United States
Environmental Protection
Agency

Industrial Environmental Research
Laboratory
Research Triangle Park NC 27711

EPA-600/7-79-224
September 1979

EPA

Adipic Acid Degradation Mechanism in Aqueous FGD Systems

Interagency Energy/Environment R&D Program Report

RESEARCH REPORTING SERIES

Research reports of the Office of Research and Development, U.S. Environmental Protection Agency, have been grouped into nine series. These nine broad categories were established to facilitate further development and application of environmental technology. Elimination of traditional grouping was consciously planned to foster technology transfer and a maximum interface in related fields. The nine series are:

1. Environmental Health Effects Research
2. Environmental Protection Technology
3. Ecological Research
4. Environmental Monitoring
5. Socioeconomic Environmental Studies
6. Scientific and Technical Assessment Reports (STAR)
7. Interagency Energy-Environment Research and Development
8. "Special" Reports
9. Miscellaneous Reports

This report has been assigned to the INTERAGENCY ENERGY-ENVIRONMENT RESEARCH AND DEVELOPMENT series. Reports in this series result from the effort funded under the 17-agency Federal Energy/Environment Research and Development Program. These studies relate to EPA's mission to protect the public health and welfare from adverse effects of pollutants associated with energy systems. The goal of the Program is to assure the rapid development of domestic energy supplies in an environmentally-compatible manner by providing the necessary environmental data and control technology. Investigations include analyses of the transport of energy-related pollutants and their health and ecological effects; assessments of, and development of, control technologies for energy systems; and integrated assessments of a wide range of energy-related environmental issues.

EPA REVIEW NOTICE

This report has been reviewed by the participating Federal Agencies, and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the Government, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

This document is available to the public through the National Technical Information Service, Springfield, Virginia 22161.

EPA-600/7-79-224

September 1979

Adipic Acid Degradation Mechanism in Aqueous FGD Systems

by

F.B. Meserole, D.L. Lewis, A.W. Nichols, and G. Rochelle

Radian Corporation
8500 Shoal Creek Blvd.
Austin, Texas 78766

Contract No. 68-02-2608
Task No. 58
Program Element No. EHE624

EPA Project Officer: Robert H. Borgwardt

Industrial Environmental Research Laboratory
Office of Environmental Engineering and Technology
Research Triangle Park, NC 27711

Prepared for

U.S. ENVIRONMENTAL PROTECTION AGENCY
Office of Research and Development
Washington, DC 20460

CONTENTS

SECTION		Page
1	Introduction	1
2	Summary of Results	3
3	Conclusions and Recommendations	6
4	Literature Review	10
	4.1 Summary	10
	4.2 Conjugated Oxidation of Carboxylic Acids	10
	4.3 Other Reactions of Carboxylic Acids	11
	4.4 Oxidative Decarboxylation by Metal Ions	18
	4.5 Health Effects	19
5	Analytical Methods	23
	5.1 Ion Chromatography	23
	5.2 Gas Chromatography	23
	5.3 Total Organic Carbon	25
	5.4 Solid Phase Characterization	26
	5.5 Carbon Dioxide	27
	5.6 Gas Chromatography-Mass Spectrometry	28
6	Results of Field Sampling Efforts	29
	6.1 Gas Phase Sampling	29
	6.2 Liquid Sampling	30
	6.3 Results of IERL-RTP Material Balance Test (10/25/78)	32
	6.4 Results of IERL-RTP Material Balance Test (11/15-16/78)	36
	6.5 Results of IERL-RTP Material Balance Test (12/18-22/78)	37
	6.6 Results of Shawnee Material Balance Test	45
	6.7 Solids Characterization	46
	6.8 Field Data Correlation	54
7	Laboratory Tests	58
	7.1 Screening Tests	58
	7.2 Mechanisms Tests	64
	Bibliography	74
	Appendix A - Analytical Methods	77
	Appendix B - Sample Chromatograms	83

LIST OF FIGURES

FIGURE		Page
4-1	Oxidative decarboxylation of adipic acid	13
6-1	Gas phase sampling train	31
6-2	IERL-RTP scrubber configuration (natural oxidation) ...	34
6-3	IERL-RTP scrubber configuration (forced oxidation)	39
6-4	IERL-RTP scrubber configuration (forced oxidation)	43
6-5	Shawnee scrubber configuration	48
6-6	Calcium sulfite hemihydrate crystals taken from EPA's Shawnee Test Facility, no additives (x500).....	51
6-7	Calcium sulfite hemihydrate crystals from natural oxidation tests at RTP, 2500 ppm adipic acid (x590) ...	51
6-8	Calcium sulfate dihydrate crystals from forced oxidation tests at RTP, 600 ppm adipic acid (x200)	52
6-9	Calcium sulfate dihydrate crystals from forced oxidation tests at RTP, 4000 ppm adipic acid (x200) ...	52
6-10	Calcium sulfate hemihydrate crystals from forced oxidation tests at RTP, 600 ppm adipic acid (x460)	53
6-11	Calcium sulfate hemihydrate crystals from forced oxidation tests at RTP, 4000 ppm adipic acid (x460) ...	53
6-12	Adipate decomposition as a function of sulfite oxidation and adipate concentration	56
7-1	Laboratory apparatus for screening tests	59
7-2	Laboratory apparatus for mechanism test with Porapak Q sorbent trap	66
7-3	Laboratory apparatus for mechanism test with recirculated gases	69
7-4	Laboratory apparatus for mechanism test with silica gel and carbon traps	72
B-1	Sample IC chromatogram with high sulfite.....	84
B-2	Sample IC chromatogram with no sulfite	85
B-3	Sample GC chromatogram	86

LIST OF TABLES

TABLE		Page
2-1	Summary of Field Sampling Results	5
2-2	Material Balance Results of Dynamic Laboratory Degradation Studies	5
3-1	Comparison of Potential Hydrocarbon Emissions from Degradation of Adipic Acid with Reported Values for Coal-Fired Industrial and Utility Boilers	8
4-1	Decarboxylation in the Air Oxidation of Cyclohexane in Acetic Acid Catalyzed by Co^{+2}	15
4-2	Rate Constants for Decarboxylation in Cumene Undergoing Oxidation for the Reaction, $R_1COOH + R\text{-}O\text{-}O\bullet \rightarrow$ Complex	16
4-3	Rate Constants for the Reaction of Cumyl Peroxide Radicals with Carboxylic Acids in Chlorobenzene	17
4-4	Toxicology of Adipic Acid and Related Compounds	20
6-1	Samples Obtained at IERL-RTP	32
6-2	Results of Analysis of IERL-RTP (10/25/78) Samples	33
6-3	Material Balance Calculations: IERL-RTP 10/25/78	35
6-4	Samples Obtained at IERL-RTP (11/15-16/78)	36
6-5	Results of Analysis of IERL-RTP (11/15/78-11/16/78) Samples	38
6-6	Material Balance Calculations: IERL-RTP 11/15/78-11/16/78	40
6-7	Samples Obtained at IERL-RTP	41
6-8	Results of Analysis of IERL-RTP (12/18/78-12/22/78) Samples	42
6-9	Material Balance Calculations: IERL-RTP 12/21/78	44
6-10	Samples Obtained at Shawnee	45
6-11	Results of Analysis of Shawnee (2/2/79) Samples	47
6-12	Material Balance Calculations - TVA's Shawnee Facility	49
6-13	Compositional Analysis of Scrubber Solids	50

LIST OF TABLES (continued)

TABLE		Page
6-14	Adipate Decomposition Data from RTP and Shawnee	55
7-1	Results of Phase One Lab-Screening Tests	60
7-2	Summary of Phase Two Lab-Screening Tests	62
7-3	Results of Sealed Flask Experiments	63
7-4	Results of Sealed Flask Experiment with Material Balance	64
7-5	Results of Mechanism Test with Porapak Q Sorbent Trap	67
7-6	Carbon Balance for Mechanism Tests Using Porapak Q Trap	65
7-7	Carbon Balance for Mechanism Test Using Porapak Q Trap; Hydrocarbon Values Neglected	68
7-8	Results of Mechanism Test with Recirculated Gases	70
7-9	Carbon Balance for Mechanism Test Using Recirculated Gases	69
7-10	Results of Mechanism Test with Silica Gel and Activated Carbon Traps	73
7-11	Carbon Balance for Mechanism Test Using Silica Gel and Activated Carbon Traps	71
A-1	Response Characteristics of Species Analyzed by Dionex	78
A-2	IC Eluents	79

SECTION 1

INTRODUCTION

The addition of weak organic acids such as adipic acid to flue gas desulfurization (FGD) wet scrubbers using limestone has been shown to benefit both SO_2 removal and limestone utilization. The value of adipic acid as a scrubber additive has been suggested in a theoretical analysis by Rochelle (1). Adipic acid has the effect of buffering scrubber solutions, thereby enhancing liquid phase mass transfer. Improved SO_2 removal can be achieved economically due to the relatively low price of adipic acid. However, long-term scrubber tests at Industrial Environmental Research Laboratory-Research Triangle Park (IERL-RTP) and EPA's test facility at the TVA Shawnee Power Plant have experienced substantial losses of adipic acid. These losses were in excess of that expected from the scrubber solution removed with the filter cake solids.

Tests have also shown that the adipic acid loss rate is considerably higher during forced oxidation runs than during natural oxidation conditions. Unaccounted losses of as much as 80% of the adipic acid make-up rate were observed in the Shawnee venturi/spray tower scrubber system.

Several possibilities could explain this disappearance including:

- inaccurate measurement of adipic acid in the scrubber solution,
- precipitation of insoluble adipate salts,
- chemical complexation and/or decomposition of adipic acid,
- biodegradation of adipic acid,
- physical adsorption on, or coprecipitation with the scrubber solids, and
- volatilization of adipic acid into the flue gas.

Radian was contracted by the Environmental Protection Agency (EPA) to select methods to accurately measure levels of adipic acid in FGD scrubber solutions and conduct material balance measurements at the IERL-RTP pilot plant and at the Shawnee Test Facility. The primary objective was to verify adipic acid loss and to determine its cause. Other objectives were to identify by-products if degradation occurs, determine mechanism, and suggest possible courses for limiting the loss.

During the period between October, 1978 and February, 1979 Radian personnel conducted three sampling trips to RTP and one sampling trip to the Shawnee Test Facility. At both facilities samples were collected at the various slurry and gas streams around the system. Analytical methods were developed for the accurate measurement of adipic acid and valeric acid in the samples and the data obtained were used to perform material balance calculations.

