pre-heater virtually eliminated.
(5) Rate dramatically increased with low SO_2 emissions.

Case 5: *Double Absorption Spent Acid Plant*

Pre-Cs Data:

(1) Used conventional catalyst in all beds; 7 % SO_2 fed.
(2) Pass 3 inlet at 410°C (770°F); heat exchange limits.
(3) Pass 4 inlet at 390°C (735°F) due to low 3rd pass temp.
(4) Emissions high (especially at startup);rate limited.

Post-Cs Information:

(1) Installed full bed of Cs-110 rings in Pass 3.
(2) Pass 3 operating very well at 410°C (770°F) inlet.
(3) Pass 4 operating very well at 425°C (800°F) inlet.
(4) Very low startup emissions; production rate increased; no gas pre-heating required after short shutdown.

Several other applications for the cesium promoted catalyst are under consideration. Scenarios have been developed for increasing the acid production rates for double absorption plants and yet maintaining the same permitted hourly SO_2 emissions. Using Cs-110 rings in the bottom pass of double absorption plants, it is possible to reduce the lbs. SO_2 per ton of acid and hence allowing for greater production at the same SO_2 ppm level in the stack.

In order to take advantage of the benefits of the cesium-promoted Cs-120 and Cs-110 catalysts, there are some considerations that need to be evaluated prior to installation. Firstly, the heat exchange capacity in the plant must be evaluated in order to insure the feasibility of reaching the lower inlet temperatures required

for the cesium catalyst beds. Secondly, there may be a greater tendency for pressure drop buildup in first passes equipped with cesium catalyst caps if the incoming gas stream is very dust-laden or contains acid mist. The highly active cesium-promoted catalyst has a more mobile molten salt than that of the conventional catalyst, which has a slightly greater tendency for accumulating incoming converter dust. The larger Cs-120 rings (12.5 mm, 1/2 in.) were developed to minimize the potential pressure drop buildup and yet maintain the required performance. The low temperature benefits of the Cs-120 rings in the first pass must be weighed against the slight possibility of higher pressure drop. Cs-110 applications in all other passes have been in operation for over two years without any indication of pressure drop buildup and/or loss of activity.

Overall, the use of the cesium-promoted catalyst in sulfuric acid converters has contributed to the significant reduction in SO_2 emissions and improved operability of the acid plants.

PORTABLE GAS ANALYSIS SYSTEM (*PeGASyS*)

The Monsanto Enviro-Chem Portable Gas Analysis System was developed several years ago to provide sulfuric acid producers with the means to fully characterize their plant operations. The PeGASyS system consists of a highly specialized gas sampling system and the state-of-the-art gas analyzer. Figure 4 shows a photograph of a portion of the gas analyzer system, including the specially design gas syringe. The analyzer is generally set up near a control room or laboratory and occupies a desk-sized space. A gas sample is taken from a slip stream of gas at the converter, heat exchanger, or absorbing tower pressure tap (or any available sampling port). The gas sample is then injected into the analyzer (state-of-the-art gas chromatograph) which accurately determines the SO_2 and O_2 levels. The PeGASyS method for characterizing the sulfuric acid plant operations is much more reliable and accurate than the standard wet chemical Reich test method. A typical sulfur burning plant can be completely analyzed in only a few hours with the PeGASyS system.

The results obtained with the PeGASyS system consist of an analysis report of the SO_2 and O_2 levels in each sample and a conversion calculation for each specific converter sample based on the inlet gas to the first bed. Figure 5 shows a typical Converter Performance Summary for a sulfur burning double absorption plant. The custom PeGASyS software also calculates gas flow rates based on the given production

rates.   Utilizing   the PeGASyS data,   the converter
performance can be effectively simulated using the Monsanto
Enviro-Chem proprietary modeling software. This information
can then be used to optimize the plant operations, adjusting
bed   inlet   temperatures,   upgrading   catalyst charges to
maximize conversion and minimize SO_2 emissions.

Another important application of the PeGASyS system is in
gas-gas heat exchanger leak detection.   The exchanger must
have shell side and tube side gas streams which contain
different SO_2 levelsin   order for the analysis   to be
effective.   Figure 6 shows the typical output for a heat
exchanger analysis.   Often, leaking   heat   exchangers
contribute to high SO_2 emissions by bleeding high SO_2 gas
directly to the stack or flooding lower pass catalyst beds
with SO_2-rich gas. Once the leaking exchanger is identified,
it can be repaired, leading to a direct reduction in the
stack emissions.

The following are case histories of typical applications of
the PeGASyS service to reducing stack emissions:

Case 1: *Spent Acid Double Absorption Plant*

    Issue: SO_2 emissions higher than expected.

    Result: PeGASyS analysis indicated that the aging first
              pass was operating at a reduced efficiency.
              Replacement of the first pass resulted in
              significant reduction in stack emissions.

Case 2: *Sulfur Burning Double Absorption Plant*

    Issue: SO_2 emissions were approaching permitted limit.

    Result: PeGASyS analysis indicated a severe leak in the
              cold heat exchanger. Following exchanger
              repair, SO_2 emissions decreased from 3.9 lbs./
              STPD to 2.0 lbs./STPD.

Case 3: *Sulfur Burning Single Absorption Plant*

    Issue: - Emissions extremely high; poor conversion.

    Result: PeGASyS analysis determined that Passes 2 and 3
              were performing very poorly. It was determined
              that low bed inlet temperatures were
              responsible. Raising the temperatures led to
              a dramatic reduction in SO_2 emissions. The
              results also indicated that a 4th pass Cs-110

application was justified. With a full 4th
pass of Cs-110 rings, this plant now has
extremely low SO_2 emissions.

Case 4: *Spent Acid Double Absorption Plant*

Issue: SO_2 emissions approaching allowed limit.

Result: PeGASyS analysis of the cold heat exchanger
identified a minute leak which was allowing
some first pass feed gas to bypass directly
to the final tower. This leak added over 200
ppm SO_2 to the stack. Repairs to this
exchanger resolved the problem.

As can be seen from these examples, the Portable Gas Analysis
System is an extremely effective tool for optimizing sulfuric
plant operations and reducing stack SO_2 emissions. In a
number of cases, the PeGASyS results have led to the
installation of Monsanto cesium-promoted catalyst which
resulted in the best overall conversion and the lowest level
of sulfur dioxide escaping to the atmosphere.

CONCLUSIONS

The effectiveness of the Monsanto Enviro-Chem cesium-promoted
catalysts (Cs-120 and Cs-110 rings) in improving sulfur
dioxide conversion and reducing stack emissions has been
demonstrated in a number of applications. The cesium
catalyst can be applied in a variety of situations which can
reduce emissions as well as enhance the versatility of the
plant operations. In many situations, the catalyst can be
used to reduce the impact of heat exchanger limitations.
Cesium catalyst effectiveness in both single absorption and
double absorption plants has been demonstrated and novel
applications are still under development.

The Monsanto Enviro-Chem Portable Gas Analysis System
(PeGASyS) has effectively been used in a variety of plants to
optimize converter performance and identify problem areas.
The results of the gas analyses are often used to identify
the most effective applications of the Monsanto Cesium
Catalyst in order to minimize SO_2 emissions and maximize
converter performance. The use of these products and
services allows for not only a positive impact on the
environment but also improved performance and profitability
for the sulfuric acid producer.

ACKNOWLEDGMENTS

REFERENCES

(1) Tandy, G. H., *J. Appl. Chem.* **6**, 68 (1956) and the references therein.

(2) Villadsen, J., and Livbjerg, H., *Catal. Rev. Sci. Eng.*, **17**, 203 (1978).