A literature survey of known decomposition mechanisms of adipic acid, and carboxylic acids in general, was conducted in order to ascertain any properties or reactions of adipic acid relevant to its stability under scrubber conditions.

Finally, a series of laboratory bench scale studies aimed at simulating scrubber conditions was conducted. These tests were designed in such a way that operating conditions were variable and degradation could be monitored by the collection and analysis of decomposition products. The results of these tasks are presented in this report.

REFERENCES

1. Rochelle, G. "The Effect of Additives on Mass Transfer in $CaCO_3$ and CaO Slurry Scrubbing of SO_2 from Waste Gases, " Ind. Eng. Chem. Fundam., 16: 67-75, 1977.

SECTION 2

SUMMARY OF RESULTS

The samples collected during this program from the RTP and Shawnee SO_2 scrubbers during the adipic acid addition tests were analyzed to determine the concentrations of adipic acid and any degradation products. Gaseous, liquid and solid samples were taken using a variety of sampling techniques and were then characterized using several analytical procedures including: ion chromatography, gas chromatography, gas chromatography-mass spectrometry, infrared spectroscopy and total organic carbon determination.

The major degradation products of adipic acid identified in the samples collected from the RTP and Shawnee test units were:

- valeric acid - $CH_3(CH_2)_3COOH$ and
- glutaric acid - $HOOC(CH_2)_3COOH$.

Trace quantities of the following were also found:

- butyric acid - $CH_3(CH_2)_2COOH$ and
- succinic acid - $HOOC(CH_2)_2COOH$.

All four of the above acids were found in the liquid phase samples, but only valeric acid was found in the scrubbed flue gases. No measurable amounts of organics could be detected in the washed solids using infrared analysis. The detection limit using this technique is about 0.1% on a weight basis.

The products measured in the samples collected during the laboratory degradation studies were the following:

- valeric acid,
- carbon dioxide,
- methane, and
- butane.

In some cases, these degradation products were found to account for most of the adipic acid lost whether in the field or laboratory tests. How-

ever, in general, only 25-50% of the adipic acid added could be accounted for. The results of the field sampling efforts associated with this program are summarized in Table 2-1. The material balance calculations were performed using analytical data measured by Radian personnel and flow rates that were supplied by on-site personnel.

In addition to the field measurements, laboratory programs were carried out to establish the conditions necessary for adipic acid degradation and to identify the degradation products. Conclusions drawn from these tests include:

- Adipic acid degradation can occur by a chemical process as opposed to a microbial process.
- The similarity in the degradation rates between the laboratory and field tests indicate the catalytic and microbial effects are small, if present.
- The oxidation of sulfite in the presence of adipic acid results in degradation, supposedly through a free-radical mechanism.

During the laboratory phase, a series of material balance tests was made using various techniques to trap low molecular weight hydrocarbon products. The results of these tests are presented in Table 2-2.

The degradation rate of adipic acid was found to depend upon the degree of sulfite oxidation and adipic acid concentration in solution. Field and laboratory data were compared using this correlation. Although there is significant scatter a general trend appears to prevail. Much of this variability may be a result of the different scrubber systems used to collect the data and different analytical techniques used to measure adipic acid.

Settling and dewatering measurements conducted at RTP on solids produced with and without the addition of adipic acid showed only slight differences due to adipic acid. The settling rates were reduced by approximately 25% and some increase in the moisture content of the filtered sludge was measured for the solids precipitated in the presence of adipic acid.

Electron micrographs of a limited number of solid samples suggest that the average particle size decreases as the adipic acid increases. However, the effect was not large enough to yield a detectable difference at Shawnee when filter-cake solids were compared with and without the use of adipic acid in the scrubber.

TABLE 2-1. SUMMARY OF FIELD SAMPLING RESULTS

Facility	Date	Scrubber Type	Oxidation Mode	Adipic Acid Decomposition (%)	Fraction of Products Measured (%)
RTP	10/25/78	TCA	Natural	28%	84-97%
RTP	11/15/78	TCA	Forced	69%	42-45%
RTP	12/18/78	TCA	Forced	54%	53%
Shawnee	2/2/79	Venturi/ Spray Tower	Forced	91%	17%

TABLE 2-2. MATERIAL BALANCE RESULTS OF DYNAMIC LABORATORY DEGRADATION STUDIES

Hydrocarbon Collection Techniques	Initial Adipic Acid (mmoles C)	Final Adipic Acid (mmoles C)	Valeric Acid (mmole C)	Methane (mmole C)	Ethane (mmole C)	Propane (mmole C)	Butane (mmole C)	CO_2 (mmole C)	Total (mmole C)
Poropak Q Trap	18.7	11.4	4.4	1.6	.4	.2	.9	1.4	20.3
Recirculation of Product	19.0	11.5	2.4	--	--	--	--	3.2	17.1
Cases	9.5	4.1	--	--	--	--	--	1.1	5.2
Silica Gel Trap	19.2	12.6	1.5	--	--	--	.02	1.6	15.7

SECTION 3

CONCLUSIONS AND RECOMMENDATIONS

The findings of this study support the field test results at RTP and Shawnee that adipic acid added to an SO_2 wet scrubber is consumed in the process. Furthermore, the degradation rate depends, in part, on the degree of sulfite oxidation occurring in the scrubber system.

The degradation products identified in the laboratory and field tests include the following:

- valeric acid,
- glutaric acid,
- butyric acid,
- succinic acid,
- butane,
- methane, and
- carbon dioxide.

No cyclopentanone, a high temperature reaction product of adipic acid, was found in any of the samples analyzed.

Adipic acid and the acidic decomposition products listed above were found in the liquid portion of slurry samples but not in the solids. No adipic acid was detected in the flue gas; however, measurable quantities of valeric acid were collected in the flue gas samples from both the RTP and Shawnee facilities. Laboratory tests generated CO_2, methane, butane and valeric acid. Due to the naturally high concentration of CO_2 in flue gases this could not be verified in the field. Attempts to measure the low molecular weight hydrocarbons such as methane and butane in the field were unsuccessful.

Additional conclusions derived from this program are summarized below:

- the decomposition of adipic acid is primarily a chemical, not a microbial process,
- the oxidation of sulfite in the presence of adipic acid was a necessary and sufficient condition for degradation to occur in a laboratory situation,

- the rate of adipic acid decomposition, $-\partial A/\partial t$, appears to be proportional to the rate of sulfite oxidation, $-\partial SO_3^{=}/\partial t$, and the adipic acid concentration in solution which can be stated mathematically as:

$$\partial A/\partial t = k\ (\partial SO_3^{=}/\partial t)\ (A) \qquad (3\text{-}1)$$

- according to Equation 3-1, reduction of the decomposition rate can be achieved by lowering the sulfite oxidation rate or the adipic acid concentration in solution,
- the literature review indicates that the decomposition products may vary depending on the relative concentrations of sulfite and oxygen during the reaction and that the decarboxylation may occur through a free radical mechanism,
- the degradation products identified in both field and laboratory test samples don't appear to pose any significant health related problems, however, valeric and butyric acids both can cause objectionable odors around the process, and
- the failure to close the material balances during forced oxidation runs at both RTP and Shawnee may result from the inability to measure some of gas phase species.

The presence of adipic acid does appear to cause some reduction in particle size of gypsum with the effect becoming greater at higher concentrations. In addition to direct evidence obtained from electron micrographs of scrubber solids, settling and dewatering tests also indicated some decrease in particle size. The effect on sludge properties does not, however, appear to be significant in practice.

Evidence of the growth of sulfur-reducing bacteria was observed in several of the slurry samples collected during the natural oxidation tests at RTP. The samples were sealed in polyethylene bottles after collection and stored at room temperature. Black deposits characteristic of metal sulfides formed in the samples and the odor of H_2S was strong when the bottles were opened. However, no similar observations have been reported at the sites used for the disposal of the RTP scrubber solid wastes.

As mentioned previously, not all of the degradation products of adipic acid were accounted for during the field sampling efforts. Probable products are methane and butane which naturally would be stripped from the scrubber into the scrubber flue gases and oxidizer vents. Since the oxidizer vents can be combined with the exit flue gases, potential hydrocarbon emission levels, assuming that all of the missing adipic acid was converted either to methane or butane, were calculated for the exhausted flue gases. The emission values calculated for both methane and butane assuming that all the degradation was either one or the other are 12,000 and 14,000 $\mu g/Nm^3$. The concentrations calculated are compared to hydrocarbon values reported for

coal-fired industrial (1) and utility boilers (2) in Table 3-1. Laboratory tests, however, indicate to as much as 50% of the degradation may be CO_2 which would not contribute significantly to the CO_2 concentration in the flue gas.

TABLE 3-1. COMPARISON OF POTENTIAL HYDROCARBON EMISSIONS FROM DEGRADATION OF ADIPIC ACID WITH REPORTED VALUES FOR COAL-FIRED INDUSTRIAL AND UTILITY BOILERS

Source	Methane ($\mu g/Nm^3$)	Butane ($\mu g/Nm^3$)	Total C_2 - C_6 (mg/Nm^3)
Industrial	15,000[1]	---	---
Utility - Lignite	3,954	---	2,070
- Bituminous	1,758	---	861
Adipic Acid Degradation[2]	12,000	14,000	---

[1]Total hydrocarbon as methane.

[2]Based on Shawnee forced oxidation tests and assuming that all the unaccounted adipic acid was converted to methane or butane.

Since material balance attempts failed to account for all of the adipic acid degradation products, additional studies are recommended to further characterize the degradation mechanism(s). Emphasis should be placed on the quantitative collection and analysis of low molecular weight hydrocarbons. Concurrent with tests to further elucidate the degradation products, experiments should be performed to study the effects of such operating parameters as:

- temperature,
- pH,
- adipic acid concentration,
- sulfite concentration,
- dissolved heavy metals, and
- free-radical scavengers.

Another area where additional work may be necessary is the development of analytical techniques that can be used in the field for the measurement of adipic acid and important degradation products.

REFERENCES

1. Leavitt, C., et al. Environmental Assessment of Coal- and Oil-Firing in a Controlled Industrial Boiler; Volume III. Comprehensive Assessment and Appendices. EPA-600/7-78-164c. Environmental Protection Agency, Research Triangle Park, North Carolina, 1978.