(3) Boghosian, S., Fehrmann, R., Bjerrum, N. J., and Papatheodorou, G. N., *J. Catalysis* **119**, 121 (1989).

(4) Villadsen, J., *U. S. Patent No. 4,193,894* (3/18/80) (assigned to Monsanto Company).

(5) Doering, F. J. and Berkel, D. A., *J. Catalysis* **103**, 126 (1987).

(6) Doering, F. J., Yuen, H. K., Berger, P. A., and Unland, M. L., *J. Catalysis* **104**, 186 (1987).

(7) Doering, F. J., Unland, M. L., and Berkel, D. A., *Chem. Eng. Sci.* **43**, 221 (1988).

Figure 1

SO$_2$ OXIDATION RATE VERSUS TEMPERATURE

In RATE

1/T (K^{-1})
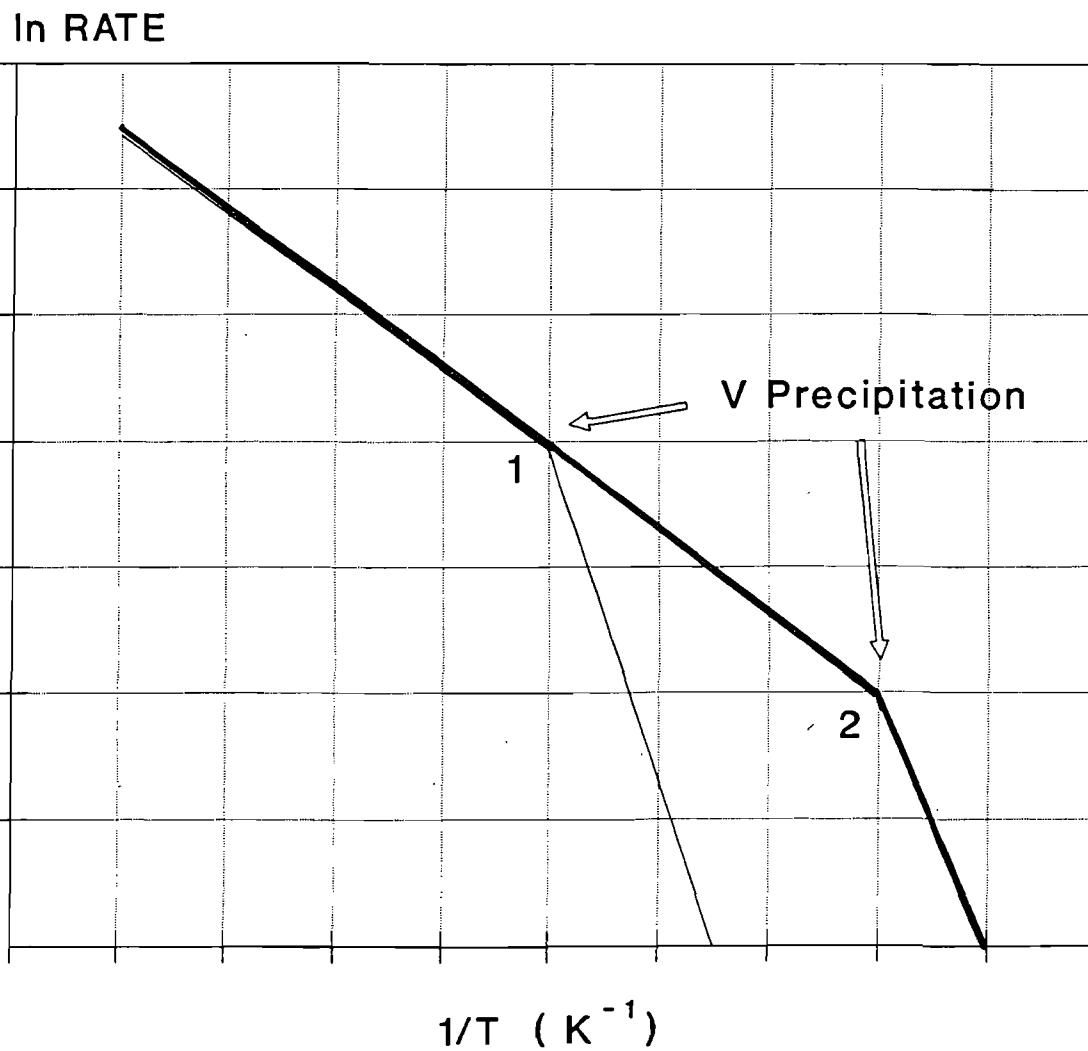
CATALYSTS:

——— CONVENTIONAL   ▬▬▬ CESIUM-PROMOTED

Figure 2

SINGLE ABSORPTION: Cs ADVANTAGE

% SO$_2$ CONVERSION

EQUILIBRIUM CURVE

1300 ppm

Min. 1460 ppm

1620 ppm

TEMPERATURE (^{o}C)
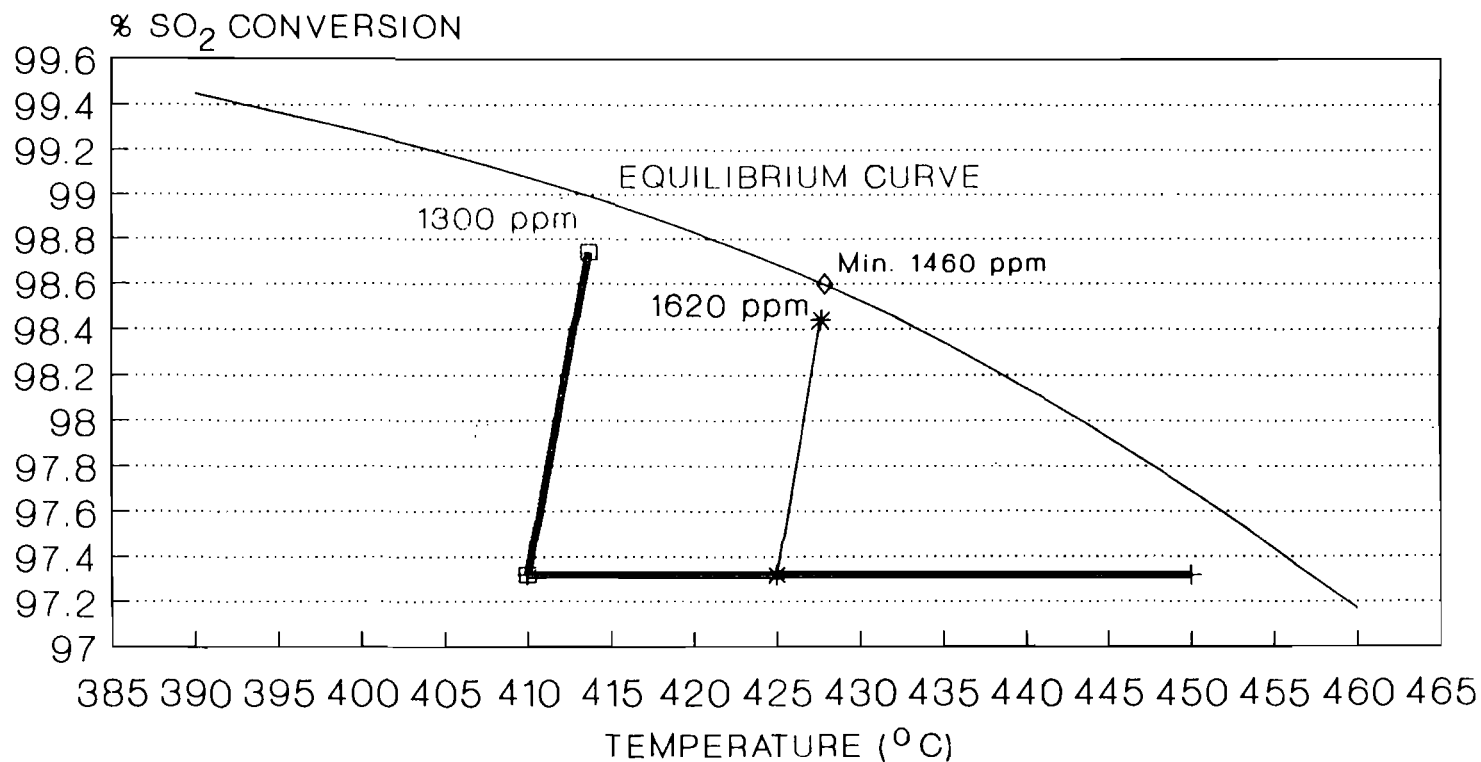
4th PASS CATALYST:

—*— LP-110   —▫— Cs-110

FEED GAS = 9 % SO$_2$, 11.9 % O$_2$
410°C = 770°F;   425°C = 797°F

Figure 3

FIRST PASS: CAPPED Cs-120 BED
SULFUR BURNING; T(INLET)= 380°C/715°F

% SULFUR DIOXIDE CONVERSION

BED DEPTH (INCHES)
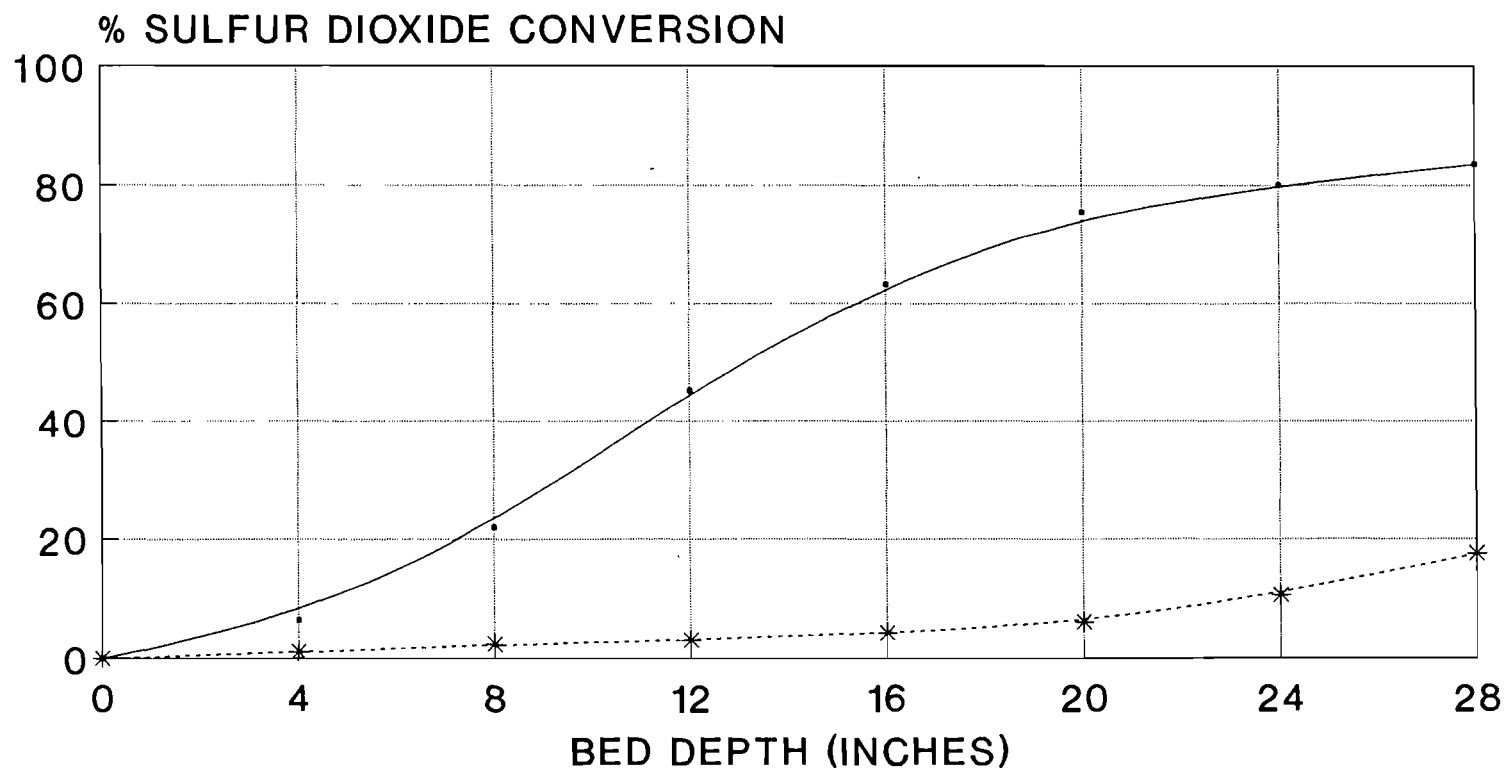
CATALYST:

—•— 8 IN. Cs CAP/LP-120   ···*··· STANDARD CATALYST

8 IN. Cs-120 CAP ON LP-120 RINGS

Figure 4

PeGASyS
Portable Gas Analysis System

Monsanto Enviro-Chem Systems, Inc.

Figure 5

MONSANTO ENVIRO-CHEM SYSTEMS, INC.
CONVERTER PERFORMANCE SUMMARY

CUSTOMER NAME: EXAMPLE 3   DATA FILE: XXX003.SAM

PLANT LOCATION: U. S. A.

PLANT NUMBER: 3

PLANT TYPE: SULFUR BURNER   DOUBLE ABSORPTION

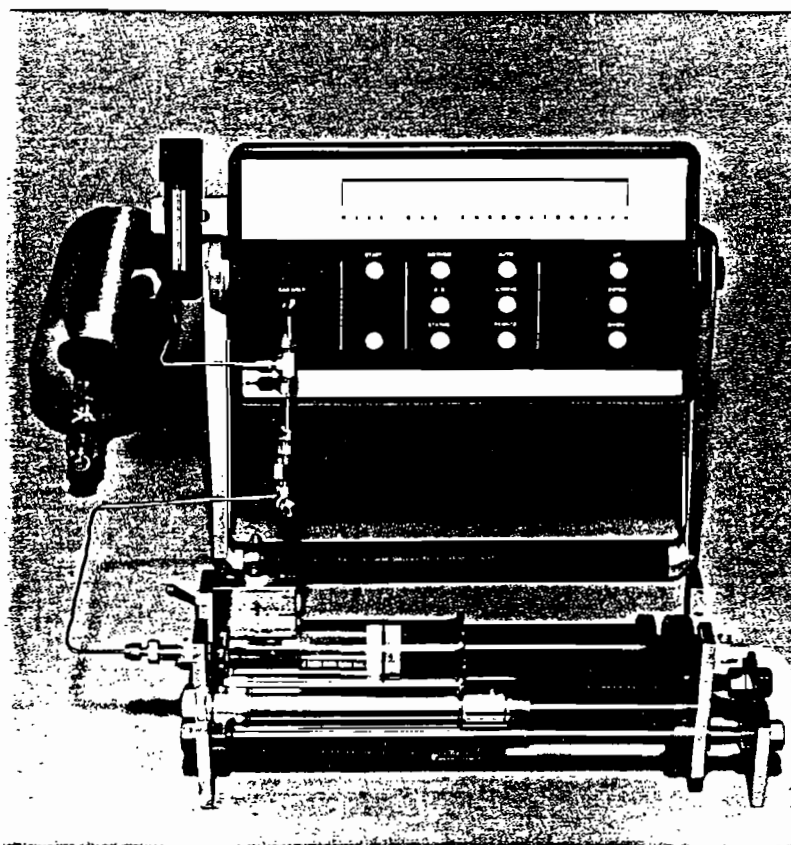| SAMPLE NO.	SAMPLE IDENTIFICATION	DATE / TIME OF SAMPLE		% SO_2	% O_2	% CONV.
5	SULFUR BURNER OUTLET	4-1-91	1600	11.209	9.506	1.563
4	FIRST PASS OUTLET	4-1-91	1600	5.135	6.998	59.394
3	SECOND PASS OUTLET	4-1-91	1600	2.088	5.638	84.269
2	THIRD PASS OUTLET	4-1-91	1600	0.911	5.144	93.257
1	FOURTH PASS OUTLET	4-1-91	1600	0.035	4.771	99.744
	SULFUR BURNER GAS			11.366	9.580	

SAMPLE NO.	SAMPLING POINT
1	OUTLET OF FINAL TOWER ABOVE MIST ELIM.
2	PASS 4 INLET AT CONVERTER TAP
3	PASS 3 INLET AT CONVERTER TAP
4	PASS 2 INLET AT CONVERTER TAP
5	PASS 1 INLET AT CONVERTER TAP

```
X X X X X X X X X X X X X X X X X X X X X X X X X X X X X X X X X X X X X X X
X                                              X                             X
X                    KG/HR.     LBS./HR.       X     CATALYST BED            X
X                  -----------------------     X     TEMPERATURES            X
X  SULFUR FEED RATE  26054.80   57441.31       X     ------------           X
X  SO2 EMISSIONS       133.04     293.30       X L/STPD  BED   °F    °C      X
X                                              X ------  ---    -     -      X
X  LBS.SO2/TON =  3.35  KG SO2/TON =  1.67     X         1 IN   779   415    X
X                                              X  31.5   1 OUT 1130   610    X
X                    NM3/HR       SCFM         X         RISE   351   195    X
X                  -----------------------     X         2 IN   824   440    X
X  AIR TO SULFUR BURNER 160139.22  94243.89    X  33.0   2 OUT  988   531    X
X  CONVERTER INLET GAS  160139.22  94243.89    X         RISE   164    91    X
X  CONVERTER OUTLET GAS 132907.50  78217.69    X         3 IN   831   444    X
X  DILUTION AIR              0.00      0.00    X  38.5   3 OUT  891   477    X
X  TOTAL GAS TO PLANT   160139.22  94243.89    X         RISE    60    33    X
X                                              X         4 IN   795   424    X
X  PRODUCTION RATE = 2100.00 SHORT TONS PER DAY X 50.5  4 OUT  844   451    X
X                                              X         RISE    49    27    X
X                                              X         5 IN                X
X                                              X         5 OUT               X
X  NOTE: ALL GAS VOLUMES ARE BASED ON          X         RISE               X
X        DRY, SO3-FREE GAS.                    X                            X
X                                              X     TOTAL R  624   346     X
X                                              X                            X
X X X X X X X X X X X X X X X X X X X X X X X X X X X X X X X X X X X X X X X
```

Figure 6

MONSANTO ENVIRO-CHEM SYSTEMS, INC.

HEAT EXCHANGER EVALUATION

DATE / TIME: 4-1-91 / 1500   FILE: INTHEX.HEX

CUSTOMER: EXAMPLE

PLANT LOCATION: U. S. A.

PLANT NUMBER: 1

PLANT TYPE: METALLURGICAL; SINGLE ABSORPTION

HEAT EXCHANGER: INTERMEDIATE HEX

```
                     ┌─────────────────┐
                     │                 │  <=====   0.237 % SO2
                     │   LOW PRESS.    │          12.750 % O2
                     │  - - - - - - -  │
                     │  │  │  │  │  │  │
                     │  │  │  │  │  │  │
 6.400 % SO2  <===== │  │  │  │  │  │  │  <=====   6.400 % SO2
14.660 % O2          │  │  │  │  │  │  │          14.660 % O2
                     │  │  │  │  │  │  │
                     │  - - - - - - -  │
 0.356 % SO2  <===== │                 │
12.801 % O2          └─────────────────┘
```
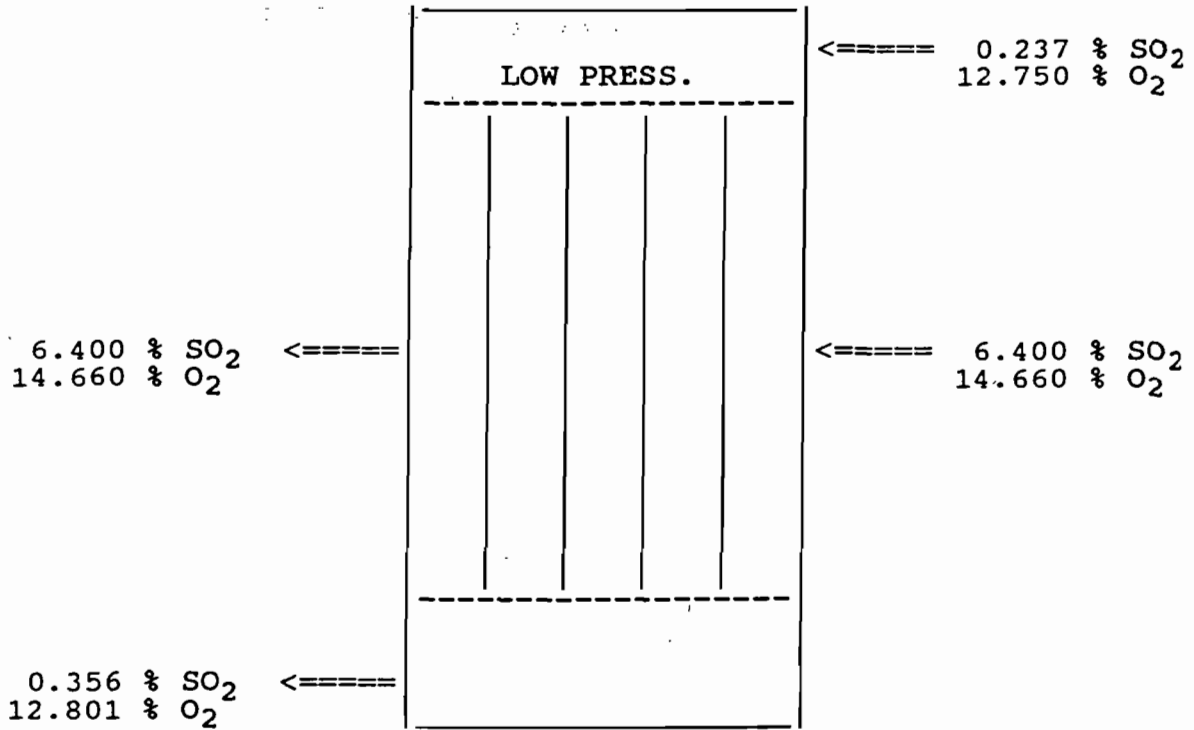
     2.0 % OF SHELL SIDE GAS IS LEAKING INTO TUBE SIDE

TUBE SIDE INLET GAS WAS SAMPLED AT:
INLET TO INTERMEDIATE HEX

TUBE SIDE OUTLET GAS WAS SAMPLED AT:
PASS 4 INLET AT CONVERTER

Comparison of Sulfuric Acid Plant Catalysts

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Introduction

The contact process for the production of sulfuric acid is based on the oxidation of sulfur dioxide to sulfur trioxide in the presence of a vanadium catalyst. From its beginnings in 1831 when Phillips of Bristol, England patented the oxidation of SO2 to SO3 over a platinum catalyst, to the modern plants of today using high activity, low pressure drop, ribbed rings of vanadium catalyst, the contact process and the catalyst it is based on have undergone significant (but subtle) changes, with the vast majority of developments in the last thirty years.