2. Personal communication from Mr. J. Warren Hammersma, TRW, Inc. to Mr. Ronald A. Venezia, EPA, 20 October 1978.

SECTION 4

LITERATURE REVIEW

4.1 SUMMARY

The most probable cause of adipic acid decomposition in limestone scrubbing systems is oxidation or decarboxylation by free radicals generated during oxidation of SO_2 species. Such conjugated oxidation of carboxylic acids has been observed, at temperatures as low as 80°C, in the air oxidation of cumene, cyclohexane, cyclohexanol and hexane. With this mechanism expected products include glutaric acid, valeric acid, and butane as well as other shorter acids and hydrocarbons. The rate of adipic acid degradation should be proportional to the rate of oxidation and to the adipic acid concentration and inversely proportional to the total concentration of dissolved SO_2.

Adipic acid degradation may be catalyzed by transition metals such as cobalt (Co) and manganese (Mn). The presence of chloride may result in chlorinated degradation products.

4.2 CONJUGATED OXIDATION OF CARBOXYLIC ACIDS

At 25-100°C aliphatic, carboxylic acids (such as adipic acid) react too slowly with free radicals to sustain continuous reaction with O_2 in aqueous or organic solvents. However, carboxylic acids will react with free radicals generated by the sustained oxidation of other species such as cyclohexane, paraffins, cumene, and cyclohexanol. An excellent review of these phenomenomena is presented by Denisov et al. (2).

The oxidation of sulfite or bisulfite undoubtedly proceeds by a free radical reaction. One example of such a mechanism is given by Chen and Barron (3) for cobalt catalyzed oxidation of sulfite:

$$SO_3^{=} + Co^{+3} \xrightarrow{k_1} Co^{+2} + \cdot SO_3^{-} \qquad (4\text{-}1a)$$

$$\cdot SO_3^{-} + O_2 \xrightarrow{k_2} \cdot SO_5^{-} \qquad (4\text{-}1b)$$

$$\cdot SO_5^{-} + SO_3^{=} \xrightarrow{k_3} SO_5^{=} + \cdot SO_3^{-} \qquad (4\text{-}1c)$$

$$SO_5^{=} + SO_3^{=} \xrightarrow{k_4} 2SO_4^{=} \qquad (4\text{-}1d)$$

$$\cdot SO_5^{-} + \cdot SO_5^{-} \xrightarrow{k_5} \text{inert products} \qquad (4\text{-}1e)$$

The rate of sulfite oxidation is determined by Reaction 4-1c and is proportional to sulfite concentration and to the concentration of the free radical, $\cdot SO_5^{=}$. Hence, with a reasonable rate of sulfite oxidation, there will be present a steady-state concentration of free radicals which usually react with sulfite but may also react with carboxylic acids or other organics which may be present.

4.3 OTHER REACTIONS OF CARBOXYLIC ACIDS

In 1M H_2SO_4 at 50-90°C, adipic acid will decompose to give CO and hydroxylvaleric acids. Decarboxylation was catalyzed by H_2SO_4. At 50°C the first order rate constant in 1M H_2SO_4 was 3.0×10^{-2} min^{-1} (4).

The Hunsdiecker reaction is used to synthesize organic bromides from carboxylic acid salts of silver or mercury (5). The proposed mechanism involves an oxidative decarboxylation:

$$Br_2O + RCO_2H \rightarrow RCO_2Br + HOBr \qquad (4\text{-}2a)$$

$$RCO_2Br \rightarrow RCO_2\cdot + Br\cdot \qquad (4\text{-}2b)$$

$$RCO_2\cdot \rightarrow R\cdot + CO_2 \qquad (4\text{-}2c)$$

$$R\cdot + RCO_2Br \rightarrow RBr + RCO_2\cdot \qquad (4\text{-}2d)$$

Kolbe electrolysis of acetate solution produces ethane via a decarboxylation:

$$RCO_2^- \rightarrow RCO_2\cdot + e^- \qquad (4\text{-}3a)$$

$$RCO_2\cdot \rightarrow R\cdot + CO_2 \qquad (4\text{-}3b)$$

$$2R\cdot \rightarrow R_2 \qquad (4\text{-}3c)$$

Similar reactions can occur by photochemical processes on semiconductor materials (6). Irradiation of $FeCl_3$ solutions at 38°C containing succinic, glutaric, or adipic acid gave β-chloropropionic acid, γ-butyrolactone and δ-chlorovaleric acid respectively (7).

Microbial decomposition of aromatic and aliphatic acids has been noted (8, 9, 10). Aliphatic acids are readily digested by sewage microorganisms (11).

At elevated temperatures (225°C) adipic acid will decompose to give cyclopentanone (12, 13). This reaction is catalyzed by $Ba(OH)_2$.

The reaction rate constants at 15°C for acid plus Co^{+3} in 1.1 M $HClO_4$ were 0.69 x 10^{-2} x 10 M^{-1} sec^{-1} for propionic acid and 1.2 x 10^{-2} M^{-1} sec^{-1} for adipic acid. The estimated rate constant for propionic acid at 55°C was 2.04 M^{-1} sec^{-1}.

Anderson and Kochi (14) investigated the reaction of Mn^{+3} with carboxylic acid in the carboxylic acid solvent at 90-125°C. The reaction with n-butyric acid proceeded slowly at 125°C and produced CO_2 and propane with minor amounts of propylene and propyl esters of butyric acid.

Oxidative decarboxylation of acids by lead tetraacetate was reviewed by Sheldon and Kocki (15). Secondary and tertiary carboxylic acids are routinely decarboxylated by Pb^{+4} in acetic acid solvent at 25-100°C. Reactions with primary acids are much slower. Reaction products include hydrocarbons and lower acids. A potential product of reaction with adipic or glutaric acids is the corresponding C_5 or C_4 lactone.

Conjugated oxidation in the presence of a transition metal may result in a synergistic effect on the rate of decarboxylation. Hence, Tinker (16) found that oxidative decarboxylation of adipic acid conjugated with cyclohexane oxidation was four times faster with 0.07 M Co^{+2} than without any catalyst.

Free radicals may attack carboxylic acids at the O-H bond of the carboxylic group or at C-H bonds of methylene groups. Attack at the O-H bond results in oxidative decarboxylation by a mechanism of the form (17):

$$R\text{-}O\text{-}O\bullet + R_1 - COOH \rightarrow R\text{-}O\text{-}OH + R_1COO\bullet \qquad (4\text{-}4a)$$

$$R_1COO\bullet \rightarrow R_1\bullet + CO_2 \qquad (4\text{-}4b)$$

The residue of the acid, $R_1\bullet$, can react with O_2 to give a peroxide radical which reacts further to end up as an acid group:

$$R_1\bullet + O_2 \rightarrow R_1\text{-}O\text{-}O\bullet \qquad (4\text{-}5a)$$

$$R_1\text{-}O\text{-}O\bullet + RH \rightarrow R_1\text{-}O\text{-}OH + R\bullet \qquad (4\text{-}5b)$$

$$R_1\text{-}O\text{-}OH \rightarrow R_1{=}\ O + H_2O \qquad (4\text{-}5c)$$

$$R_1{=}O + O_2 \rightarrow R_1OOH \qquad (4\text{-}5d)$$

The acid residue, $R_1\bullet$, may also react with other species to extract H and end up as a hydrocarbon R_1H. Hence, the oxidative decarboxylation of adipic acid can give valeric acid (CH_3-$(CH_2)_3$-COOH) or glutaric acid (HOOC-$(CH_2)_3$-COOH) as well as producing CO_2. The products are also subject to oxidative decarboxylation and can give the full series of lower acids and hydrocarbons as shown in Figure 4-1. The C_3 dicarboxylic acid (malonic) is unstable and decomposes to CO_2 in an oxidizing environment.

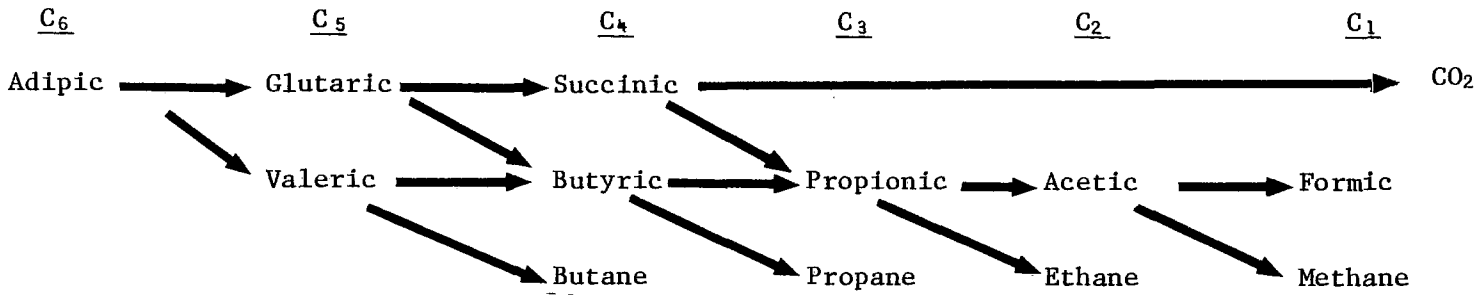


Figure 4-1. Oxidative decarboxylation of adipic acid.

Oxidation of the C-H bonds in dicarboxylic acids produces no hydrocarbons or monocarboxylic acids, but results in lower dicarboxylic acids (2). Hence, attack of adipic acid can result in glutaric and succinic acids as well as CO_2. Malonic (C_3) and oxalic (C_2) acids are unstable and decompose quickly to CO_2.

Tinker (16) studied decarboxylation of adipic acid conjugated with the air oxidation of cyclohexane at 90-150°C catalyzed by cobalt in acetic acid solvent. The carboxylic groups of acetic, succinic, glutaric, and adipic acid were tagged with C^{14}. The evolution of tagged CO_2 was followed as a function of time. In the absence of cyclohexane, adipic acid did not decarboxylate. The amount of decarboxylation was proportional to the acid concentration and to the amount of O_2 consumed. The relative rate of decarboxylation, % decomposition/O_2 consumed per liter, was approximately independent of acid concentration and O_2 consumption. As shown in Table 4-1, the relative rate of decarboxylation was a function of temperature and increased about a factor of six from 90°C to 150°C. The relative decarboxylation rates of succinic and glutaric acids were about half that of adipic acid. Acetic acid was very stable. Cobalt was not necessary for decarboxylation, but did catalyze it significantly.

Emanuel Berezin, et al. (2) have studied decarboxylation of monocarboxylic acids in heptane or octadecane undergoing oxidation at 130°C. The decarboxylation rate is the same for propionic, n-butyric, and valeric acids, but about 50% less for acetic acid.