This paper will review the basic principals of the catalytic sulfuric acid process, and using a summary of operating data compare the three catalysts normally used in North America in the areas of conversion efficiency, activity, ignition temperature, loss in activity over time and screening losses. The paper will also review the advantages and problems with extensive plant converter testing using gas chromatography, Reich or other test methods.

Background

Before 1900, essentially all sulfuric acid was produced by the "Chamber" process, where nitrogen oxides were used to catalyze the oxidation of sulfur dioxide to sulfur trioxide. Plant size was small, unusually less than 50 STPD, and product acid strength limited to 65% to 75% sulfuric acid. The development of the chemical (dye) industry and the need for gun powder in the late 1800's necessitated a process to produce high strength sulfuric acid and Oleum. Early work (1870's - 1910) based on platinum as a solid catalyst, usually as platinum impregnated asbestos gauze, was the first technical and economic application of the "Contact" process. The high cost of platinum and its susceptibility to poisoning by many materials (notably arsenic present in the roaster gas streams of the day), led to the development of vanadium pentoxide based catalysts using alkali metal prompters on a porous silica carrier in the early 1900's (BASF patent of 1913). This is essentially the vanadium based catalyst used today. The following table shows the transition from the Chamber to Contact process:

Transition to the Contact Process

		1910	1930	1950	1960	1980
Contact Process	%	20	27	75	85	100
Chamber Process	%	80	73	25	15	0

Vanadium Catalyst

Vanadium catalyst usually contains 6% - 9% vanadium pentoxide with alkali metal promoters. The promoters are potassium sulfate with an atomic ratio of potassium to vanadium of 2 - 4 and a small amount of sodium sulfate to adjust (lower) the eutectic melt temperature of the mixture. The active components are supported on a highly porous silica base (diatomaceous earth).

In 1948 Topsoe & Nielsen demonstrated catalyst at operating temperatures exists as a melt within the pores of the silica support. The melt consists of vanadium sulfur complexes dissolved in pyrosulfates. In other words, the oxidation of sulfur dioxide to sulfur trioxide is a homogeneous reaction in the liquid film covering the surfaces of the support and not the heterogeneous reaction it would appear to be. The activity of the catalyst is from active species of vanadium pentoxide (V_2O_5), with the mechanism involving changes in the valence of vanadium.

The reaction rate is the result of many factors, including; the solubility of SO_2, SO_3 and oxygen in the melt, mass transfer limitations, the concentration of the active catalyst components and their solubility's in the melt, the porosity and pore size distribution of the silica support, as well as other less obvious factors (manufacturing process, etc.). The effect and interaction of each variable is not completely defined, so changes leading to improvements are more by trial and error than science. The difference between conversion predicted by rate equations and conversion actually obtained is accounted for by adding a so called "catalyst effectiveness factor" or fudge factor to the rate equation. The reaction rate can be described by the following relationship:

$$r = k\,[p(SO_2)^l\,p(O_2)^m\,p(SO_3)^n]\;K_{act}\;K_{eff}$$

r = reaction rate - g mole SO_2/g catalyst, sec
k = rate constant - function on catalyst properties
$p()^x$ = partial pressure of components
K_{act} = adjustment factor for catalyst activity
K_{eff} = adjustment factor for system unknowns

The acknowledgment of the reaction taking place in the liquid melt leads to an understanding of catalyst ignition temperature as the temperature at which the melt first forms. The decrease in activity at low temperature is explained by the precipitation of some of the vanadium

compounds reducing the concentration of the vanadium in the melt. The loss in catalyst activity at high temperature is attributed to the melt exceeding the capacity of the catalyst pores, with the liquid melt forming large inactive globules. The "old wives tale" of catalyst having a memory - once operated at high temperature, it must always be operated at high temperature - is explained by the loss in activity from melt components flowing out of the catalyst.

Sulfur dioxide to sulfur trioxide equilibrium is determined by the following equation:

$$Kp = \frac{p(SO3)}{p(SO2)\,p(O2)^{.5}}$$

A typical equilibrium curve showing operating lines for a four bed single or double absorption system is shown in Figure 1. The figure shows the change in the equilibrium curve resulting from the removal of SO3 in the interstage absorber (upper equilibrium line), and the reason the double absorption process increases conversion of SO2 to SO3 from 98.5% to 99.7%.

A review of the equilibrium equation indicates increasing pressure will increase equilibrium conversion. Figure 2 shows the effect of increasing pressure. In the example shown, increasing pressure from 1.3 bar (3.8 psi) to 10 bar (127 psi) will increase equilibrium conversion in a first catalyst stage from 63% to 75%. In the late 1960's, I did extensive work developing and evaluating a pressure process for sulfuric acid production - looking at single absorption at pressure versus double absorption. The conclusion of that work indicated double absorption could not be avoided at reasonable pressures to meet 99.7% conversion, eliminating the pressure process from economic consideration. In the mid 1970's, Krebs built a plant at PCUK in France based on the pressure process. The plant was a double absorption unit operating at 70 psi. Analysis indicated capital cost savings compared to the conventional double absorption route to be small (< 10%), with the plant experiencing extremely high corrosion and low energy efficiency.

Another route to increased conversion is to increase the oxygen concentration in the converter gas by using enriched air or pure oxygen. Analysis indicates improved conversion efficiency, but not enough to eliminate double absorption. A process using pure oxygen was evaluated in the late 1960's as an alternate to double absorption. The system was not economically sound due to the continuing cost of oxygen. No plants based on pure oxygen have been built. A number of spent acid regeneration plants use enriched air to overcome capacity limitations in the gas cleaning sections of the plant, and oxygen use to enrich the gas in the contact section is being used in a few places. The cost is a balance of the need for additional capacity versus the continuing cost of oxygen.

Catalyst Shape and Composition

In the 1960's and early 1970's catalyst was in the form of pellets, usually 1/4" and 5/32" diameter by 0.3" to 0.6" long (6 mm & 4 mm diameter by 8 mm - 15 mm long). The catalyst normally contained 6% to 8% V2O5, and was sold in North America by many vendors:

Stauffer   Allied
Cyanamid   Monsanto
BASF   Topsoe
Catalyst & Chemicals   Imperial Smelting

In the mid to late 1970's lower pressure drop through the catalyst bed was achieved by the use of a larger diameter pellet, 8 mm in diameter or 5/16" rather than 6 mm diameter. This size pellet was heavily promoted by Monsanto as 516 catalyst. At about the same time Topsoe introduced the ring shape catalyst to the North American market. Topsoe claimed significantly lower pressure drop and greater dust holding capacity. Initial installations used ring catalyst to top off the pellets in the first catalyst bed. Data showed lower initial pressure drop, and lower rate of pressure drop build-up (greater dust holding capacity). Complete first beds of ring catalyst showed acceptable activity and conversion while maintaining the low pressure drop and pressure drop build-up. Ring catalyst allowed an increase in operating time between turnarounds from 12 months to 18 - 24 months. It took a number of years for ring catalyst to be accepted and used in the entire converter. Now the three principal catalyst suppliers to North America (Topsoe, BASF, Monsanto) all offer ring shaped catalyst - with pellet and 516 catalyst essentially obsolete. The most recent change in catalyst shape has been the ribbed ring, offered by Topsoe as "Daisy" and BASF as "Star" rings, providing about 20% lower pressure drop than the normal 10 mm rings.