Russian workers have studied the decarboxylation of aliphatic acids in cumene undergoing oxidation from 80°C to 140°C (2). The decarboxylation of acetic, n-butyric, isobutyric, and stearic acids takes place as low as 80°C. The relative rates for acetic, n-butyric, n-valeric, and isobutyric acids are 0.25, 1.0, 1.0, and 5.0, respectively. At 135°C, nonane was detected in the decarboxylation of decanoic acid. The quantity of nonane increased with a decrease in O_2 pressure.

In the oxidation of cumene, it was determined that the primary reaction resulting in decarboxylation was attack of a peroxy-radical at the α-methylene group. Rate constants for this reaction are given in Table 4-2. The rate is uniform for unbranched monocarboxylic acids and is about four times less with dicarboxylic acids.

Denisov et al. (2) have measured the overall rate of reaction of cumyl peroxide radicals with acids in chlorobenzene solvent. The rate constants and activation energies are given in Table 4-3. Longer chain acids react faster because there are more available C-H bonds. Dicarboxylic acids react about six times faster than monocarboxylic acids with an equal number of carbon atoms.

TABLE 4-1. DECARBOXYLATION IN THE AIR OXIDATION OF CYCLOHEXANE (3.3 M) IN ACETIC ACID (9.75 M) CATALYZED BY Co^{+2} (3.3×10^{-2} M)

Acid	T(°C)	% Decarboxylation[a]/O_2 Consumed (% M^{-1})
Adipic	90	1.8[b]
	90	1.3
	90	1.1[c]
	125	1.8
	150	8.3
	150	2.8[d]
	150	10.0[e]
Glutaric	90	0.9
	150	4.3
Succinic	90	0.9
	150	4.1
Acetic	90	0.03
	115	0.1
	150	0.6

[a] 3.0 moles O_2 consumed/liter unless noted otherwise

[b] 0.9 moles O_2/liter

[c] 4.2 moles O_2/liter

[d] no cobalt

[e] $Co^{+2} = 6.6 \times 10^{-2}$ M

TABLE 4-2. RATE CONSTANTS FOR DECARBOXYLATION IN CUMENE UNDERGOING OXIDATION, FOR THE REACTION, $R_1COOH + R\text{-}O\text{-}O\bullet \rightarrow$ COMPLEX (DENISOV et al. 1977)

Acid	Rate-constant (ℓ/mole-sec) 120°C	125°C
Isobutyric	--	3.2
n-Butyric	--	1.5
n-Valeric	--	1.6
Decanoic	--	1.7
Stearic	--	1.9
Sebacic	0.58	--
Azelaic	0.44	--
Pimelic	0.25	--

TABLE 4-3. RATE CONSTANTS FOR THE REACTION OF CUMYL PEROXIDE RADICALS WITH CARBOXYLIC ACIDS IN CHLOROBENZENE (DENISOV, et al., 1977)

Acid	k(liters/mole-sec)			Activation energy (kcal/mole)
	110^0C	130^0C	55^0C[a]	
Acetic	0.13		$0.4 \cdot 10^{-2}$	16.2
Propionic	0.17		$0.6 \cdot 10^{-2}$	15.1
n-Butyric	0.25		$1.0 \cdot 10^{-2}$	14.8
Isobutyric	0.46		$2.4 \cdot 10^{-2}$	13.4
Valeric	0.31		$1.1 \cdot 10^{-2}$	15.1
Glutaric	--	1.8	$6.9 \cdot 10^{-2}$	11.4
Pimelic	--	2.4	$10 \cdot 10^{-2}$	11.0
Suberic	--	3.2	$12 \cdot 10^{-2}$	11.4

[a]Estimated

It appears that free radical attack at both the O-H and C-H bonds is possible. Therefore, we can expect the products of decomposition to include glutaric and succinic acids, monocarboxylic acids from valeric to formic, and hydrocarbons from butane to methane. The distribution of products should depend upon the ratio of O_2 to SO_2 in the solution.

If the rate of decomposition of adipic acid is proportional to the concentrations of adipic acid and free radical then:

$$\text{decomposition rate} = k_d\ [R\bullet]\ [\text{Adipic}] \tag{4-6}$$

Assuming that the rate of oxidation is proportional to the concentration of free radical and SO_2 species gives:

$$\text{oxidation rate} = k_o\ [R\bullet][SO_2]_T \tag{4-7}$$

Combining Equations 4-6 and 4-7, the ratio of decomposition rate to oxidation rate can be expressed as follows:

$$\frac{\text{moles adipic decomposed}}{\text{moles } SO_2 \text{ oxidized}} = \frac{k_d\ [\text{adipic}]_T}{k_o\ [SO_2]_T} \tag{4-8}$$

The ratio k_d/k_o may be a function of pH, since the actual adipic and SO_2 species will depend upon pH and may react at different rates with the free radical.

4.4 OXIDATIVE DECARBOXYLATION BY METAL IONS

Transition metal ions such as Co^{+3}, Mn^{+3}, Pb^{+4}, and Ce^{+4} react with carboxylic acids at 25-100°C and result in decarboxylation. Typical conditions for such reactions require organic solvents such as acetic acid or aqueous solutions at pH 0-2. The rate of reaction with aliphatic acids is greatest when the α-carbon is tertiary (isobutyric acid) and least when it is primary (acetic acid).

Clifford and Waters (18) measured the rate of reaction of Co^{+3} with several carboxylic acids at 10-35°C in 1.1 M perchloric acid. They postulated a reaction mechanism of the form:

$$RCO_2H + Co(H_2O)_6{}^{3+} \xrightarrow{k_2} R\bullet + CO_2 + Co^{2+} + H^+ + 6H_2O \tag{4-9a}$$

$$R\bullet + Co^{3+} \rightarrow R^+ + Co^{2+} \tag{4-9b}$$

$$R^+ + H_2O \rightarrow ROH + H^+ \tag{4-9c}$$

4.5 HEALTH EFFECTS

Toxicology data for adipic acid and several identified and potential degradation products were obtained from the Dangerous Properties of Industrial Materials (19), Toxic and Hazardous Industrial Chemicals Safety Manual for Handling and Disposal with Toxicity and Hazard Data (20), Registry of Toxic Effects of Chemical Substances (21) and Federal Register (22). These findings are summarized in Table 4-4. Both adipic and butyric acid are listed in EPA's hazardous substances list in Category D with a reportable quantity (RQ) consisting of 5000 lbs (2270 Kg). Thus, permits will be required to discharge these two compounds.

TABLE 4-4. TOXICOLOGY OF ADIPIC ACID AND RELATED COMPOUNDS

Compound	Synonym	Toxicity: Toxic Dose	Toxicity: Comments	Reportable Quantities of Hazardous Substances*: Category	Reportable Quantities of Hazardous Substances*: RQ in pounds (kilo)
Adipic Acid	Hexanedioic Acid	orl-rat LDLO:3600 mg/Kg ipr-rat LD50:275 mg/Kg orl-mus LD50:1900 mg/Kg ipr-mus LD50:275 mg/Kg ivn-mus LD50:680 mg/Kg	Food additive	D	5000(2270)
Valeric Acid	Pentanoic Acid	ivn-mus LD50:1290 mg/Kg orl-mus LD50:500 mg/Kg scu-mus LD50:3590 mg/Kg	Corrosive, unpleasant odor		
Glutaric Acid	Pentanedioic Acid	No data found			
Cyclopentanone	Ketocyclopentane	ipr-mus LD50:1950 mg/Kg	Moderately flammable		
Butane	Methylethylmethane Butyl Hydride	ihl-rat LC50:658 mg/m3 TVL-air:500 ppm	Flammable		
Butyric Acid	Butanoic Acid	orl-rat LD50:2940 mg/Kg ivn-mus LD50:800 mg/Kg orl-rbt LDLo:3600 mg/Kg	Flammable, unpleasant odor	D	5000(2270)

Abbreviations:
orl - oral
rat - rat
ipr - intraperitoneal
mus - mouse
ivn - intraveneous
scu - subcutaneous
ihl - inhalation
TLV - threshold limit value
rbt - rabbit

LDLO - lowest published lethal dose
LD50 - lethal dose 50 percent kill
LC50 - lethal concentration 50 percent kill
LDLo - lowest published lethal concentration
m3 - cubic meter

* Taken from the EPA hazardous substances list contained in the Federal Register, Vol. 44 No. 34 - 16 February, 1979 (p 10280-10282)

REFERENCES

1. Rochelle, G. "The Effect of Additives on Mass Transfer in $CaCO_3$ and CaO Slurry Scrubbing of SO_2 from Waste Gases," Ind. Eng. Chem. Fundam., 16: 67-75, 1977.

2. Denisov E. T., N. I. Mitskevich, and V. E. Agabekov. Liquid-phase Oxidation of Oxygen-containing Compounds. Consultants Bureau, New York, 1977.

3. Chen, T., and C. H. Barron. Ind. Eng. Chem. Fundam., 11:466, 1972.

4. Kiseleva, R. A. and M. S. Dudkin. Zh. Prik, Khim., 40:2513, 1967.

5. Bunce, N. J. J. Org. Chem., 37:664, 1972.

6. Kraeutler, B.; Bard, A. J. J. Am. Chem. Soc., 100(19):598-2-92, 1978.

7. Kuhnle, J. A., R. E. Lundin, and A. C. Waiss. J.C.S. Chem Com., 287, 1972.

8. Keith, C. L., et al. Arch. Microbiol., 118 (2):173-176, 1978.

9. Grula, M. M., Grula, E. A. BERC-RI-76-6, 1976. 61 pp.

10. Hammond, M. W., Alexander, M. Environ. Sci. Technol., 6(8):732-735, 1972.

11. Dias, F. F. and M. Alexander. Appl. Microbiol., 22:1114, 1971.

12. Messier, F.; DeJongh, D. C. Can. J. Chem., 55:2732-2740, 1977.

13. Potai, S. The Chemistry of Carboxylic Acids and Esters. Interscience, New York, New York, 1969.

14. Anderson, J. M. and J. K. Kochi. J. Am. Chem. Soc., 92:2450, 1970.

15. Sheldon, R. A. and J. K. Kochi. In: Organic Reactions, W. G. Danben, ed. 1972.

16. Tinker, H. B. J. Catalysis, 19:237, 1970.

17. Berezin, I. V., E. T. Denisov, and N. M. Emanuel. The Oxidation of Cyclohexane. Pergamon, New York, 1964.

18. Clifford, A. A. and W. A. Waters. J. Chem. Soc., 2796, 1976.

19. Sax, N. Irving. Dangerous Properties of Industrial Materials, 4th ed. Van Nostrand-Reinhold, New York, New York, 1975.

20. International Technical Information Institute. Toxic and Hazardous Industrial Chemicals Safety Manual for Handling and Disposal with Toxicity and Hazard Data. Tokyo, 1976.

21. Christensen, Herbert E. and Edward J. Fairchild, eds. Registry of Toxic Effects of Chemical Substances. NIOSH, Rockville, Maryland, 1976.

22. Federal Register, "Hazardous Substances", EPA, Vol. 44 No. 34 - Friday, February 16, 1979.

SECTION 5

ANALYTICAL METHODS

A variety of analytical methods were employed in the analysis of samples collected during field testing and those generated in the laboratory experimentation. The following sections address each of the methods which were used, with emphasis on application, problems and accuracy.

5.1 ION CHROMATOGRAPHY

Ion chromatography (IC) is a relatively new technique for identifying and quantifying ions in solution, which offers the advantage of direct measurement of the concentration of the ions of interest. Ion exchange columns are used to separate the ions which are then detected by a conductivity meter. At low concentrations conductivity is directly proportional to concentration and is virtually linear. Concentrations of ions in the sample are determined by comparison with standard solutions. Identification of ionic species is based upon retention time of the ion in the system, which is a function of the affinity of that ion for the separator column under a given set of operating conditions. The retention time of specific ions is determined by analysis of standard solutions containing the species of interest. A Dionex Model 14 ion chromatograph was used for all IC work done on this project. Operating conditions are detailed in Appendix A with other pertinent information.

Ion chromatography was used as the principal method for quantitative determination of adipic acid concentration in all phases of this project. All material balance calculations related to testing at the IERL-RTP facility (Section 6) are based on adipic acid concentrations as measured by IC. Also, IC analyses were used for measurement of adipic acid degradation in all laboratory tests conducted as part of this project. In addition, IC analyses of liquid samples taken from the bench scale test apparatus during test runs were used to semi-quantitatively assess sulfite oxidation during the course of the experiment. This was done by comparing relative concentrations of $SO_4^{=}$ and $SO_3^{=}$ in the liquid phase of the test mixture.

Although IC analyses were found to be the most reliable means for quantifying adipate concentrations in FGD slurry samples and synthetic slurry samples, the method does present certain problems and disadvantages. The most significant problem encountered in the IC analyses was that of variations in peak resolution, with the sulfite and adipate peaks being the most difficult to resolve. The evaluation of IC data requires esta-

blishing a standard curve relating peak height to concentration. Poor resolution of the peaks in a standard or a sample gives rise to difficulties in measuring peak heights accurately, since the 'true' baseline is difficult to establish. Several factors tend to affect the resolution which can be achieved with IC. In several instances, observed decreases in the ability of the instrument to give good resolution of the adipate peak under a given set of conditions were traced to deterioration of the ion separator column. In some instances, regeneration procedures restored the column to previous performance levels. In other instances, it was necessary to modify parameters such as eluent strength to achieve acceptable resolution. In the most extreme cases, the separator column had to be replaced to bring instrument performance to an acceptable level. In order to achieve good resolution of the adipate peak, especially in the presence of sulfite, conditions had to be maintained such that each sample injection required some 18-24 minutes to elute all species completely.

The large number of samples collected and generated during the course of this project precluded replicate IC analysis of every sample. A large number of samples were analyzed two or more times, however, especially during the laboratory testing phase of the program. When replicate analyses were performed, the mean value is reported. The analytical data from twenty two samples which were analyzed two or more times were statistically evaluated to determine the accuracy of the method. The number of repeat analyses of a given sample ranged from two to seven, and were separated in time by up to several weeks. For each sample, the mean and root mean square (RMS) error were calculated. The RMS error was calculated to be 7% over the range of adipic acid concentrations measured (see data tables inSection 6). Thus, based upon the above error value, calculated material imbalances of greater than 10% are statistically valid.

5.2 GAS CHROMATOGRAPHY

Slurry and gas samples obtained from IERL-RTP and Shawnee facilities were analyzed for adipic, valeric, glutaric, and butyric acids by gas chromatography (GC). Gas samples obtained during the laboratory test studies were analyzed for low molecular weight hydrocarbons by GC. Operating conditions for GC analyses are detailed in Appendix A.

Slurry samples, NaOH impinger solutions and XAD-2 sorbent samples were prepared for analysis by extraction, concentration and derivitization. Liquid samples were acidified to pH 1 with concentrated HCl and then extracted with diethyl ether by either continuous extraction or separatory funnel extraction. Solid samples were extracted with diethyl ether in a Soxhlet extractor. The extracts were then concentrated and treated with diazomethane in order to form the methyl esters of any carboxylic acids present.

Individual samples were analyzed on the GC by direct injection. A flame ionization detector (FID) was employed in the analysis due to its sensitivity to all organic compounds. Identification of compounds in the samples was made by comparison of retention times with those of known standards prepared in the laboratory. A compound having the same retention time as a standard compound was identified as that compound. While this method of analysis is useful for the identification of a wide variety of compounds, it is at best semi-quantitative. Several prepared solutions of adipic acid ranging from 1500 ppm to 2500 ppm were extracted and analyzed. The apparent recovery ranged from 84% to 118%. Duplicate injections of standards indicate a variation between injections of up to 11%.

Multiple extractions and analyses of valeric acid standard solutions indicate an extraction and concentration efficiency of about 60%. Duplicate injections of samples indicate a variation between injections of up to 15%.

Gas samples from the laboratory degradation tests were of two types: headspace gases and gases purged from sorbent traps. The gases were sampled with a gas-tight syringe and loaded into a sample loop for injection onto the column. An FID detector was again chosen for the analysis. Peaks were identified by comparison of retention times with those of a standard gas mixture.

As in the case of the field sample analysis the specificity of this method is limited only by the reliability of assigning a positive identification to a peak with the same retention time as a standard. Accuracy is dependent on a number of factors including the degree of mixing of the gas and the reproducibility of the injection technique. A sample was analyzed four times with an average concentration of 41.1 ppm butane. The average deviation was found to be $\pm$ 3.4 ppm or $\pm$ 8.3%.

5.3 TOTAL ORGANIC CARBON

Ion chromatography was chosen as the method for quantitative adipic acid analyses of samples collected and generated during the course of this project. While the method has been demonstrated to give reliable values for adipate in solution, its ability to detect other organic species which might be present as a result of adipic acid degradation is not well documented. For this reason, all field samples which were analyzed by IC were also analyzed for total organic carbon (TOC). A Dohrmann DC-52D total organic carbon analyzer was used for these analyses. This instrument couples oxidative-reductive pyrolysis with a flame ionization detector (FID). A carbonate bypass system eliminates instrument response to inorganic carbonates (HCO_3^- and $CO_3^=$). Methane and ethane are vented during the carbonate bypass sequence; all other organic species are stoichiometrically converted to methane and detected by the FID. Data obtained by TOC analyses were primarily used for comparison to data obtained by GC and IC methods.

The TOC method is not specific for a particular organic species, such as adipic acid. Quantitative determination of a given species is possible only if it is the only one present. If, however, the concentration of one compound has been determined by some other method, additional carbon indicates the presence of other organics in the sample. Contamination can give rise to indications of extraneous carbon if care is not taken in sample handling. Filtration of samples through cellulose filters was found to give greatly inflated TOC values. For this reason, all field samples were filtered using polycarbonate membrane filters. Analytical data on twenty one samples collected at RTP during the first and second sampling trips were statistically evaulated to estimate the accuracy of the TOC method. The number of replicate analyses performed on any given sample ranged from two to fifteen. These analyses were performed over a period of several days and all analyses of a given sample were not necessarily done on the same day. The standard deviations expressed as percents of the means ranged from 0.4% to 10.5% with an average of 3.8%.

5.4 SOLID PHASE CHARACTERIZATION

5.4.1 Sulfite Analysis

Solids obtained from bench scale degradation studies were analyzed for their sulfite concentration by an iodometric titration with sodium arsenite.

In this procedure the sample is added to an excess of buffered iodine solution. The iodine remaining after the stoichiometric oxidation of sulfite is titrated with standard sodium arsenite solution. An amperometric dead-stop method was used for the endpoint detection. The analytical procedure is detailed in Appendix A.

5.4.2 Infrared Absorption Spectrophotometry

Calcium sulfite solids, generated to simulate scrubber solids in the bench scale tests, were analyzed by infrared spectrophotometry using a Perkin Elmer Model 283 spectrophotometer. This analysis provided a preliminary qualitative characterization of the $CaSO_3$ solids. A verification of the solids' sulfite concentration was later made using an iodometric titration method.

Infrared analysis was also performed on field samples collected from the IERL-RTP pilot facility. These samples included adipic acid feed and scrubber filtrate solids from the reaction tank.

The major limitation of infrared analysis is that the technique is primarily qualitative. However, with care the relative amounts of $CaCO_3$, $CaSO_4 \cdot 2H_2O$ and $CaSO_3 \cdot \frac{1}{2}H_2O$ in scrubber solid samples can be determined pro-

viding limestone utilization and oxidation ratios. The detection limit for organic compounds in the solids by direct infrared analysis is approximately 0.1% or 1000 ppm.

5.4.3 Organic Analysis

In addition to the infrared analysis a direct extraction procedure was used to determine the organic content of the solids. The dried solids were placed in a sohxlet extractor and diethylether was used as the extractant. The ether was subsequently removed and analyzed for extracted organics using the methylation-GC technique used in the liquid phase analyses. No organics were detected above the 10 ppm (in the solids) detection limit of this procedure. However, since the solids were not dissolved in this procedure organics incorporated in the solids would not be detected. Metal salts of organic acids present in the solid phase would not be measured using this technique. Future studies are needed to investigate the organic content of the scrubber solids.

5.5 CARBON DIOXIDE

The flow-through laboratory tests described in Section 7 employed sodium hydroxide impingers for trapping carbon dioxide generated in the decarboxylation of adipic acid. These NaOH solutions were analyzed for CO_2 using a non-dispersive infrared CO_2 analyzer. In this system, CO_2 is liberated after injection of the sample into an acid solution. The CO_2 is detected by the infrared analyzer and monitored by a recorder equipped with a disc chart integrator. The integrated peak area is then used to determine the amount of CO_2 present in the sample.

Samples of the NaOH solution used to trap CO_2 were preserved prior to analysis by addition of an ammonia-EDTA buffer solution to maintain a pH of $\sim$10. Samples of this buffer solution and of the stock NaOH solution were analyzed to determine background levels of CO_2 present in these solutions. These blank values were taken into account in the calculation of the amount of CO_2 generated in the degradation reaction.