In addition to catalyst shape changes, in the last twenty years catalyst composition changes have provided improved performance permitting 99.7% conversion in a double absorption plant with increasing SO2 gas strengths (9.5% - 10% in the 1970's to 11.5% - 11.75% today). A catalyst with 6% - 8% V2O5 is used in the first and second beds of the converter to attain resistance to activity loss at high temperature and maintain high temperature strength (reduced screening loss). The lower vanadium content - lower activity is offset by the higher average operating temperature of the upper beds, resulting in a high reaction rate and acceptable catalyst loading and approach to equilibrium. A catalyst with 7% to 9% V2O5 is used in the third and fourth catalyst beds to provide higher activity, lower ignition temperature and high reaction rate at the lower average operating temperature. The higher vanadium, lower bed catalyst has 10% to 20% greater activity than the 6% - 8% V2O5 upper bed catalyst.

The most recent catalyst development (re-invention of a 1948 discovery) is the so called "Cesium Catalyst". Cesium catalyst is really a 6% - 8% V2O5 catalyst with the formulation adjusted by substituting cesium for a portion of the potassium promoter. The use of cesium doubles the activity of the catalyst in the low temperature region, permitting continuous operation at bed inlet temperatures in the 720 F - 730 F region. The high cost of cesium promoted catalyst (about 2.5 times standard catalyst) limits its use to special applications.

The various catalyst shapes are shown in Figures 3 and 4. The following tables compare catalyst size and composition.

Shape

		Pellet	Pellet	Ring	Ribbed Ring
Diameter	mm	6	8	10	12
Length	mm	8	12 - 15	9 - 14	10
Pressure Drop	"H2O	1.0	0.9 - 0.95	0.5	0.4

Composition

	V2O5 Content	Comments
Upper Bed Catalyst	6% to 8%	High Temperature Operation Hardness & Temperature Resistance
Lower Bed Catalyst	7% to 9%	Low Temperature Operation High Activity - Softer Catalyst
Cesium Catalyst	6% to 8%	High Activity at Low Temperature (720 F) Can be Sticky at High Temperature

Catalyst Operation Analysis

Over the last ten years Acid Engineering & Consulting, Inc. has been involved with the operation of over one-hundred sulfuric acid plants around the world. In many cases data collected included information on various catalysts, including conversion efficiency, ignition temperature, loss in activity, screening loss, pressure drop and pressure drop build-up. A statistical analysis was performed on the data and the resulting observations are presented below. The analysis was made for the three main North America catalyst suppliers, Topsoe, BASF, and Monsanto, identified as supplier "A", "B", and "C". Note: If the analysis is on target, acid plant operators should be able to connect the supplier with their performance data.

Conversion Efficiency - The data suggests little significant difference in overall conversion efficiency between the three suppliers. Conversion efficiency analysis was complicated by many operating plants with more than one manufacturers catalyst in the converter, and many with two or three suppliers catalyst in a particular bed. Although there was some statistical difference, one could not use the conversion efficiency difference to tell which catalyst was in a particular converter.

Loss in Activity - The reduction in activity of a particular catalyst over time was determined by a review of catalyst suppliers activity test results and operating data showing changes in bed inlet and exit temperatures and conversions over time. The results were based on plants operating with high converter inlet SO2 concentrations resulting in bed 1 exit temperatures of 1140 F to 1160 F. The table below summarizes the activity loss over an 18 month to 24 month period for ring catalyst.

Loss in Activity (18 - 24 Months)

	Supplier "A"	Supplier "B"	Supplier "C"
Bed 1	20% - 35%	9% - 12%	9% - 13%
Bed 2	8% - 12%	5% - 8%	5% - 8%
Bed 3	< 5%	< 5%	< 5%
Bed 4	< 5%	< 5%	< 5%

The data indicates supplier "A" upper bed catalyst looses activity at a significantly higher rate than the others, about 2 to 3 times the activity loss between turnarounds. This would suggest a formulation problem resulting in the melt solution leaving the pores of the catalyst when operating at high temperature. The data is consistent over many years, eliminating the possibility of a bad batch or run of catalyst causing the results. In fact, for many years this supplier recommended limiting first bed exit temperature to less than 1125 F.

Screening Loss - Data for screening loss was based on ring catalyst, vacuum screened per suppliers instructions, usually by the same two commercial catalyst screening companies. The wide variation in the data for a particular supplier is attributed to operating time at high temperature, screening rate and the amount of broken pieces returned to the converter.

Screening Loss (% of Bed)

	Supplier "A"	Supplier "B"	Supplier "C"
Bed 1	25% - 40%	10% - 15%	11% - 16%
Bed 2	20% - 30%	9% - 15%	10% - 15%
Bed 3	15% - 20%	8% - 14%	8% - 14%
Bed 4	12% - 17%	8% - 12%	8% - 12%

The data is consistent, indicating a problem with supplier "A" catalyst, especially in the high temperature area, suggesting a formulation problem (high screening loss and loss in activity). The data is from many plants over a number of years with more data points for beds 1 and 2, and limited data for beds 3 and 4.

Pressure Drop Build-up -   Data for sulfur burning plants was analyzed to determine differences in the rate of pressure drop build-up over an 18 month operating period between turnarounds. The analysis was complicated by unknown variations in the ash content of the sulfur and the amount of broken pieces returned to the converter after screening. After some

adjustment for bed area, gas velocity, etc., the data indicated no significant difference in the rate of pressure drop build-up between the three catalysts.

Comparison Summary

Overall the catalyst comparison indicates supplier "A" has a problem with its upper bed ring catalyst when operated at high gas strength - high temperature (exit temperatures above 1130 F), resulting in excessive loss of activity over time and screening losses two to three times the others. In fact, the high screening loss and subsequent make-up with fresh catalyst obscures the activity loss problem, so overall plant conversion efficiency is maintained. Based on the analysis, supplier "B" and "C" catalyst are close in all aspects studied, with supplier "A" upper bed catalyst of lower overall performance.

Cesium Promoted Catalyst

Cesium promoted catalyst is offered by the three North American suppliers. The high cost, about 2.5 - 3 times conventional catalyst, has limited use to special situations. Cesium catalyst is rarely used in sulfur burning plants, but has found some advantages in spent acid regeneration and metallurgical plants. The catalyst has been used as a top layer of the first catalyst bed to provide operation at 720 F - 730 F, reducing gas heat exchanger requirements, while allowing restart of the plant when the catalyst bed is at 600 F.

Early installations of cesium promoted catalyst experienced severe pressure drop build-up. Pressure drop in some plants increased 30" to 60" H2O in a few months. Investigation indicated the plants experiencing the problem were operating at first bed inlet temperature of 780 F to 820 F, while plants without problems operated at 720 F to 740 F. The operating data indicates the cesium catalyst becomes very sticky at elevated temperatures. Recently, Topsoe has reformulated their cesium catalyst so it can be operated at low or high temperature without the pressure drop build-up problem. The other suppliers are expected to produce an adjusted formulation in the near future.

Converter Testing

Traditionally catalyst performance evaluations are made by reviewing bed inlet temperatures and temperature rise, inlet SO_2 gas strength and overall conversion efficiency. Changes in these operating variables, although small from day to day, are good indicators of catalyst bed performance over time. Recently, one catalyst supplier has offered portable gas chromatograph testing of converter systems. The tests provide the composition of gas into and out of each catalyst bed. Comparing actual bed conversion with calculated conversion and equilibrium would be a superior way of determining catalyst activity - performance.

Acid Engineering & Consulting, Inc. has reviewed the results of a number of gas chromatograph tests of converter systems. In most cases, the test data was consistent with evaluations based on traditional methods, and was a useful tool in determining catalyst activity - replacement requirements for an upcoming turnaround. In a number of cases, the test results were obviously incorrect and the interpretation of the results flawed and self-serving. Objectivity comes into question when the one doing the testing is selling catalyst or testing his own catalyst to show how good it is, or how bad a competitors is. In one case, the test data indicated 7% to 8% conversion of SO_2 to SO_3 in the sulfur furnace - well above equilibrium. This was coupled with extremely low conversion in the first catalyst bed, indicating low catalyst activity and the need for additional replacement catalyst. In another case, a spent acid regeneration plant was experiencing conversion efficiency problems (very low first bed temperature rise) after a major plant modification. The catalyst in the first bed was changed, but the same problem persisted. Gas chromatograph tests (purchased with the replacement bed of catalyst) were run at various O_2/SO_2 ratios (0.72 to 0.92) and SO_2 gas strengths (9.4% - 10.7%). Note: Most sulfur burning plants operate at O_2/SO_2 ratios of 0.75 to 0.77 and SO_2 gas strengths of 11.5% - 11.75%. The test results are summarized below:

Plant Test Data

	Run 1	Run 2	Run 3
O_2/SO_2 Ratio	0.72	0.86	0.92
Overall Conversion	90.8%	94.2%	95.4%
Bed 1 Catalyst Activity	104%	83%	82%

Note: Catalyst activity dropped 22% between test runs 1 and 3. This was reported as "catalyst activities are in the normal range".

The conclusion presented by the testing company - catalyst supplier was the plant design at 0.75 O_2/SO_2 ratio and 97% conversion in a single absorption plant was not possible with the catalyst type, volume and O_2/SO_2 ratio. However, the catalyst supplier - testing company would be happy to study ways to achieve plant conversion and capacity, although they stated "there are no clear cut, low cost ways to do this". Note: Acid Engineering & Consulting, Inc. adjusted plant operating conditions and in four hours the plant was able to meet design capacity at an O_2/SO_2 ratio of 0.75 with conversion exceeding 98%. In this case, knowledge and experience was able to do what blind or self-serving testing could not do - get the plant operating at or above design without additional catalyst or costly modifications.

Conclusion

This work was intended to provide an understanding of sulfuric acid plant catalysts and to present a comparison of the three catalysts used in North America. Data from many plants over a number of years was reviewed, adjusted and evaluated to obtain comparative catalyst performance. The data indicated suppliers "B" and "C" catalyst to be about equal in each of the areas examined, with supplier "A" catalyst of lower performance (activity loss over time and high screening loss).

If some have a better understanding of sulfuric acid plant converter operation and catalysts, and supplier "A" is encouraged to improve their catalyst, the time and effort spent on this work will have been justified.
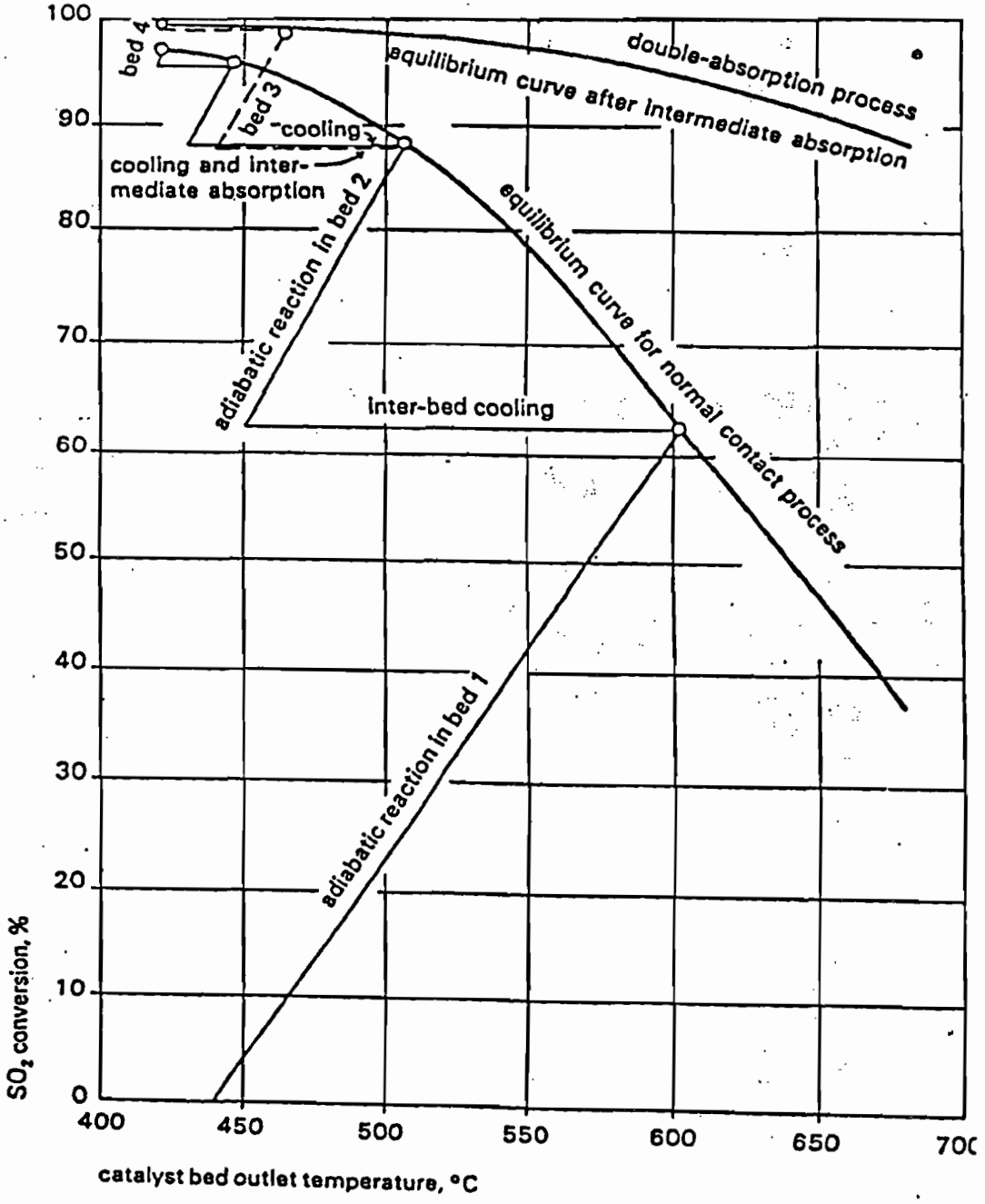
Figure 1