This method of CO_2 determination is quite specific, especially when the sample matrix is well defined as in this application. The analyzing unit allows samples to be analyzed without introducing atmospheric carbon dioxide. Water vapor is removed from the gas stream by a series of drying tubes upstream of the detector. By using peak area instead of peak height, inaccuracies due to varying pH in the acid pool are virtually eliminated.

5.6 GAS CHROMATOGRAPHY-MASS SPECTROMETRY

The tenax tubes, VOA's and some extracts were analyzed utilizing a Hewlet-Packard 2982A combined gas chromatograph-mass spectrometer (GC-MS). A Hewlett-Packard 5934A Data System was used for the collection, storage, and retrieval of data.

The GC-MS instrument consists of a Hewlett-Packard 5710A gas chromatograph and a Hewlett-Packard 5982A dodecapole mass spectrometer and GC-MS interfaces. The instrument is equipped with a dual ion source for operation in the electron impact or chemical ionization mode. The major features of the system include: 3-1,000 amu mass range covered in a single scale; adjustable scan rate of 325 amu/sec.; sensitivity to picogram levels, even with large samples; provision for membrane and jet separators; AID measurements at every 0.1 amu; and resolution permitting full separation of half masses.

SECTION 6

RESULTS OF FIELD SAMPLING EFFORTS

During the course of this program Radian personnel conducted four field sampling trips. Three of these trips were to the RTP pilot unit and one to EPA's Shawnee test facility. Samples were collected during adipic acid addition tests to measure adipic acid and degradation products around the systems. The objective was to identify the degradation products and determine the relative amounts leaving the systems in the various exit streams such as the filter cake and scrubbed flue gases.

The sampling procedures and analytical results of the field studies are presented in this section.

6.1 GAS PHASE SAMPLING

The inlet and outlet flue gases and the oxidizer vent, in the case of forced oxidation, were sampled to measure the vapor concentration of any volatile degradation products. Prior to and during gas sampling, several parameters were measured in order to characterize the gas streams:

- gas flow rate,
- absolute pressure,
- temperature,
- percent CO_2 and O_2, and
- percent H_2O.

The gas flow rate was determined through the use of an S-type pitot tube used in conjunction with either a water manometer or a 0 to 1 inch magnehelic

gauge. The stack pressure was determined by disconnecting one leg of the pitot tube and measuring the pressure with a water manometer. The barometric pressure was determined by a barometer. The stack temperature was determined by insertion of a thermometer into the gas stream. Carbon dioxide and oxygen concentrations were determined by Orsat tests. Percent moisture was determined by drawing a known amount of stack gas through a pre-weighed, ice-cooled water impinger followed by a silica-gel impinger. The impingers were then weighed to determine the amount of moisture collected.

Flue gas samples were collected in a number of different ways. They include:

- XAD-2 resin traps (RTP only)
- Tenax sorbent traps (RTP only)
- NaOH impingers (RTP and Shawnee)
- Porapak Q sorbent traps (Shawnee only)

The XAD-2 resin traps were designed to collect semi-volatile and volatile organic compounds. The traps consisted of a 10 inch long by one inch diameter stainless steel tube packed with approximately 100 ml of the resin. The sampling train consisted of a six inch stainless steel probe followed by a Gelman filter. The resin canister was then attached and followed by a cooled dry impinger to eliminate moisture. The impinger was followed by a diaphragm pump, a needle valve to control flow and a dry gas meter. A diagram of the sampling train can be seen in Figure 6-1.

The Tenax sorbent traps were designed to trap medium molecular weight volatile compounds. They consisted of a 12 inch long by 1/8 inch diameter stainless steel, glass lined tube packed with Tenax GC 60/80 followed by silica gel 35/60 mesh. The sampling train was identical to that used for the XAD-2 canister.

The NaOH impingers were designed to trap volatile carboxylic acids. Two Smith-Greenburg impingers charged with 1N NaOH were used in each run. The sampling train was identical to that used previously.

The Porapak sorbent traps were designed to trap low molecular weight hydrocarbons. They consisted of a 24 inch long by 3/8 inch diameter stainless steel tube packed with approximately 30 ml of Porapak Q 100/120. During the run, the trap was preceded by one NaOH impinger. The sampling train was identical to that used previously.

6.2 LIQUID SAMPLING

Slurry samples were filtered on site through polycarbonate membrane filters into sample containers. A stainless steel filter holder was used in conjunction with a peristaltic pump. Solids were removed from the filter and placed in a sample container.

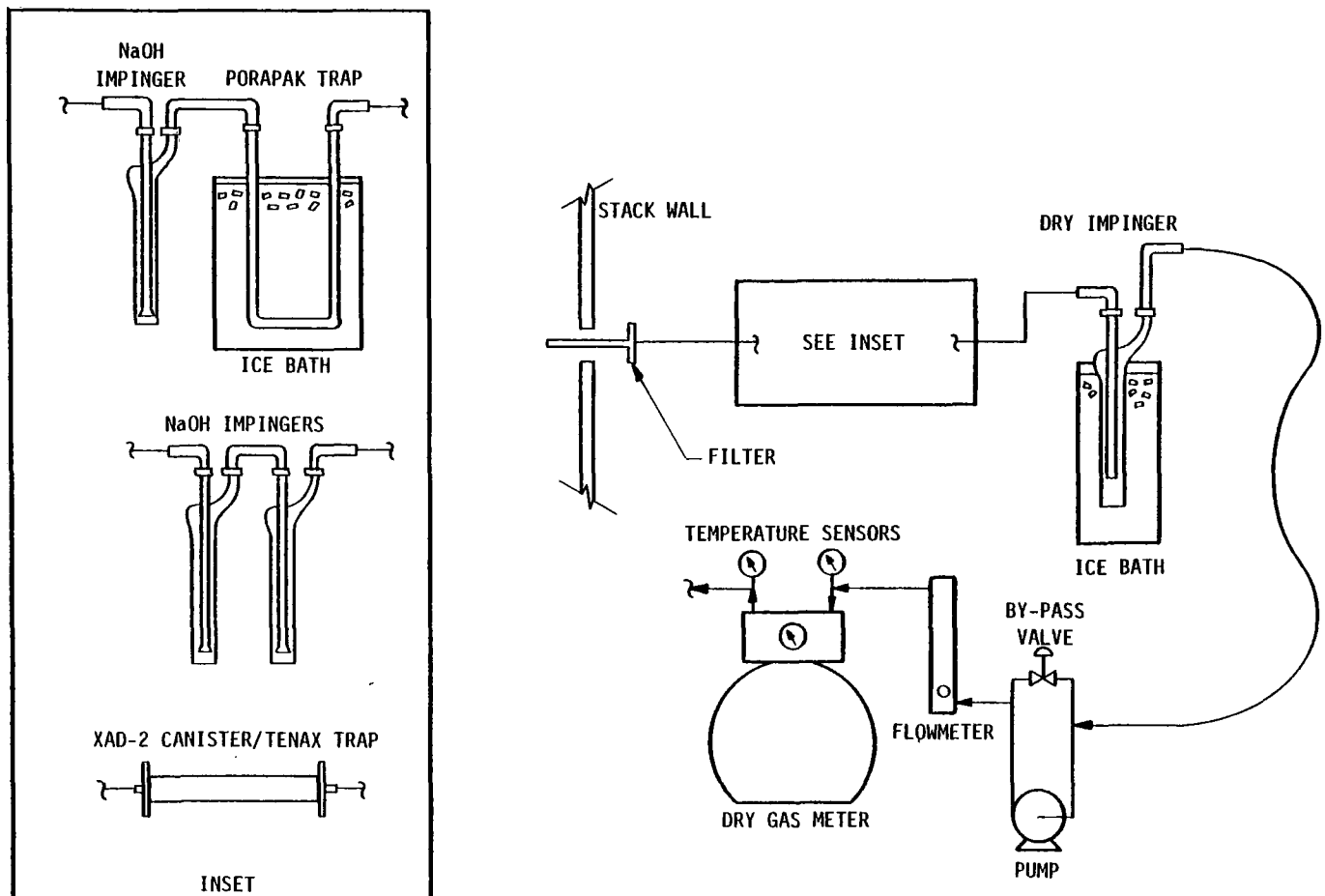


Figure 6-1. Gas phase sampling train.

6.3 RESULTS OF IERL-RTP MATERIAL BALANCE TEST (10/25/78)

During the week of October 22, Radian personnel conducted a field trip to IERL-RTP to sample the process streams around the pilot SO_2 scrubber during natural oxidation conditions. The samples taken are summarized in Table 6-1.

TABLE 6-1 SAMPLES OBTAINED AT IERL-RTP

Sampling Point	Type of Sample
1. Scrubber Flue Gas Outlet	XAD-2 resin (2) NaOH impinger Tenax adsorbent (2)
2. Scrubber Outlet Slurry	Filtered liquid (4) Filtered solids (4) Volatile organics, unfiltered (4)
3. Scrubber Feed Slurry	Same as #2 plus Tenax adsorbent (2) of head space
4. Adipic Acid Feed	Liquid composite
5. Filter Cake	Solid Sample
6. Filtrate from Filter	Filtered liquid Volatile organics, unfiltered

Slurry samples were analyzed by gas chromatography (GC), ion chromatography (IC), and total organic carbon (TOC) analysis. Flue gas samples were analyzed by GC. The only degradation products identified were valeric and glutaric acids. Results of these analyses are shown in Table 6-2.

Analysis of volatile organics samples by gas chromatography/mass spectrometry (GC-MS) showed only trace amounts of organic materials at the ppb level.

The configuration of the IERL-RTP scrubber under natural oxidation conditions can be seen in Figure 6-2. Adipic and valeric acid concentrations and mass flows are indicated.

TABLE 6-2 RESULTS OF ANALYSIS OF IERL-RTP (10/25/78) SAMPLES (NATURAL OXIDATION TESTS)

Stream/Set	Time	GC Adipic Acid (mg/ℓ)	GC Adipic Acid (mmoles C/ℓ)	GC Valeric Acid (mg/ℓ)	GC Valeric Acid (mmoles C/ℓ)	GC Glutaric Acid (mg/ℓ)	GC Glutaric Acid (mmoles C/ℓ)	IC Adipic Acid (mg/ℓ)	IC Adipic Acid (mmoles C/ℓ)	IC Chloride (mg/ℓ)	IC Sulfate (ppm)	TOC Organic Carbon (mmole C/ℓ)	TOC Sum of Species (mmole C/ℓ)
								RTP[1]					
Scrubber Outlet Slurry													
I	1130-1300	2,060	85	70	3	10	<1	2,560	105	4,790	10,760	114	108
II	1345-1430							2,410	99	4,540	11,140	118	102
III	1530-1650							2,560	105	4,720	11,430	112	108
IV	1730-1745							2,560	105	4,610	10,760	113	108
							Avg.	2,520	104	4,670	11,020	113	107
Scrubber Feed Slurry													
I	1130-1300	2,260	93	70	3	10	<1	2,410	2,150 99	4,610	10,470	112	102
II	1345-1430							2,560	105	4,720	12,010	113	108
III	1530-1650							2,630	108	4,790	12,300	115	111
IV	1730-1745							2,480	2,130 102	4,820	15,370	111	105
							Avg.	2,520	104	4,740	12,540	113	107
Filtrate from Filter	1530-1650	2,070	85	80	4	20	1	2,410	99	4,720	10,760	107	104
Adipic Acid Feed Composite	1130-1745	10,610	436	ND[2]		ND		9,500	390	ND	49,470	406	390
Flue Gas[3]													
XAD-2	1200-1400	ND		1.0	<1								
XAD-2	1600-1800	ND		2.3	<1								
NaOH impinger	1430-1455	ND		0.7	<1								

[1]Concentration as analyzed by Acurex personnel on-site

[2]"Not detected"

[3]Concentrations are expressed as ppmv

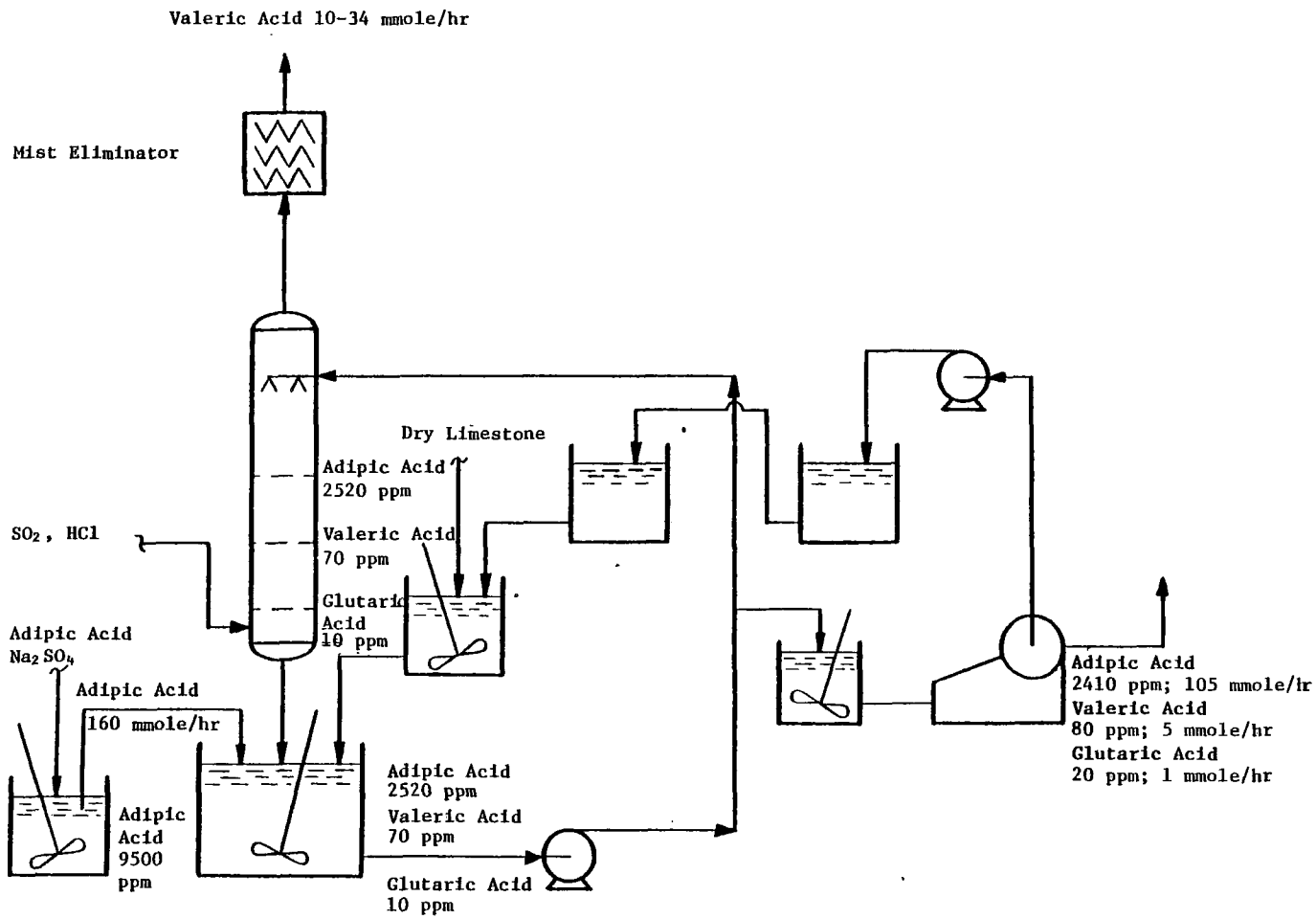


Figure 6-2. IERL-RTP scrubber configuration (natural oxidation).

TABLE 6-3. MATERIAL BALANCE CALCULATIONS: IERL-RTP 10/25/78[1]
(NATURAL OXIDATION TESTS)

	Process Stream	Concentrations			Stream Flow Rate (ℓ/hr)	Species Flow Rates			Total (mmole/hr)
		Adipic Acid (mmole/ℓ)	Valeric Acid (mmole/ℓ)	Glutaric Acid (mmole/ℓ)		Adipic Acid (mmole/hr)	Valeric Acid (mmole/hr)	Glutaric Acid (mmole/hr)	
Inlet	Adipic acid feed	72.7	--	--	2.2	160	--	--	160
								Total Inlet	160
Outlet	Outlet flue gas	--	$3\text{-}10 \times 10^{-5}$	--	3.4×10^{5}	--	10-34	--	10-34
	Filter cake liquor	16.5	0.8	0.2	6.0	99	5	1	105
	Scrubber liquor losses	17.3	0.7	0.8	1.0	17	1	1	19
								Total Outlet	134-158
								Recovery Fraction	84-99%
								Adipic Acid Degradation	28%

[1]Blowdown data based on IERL-RTP calculations for this period

As can be seen from Figure 6-2, the rate of valeric acid loss in the flue gas is in the range of 10 mmole/hr to 34 mmole/hr. Since the adipic acid feed rate to the scrubber is 160 mmole/hr, the loss of valeric acid represented from 6% to 21% of the amount of adipic acid fed into the system.

To assess whether the measured gas phase concentrations of valeric acid are reasonable, the stripping rate or change in the liquid phase valeric acid concentration across the scrubber was calculated. Using the extreme values of valeric acid measured in the gas phase, the change in the liquid concentration would range from 0.2 to 0.8 mg/ℓ. This represents a change in the liquid phase concentration, 70 mg/ℓ, or less than 2%, which considering the boiling point of valeric acid, seems reasonable. However, a direct measure of the change in the liquid concentration of valeric acid across the scrubber would be difficult.

The material balance for adipic acid and its degradation products shown in Table 6-3 closes within 15% or less depending on which gas phase valeric acid value is correct. Approximately 28% of the adipic acid added during the natural oxidation tests is degraded. Valeric acid appears to be the major decomposition product with most of the valeric discharged in the outlet flue gas. Some glutaric acid was also found in the aqueous solutions within the scrubber system but none in the flue gases.

6.4 RESULTS OF IERL-RTP MATERIAL BALANCE TEST (11/15-16/78)

During the week of November 13, Radian personnel conducted a field trip to IERL-RTP to sample the process streams around the pilot SO_2 scrubber during forced oxidation testing. The samples taken are summarized in Table 6-4.

TABLE 6-4. SAMPLES OBTAINED AT IERL-RTP (11/15-16/78)

Sampling Point	Type of Sample
1. Scrubber Flue Gas Outlet	XAD-2 resin (2) NaOH impinger (2) Tenax adsorbent (2)
2. Scrubber Outlet Slurry	Filtered liquid (4) Filtered solids (4) Volatile organics, unfiltered
3. Scrubber Feed Slurry	Same as #2
4. Adipic Acid Feed	Liquid composite

(continued)

TABLE 6-4. Continued

Sampling Point	Type of Sample
5. Filter Cake	Solid sample
6. Filtrate from Filter	Filtered liquid
7. Flue Inlet to Scrubber	XAD-2 resin NaOH impinger Tenax adsorbent
8. Oxidizer Air Vent	NaOH impinger

Slurry samples collected at IERL-RTP were analyzed by gas chromatography (GC), ion chromatography(IC), and total organic carbon (TOC) analysis. Flue gas samples were analyzed by GC. Results of these analyses are shown in Table 6-5. In addition, tenax adsorbent samples of the flue gas outlet and flue inlet to scrubber were analyzed by GC-MS and compared. Differences due to the scrubber were too insignificant and poorly resolved to warrant meaningful identification.

The configuration of the IERL-RTP pilot scrubber under forced oxidation conditions can be seen in Figure 6-3. Adipic and valeric acid concentrations and mass flows are indicated in the appropriate places.

The rate of valeric acid loss indicated in Figure 6-3 is in the range of 1.4 mmole/hr to 6.5 mmole/hr. The adipic acid feed rate was 127 mmole/hr. Therefore, the amount of adipic acid lost as valeric acid in the flue gas is in the range of 1% to 5% of that added.

The material balance for adipic acid and its degradation products shown in Table 6-6 closes only within 58% or less depending on which gas phase valeric acid value is correct. Approximately 69% of the adipic acid added during this forced oxidation test is degraded. Again valeric acid appears to be the major decomposition product, but in this case glutaric acid makes a significant contribution to the material balance. Valeric acid is discharged in the flue gas and liquor while glutaric acid is discharged only in the liquor.