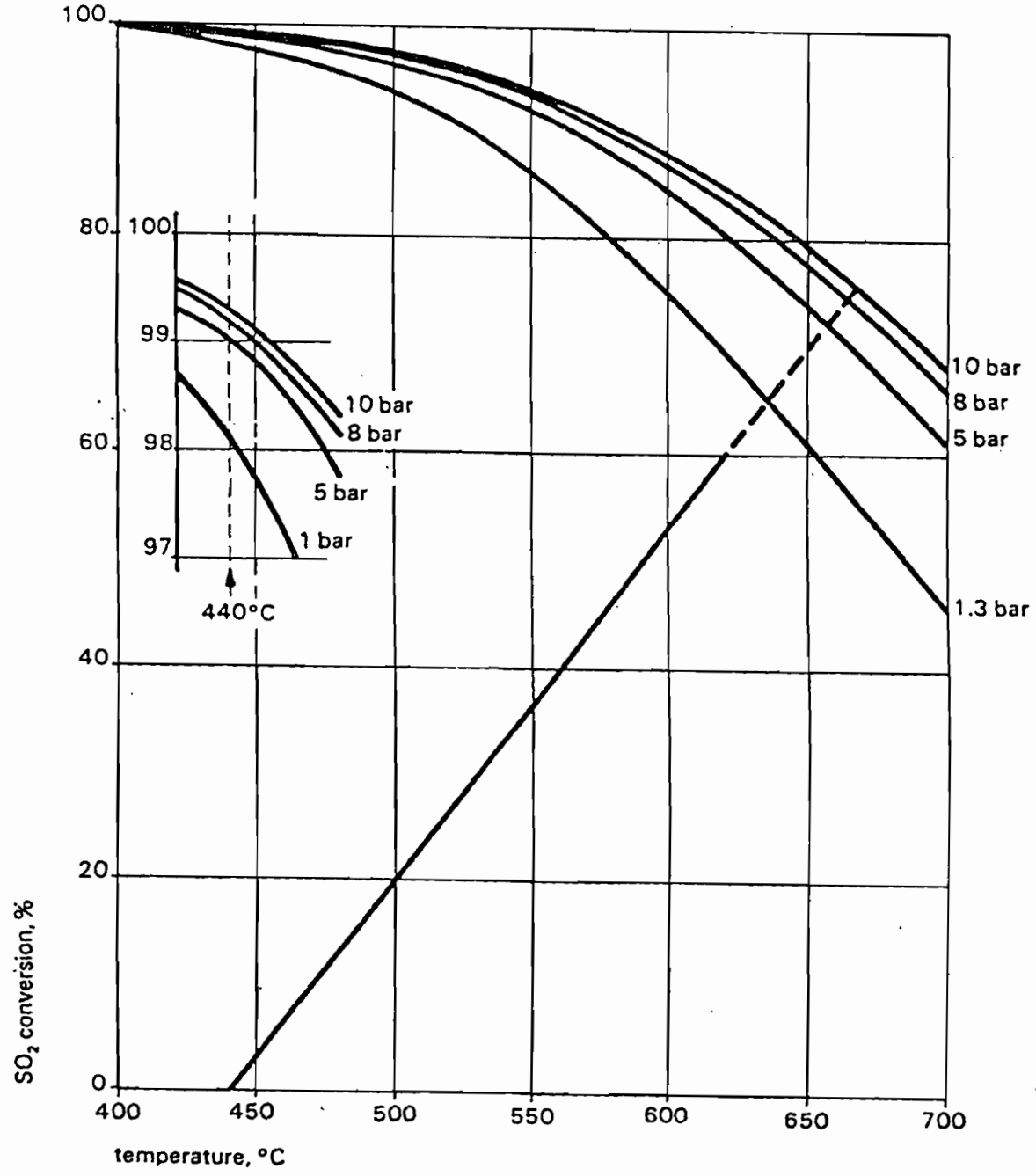## Converter Equilibrium

Figure 2

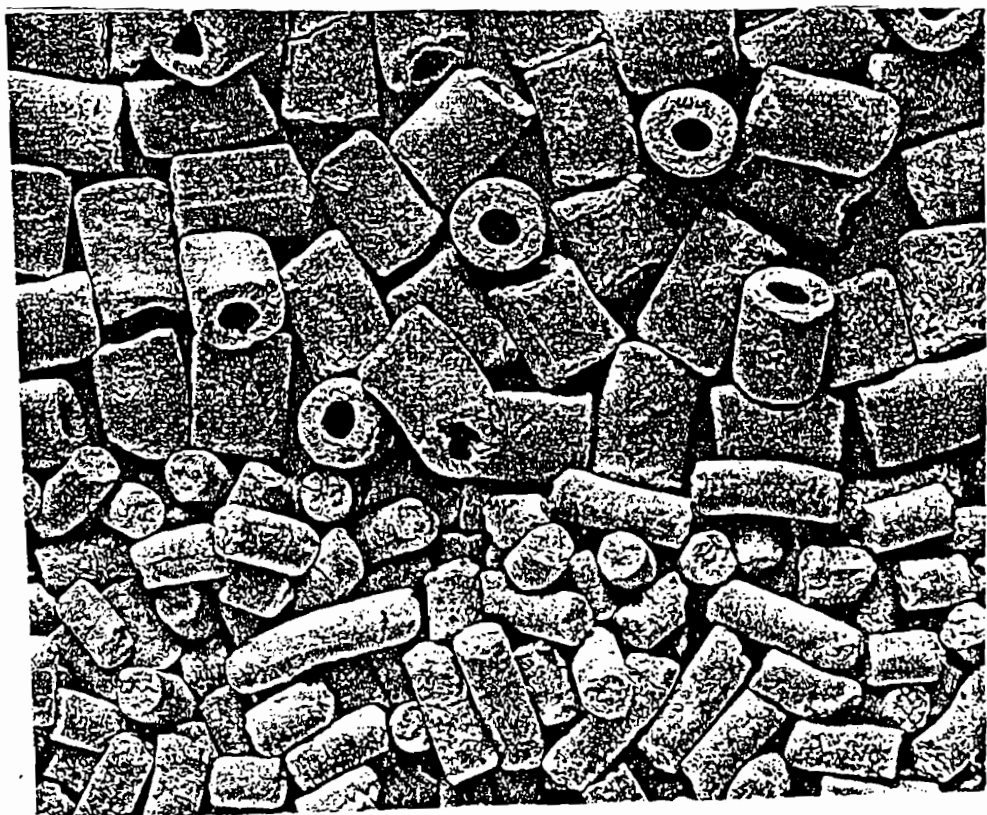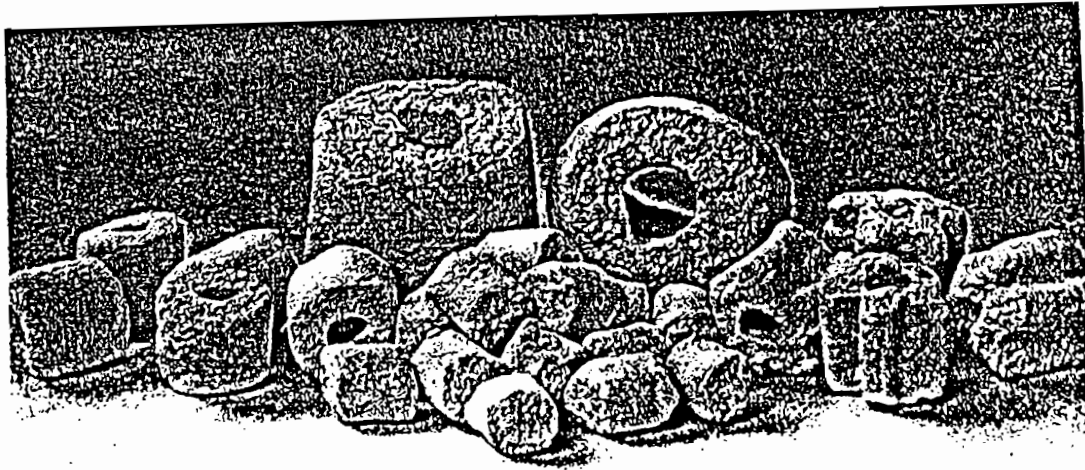## Pressure Effect on Equilibrium

Figure 3

Catalyst Shapes & Sizes

Figure 4

Catalyst Shapes & Sizes