6.5 RESULTS OF IERL-RTP MATERIAL BALANCE TEST (12/18-22/78)

During the week of December 18, Radian personnel conducted a field trip to IERL-RTP to sample the process streams around the pilot SO_2 scrubber during forced oxidation testing. The samples taken are summarized in Table 6-7

TABLE 6-3 RESULTS OF ANALYSIS OF IERL-RTP (11/15/78-11/16/78) SAMPLES
(FORCED OXIDATION TESTS)

Stream/Set	Time	GC						IC						TOC	Sum of Species
		Adipic Acid (mg/ℓ)	Adipic Acid (mmoles C/ℓ)	Valeric Acid (mg/ℓ)	Valeric Acid (mmoles C/ℓ)	Glutaric Acid (Estimated) (mg/ℓ)	Glutaric Acid (Estimated) (mmoles C/ℓ)	Adipic Acid (mg/ℓ)	Adipic Acid (mmoles C/ℓ)	Chloride (mg/ℓ)	Sulfate (mg/ℓ)	Organic Carbon (mmoles C/ℓ)	(mmoles C/ℓ)
								RTP[1]		RTP[1]	RTP[1]		
Scrubber Outlet Slurry													
I	1345-1415							730	30	9080	2500	59	37
II	2120-2130	Composite 810	33	80	4	70	3	660 760	27	8960 1040	2500 2680	46	34
III	0600-0610							790	32	9700	2570	55	39
IV	1340-1350							880	36	9870	2740	51	43
								Avg. 760	31	Avg. 9400	2580	Avg. 53	Avg. 38
Scrubber Feed Slurry													
I	1345-1415							590	24	8960	2500	55	32
II	2120-2130	Composite 860	35	100	5	70	3	730 760	30	9080 1030	2500 2760	55	32
III	0600-0610							800	33	9820	2400	57	41
IV	1340-1350							730	30	9650	2830	64	38
								Avg. 710	29	Avg. 9380	2560	Avg. 58	Avg. 37
Filter Liquor IV	1500	580	24	50	2	50	2	440	18	6370	2160	34	22
Adipic Acid Feed	Composite	7920	325	ND[2]		ND		8040	330	ND	38900	324	330
Flue Gas[3]													
XAD-2 I	1310-1510	ND		0.07	<1								
NaOH Impinger I;III	Composite	ND		0.3	<1								
Sparge Outlet NaOH Impinger II	2158-2223	ND		0.4	<1								

[1]Concentration as analyzed by Accurex personnel on site
[2]"Not Detected"
[3]Concentrztions expressed as ppmv

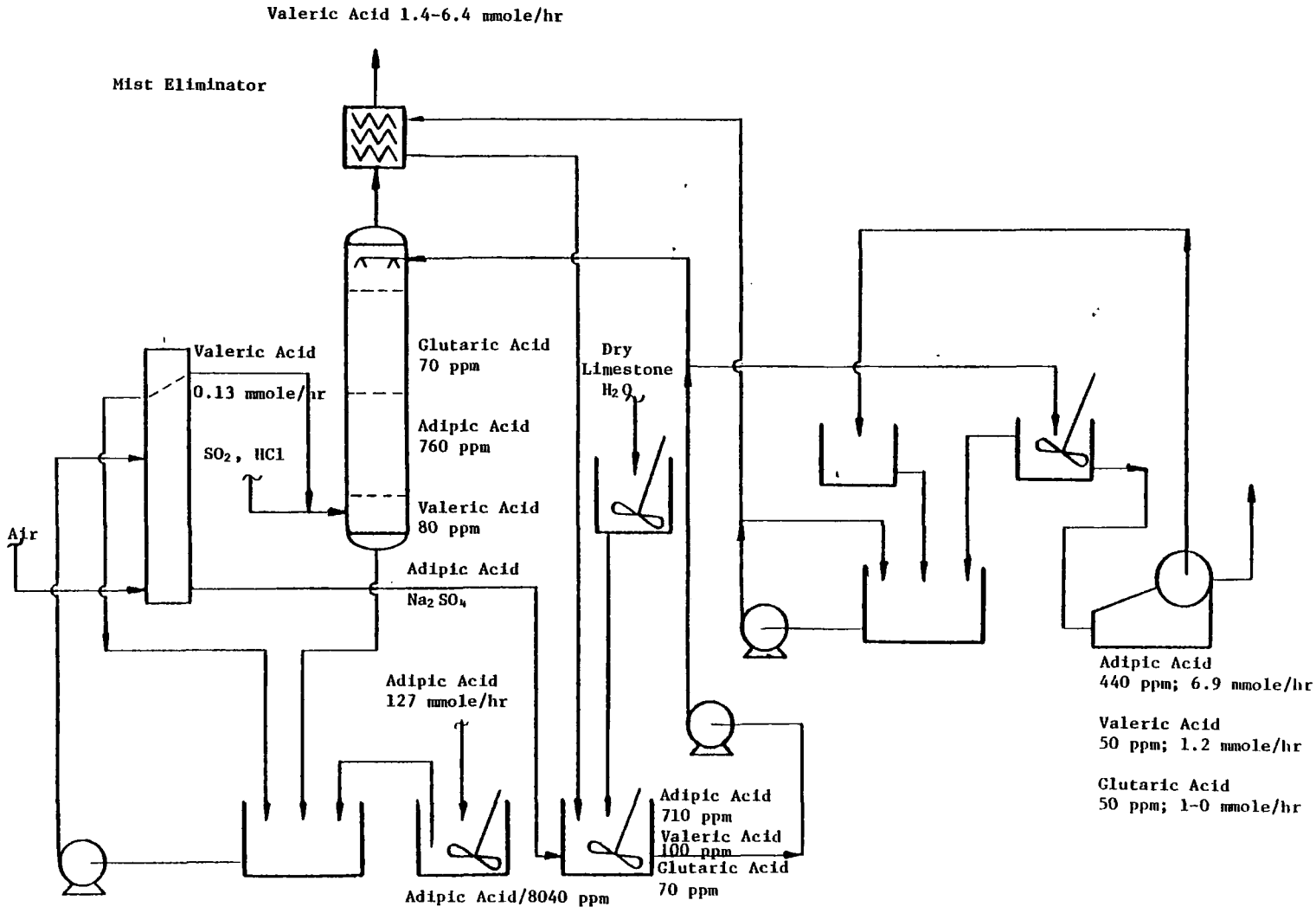


Figure 6-3. IERL-RTP scrubber configuration (forced oxidation).

TABLE 6-6 MATERIAL BALANCE CALCULATIONS; IERL-RTP 11/15/78-11/16/78[1]
(FORCED OXIDATION TESTS)

	Process Stream	Concentrations			Stream Flow Rate	Species Flow Rate			
		Adipic Acid (mmole/ℓ)	Valeric Acid (mmole/ℓ)	Glutaric Acid (mmole/ℓ)	(ℓ/hr)	Adipic Acid (mmole/hr)	Valeric Acid (mmole/hr)	Glutaric Acid (mmole/hr)	Total (mmole/hr)
Inlet	Adipic acid feed	55.0	--	--	2.3	127	--	--	127
								Total Inlet	127
Outlet	Outlet flue gas	--	$3\text{-}13 \times 10^{-6}$	--	4.8×10^{5}	--	1.4-6.4	--	1.4-6.4
	Filter cake liquor	3.0	0.5	0.4	2.3	6.9	1.2	1.0	9.1
	Scrubber liquor losses[2]	5.0	0.9	0.5	6.6	33	5.9	3.3	42.2
								Total Outlet	52.7-57.7
								Recovery Fraction	42 - 45%
								Adipic Acid Degradation[3]	69%

[1] Blowdown data based on IERL-RTP calculations for this period.

[2] Incidental scrubber solution losses other than those associated with the filter cake.

[3] Degradation is defined as the difference between the adipic acid feed rate and the measured discharge rate.

TABLE 6-7 SAMPLES OBTAINED AT IERL-RTP

Sampling Point	Type of Sample
1. Scrubber Flue Gas Outlet	XAD-2 resin (composite) NaOH impinger (composite) Tenax adsorbent (4)
2. Scrubber Outlet Slurry	Filtered liquid (8) Filtered solids (8) Volatile organics (8)
3. Scrubber Slurry Hold Tank	Filtered liquid (4) Filtered solids (4) Volatile organics (4)
4. Adipic Acid Reaction Tank	Filtered liquid (7) Filtered solids (5) Volatile organics (5)
5. Adipic Acid Feed	Liquid composite
6. Filter Cake	Solid Sample (2) Volatile organics (2)
7. Filter Liquor	Filtered liquid (2)
8. Inlet to Flue	XAD-2 resin NaOH impinger Tenax adsorbent
9. Oxidizer Air Vent	NaOH impinger Tenax adsorbent

Slurry samples collected at IERL-RTP were analyzed by GC, IC and TOC. Flue gas samples were analyzed by GC. Results of these analyses are shown in Table 6-8.

The configuration of the scrubber under forced oxidation conditions is shown with adipic and valeric acid concentrations and mass flows in Figure 6-4.

The average rate of valeric acid loss indicated in Figure 6-4 is 8.3 mmole/hr. The adipic acid feed rate measured by Radian personnel for the period during which samples were analyzed was 520 mmole/hr. The loss as valeric acid accounts for 1.6% of the adipic acid added.

TABLE 6-8. RESULTS OF ANALYSIS OF IERL-RTP (12/18/78-12/22/78) SAMPLES (FORCED OXIDATION TESTS)

Stream/Set	Time	GC Adipic Acid (mg/ℓ)	GC Adipic Acid (mmoles C/ℓ)	GC Valeric Acid (mg/ℓ)	GC Valeric Acid (mmoles C/ℓ)	GC Glutaric Acid (mg/ℓ)	GC Glutaric Acid (mmoles C/ℓ)	IC Adipic Acid (mg/ℓ)	IC Adipic Acid (mg/ℓ) RTP[1]	IC Adipic Acid (mmoles C/ℓ)	TOC Organic Carbon (mmoles C/ℓ)	Sum of Species (mmoles C/ℓ)
Scrubber Outlet Slurry (SE)	12/21/78											
IX	1315	3,070	126	280	14	320	12	3,360		138	210	164
X	2150	3,370	138	120	6	160	6	3,870		159	224	171
Scrubber Feed Slurry (HT)												
IX	1350	3,620	149	120	6	190	7	3,480	3,875	143	203	156
X	2210	2,260[2]	93[2]	180	9	180	7	4,400	2,950	181	229	197
Filter Liquor XI	2/22/78 070	1,980[2]	81[2]	120	6	190	7	4,290		176	152	189
Adipic Feed	composite	11,180[2]	459[2]	ND[3]		ND		26,520		1,090	1,334	1,090
Flue Gas[7]												
XAD-2	composite			0.43								
NaOH Impinger	composite			0.41								
Sparge outlet	1320			0.23								

[1]Concentration as analyzed by Accurex personnel on site

[2]Inefficient extraction is indicated

[3]"Not detected"

[7]Concentrations are expressed as ppmv

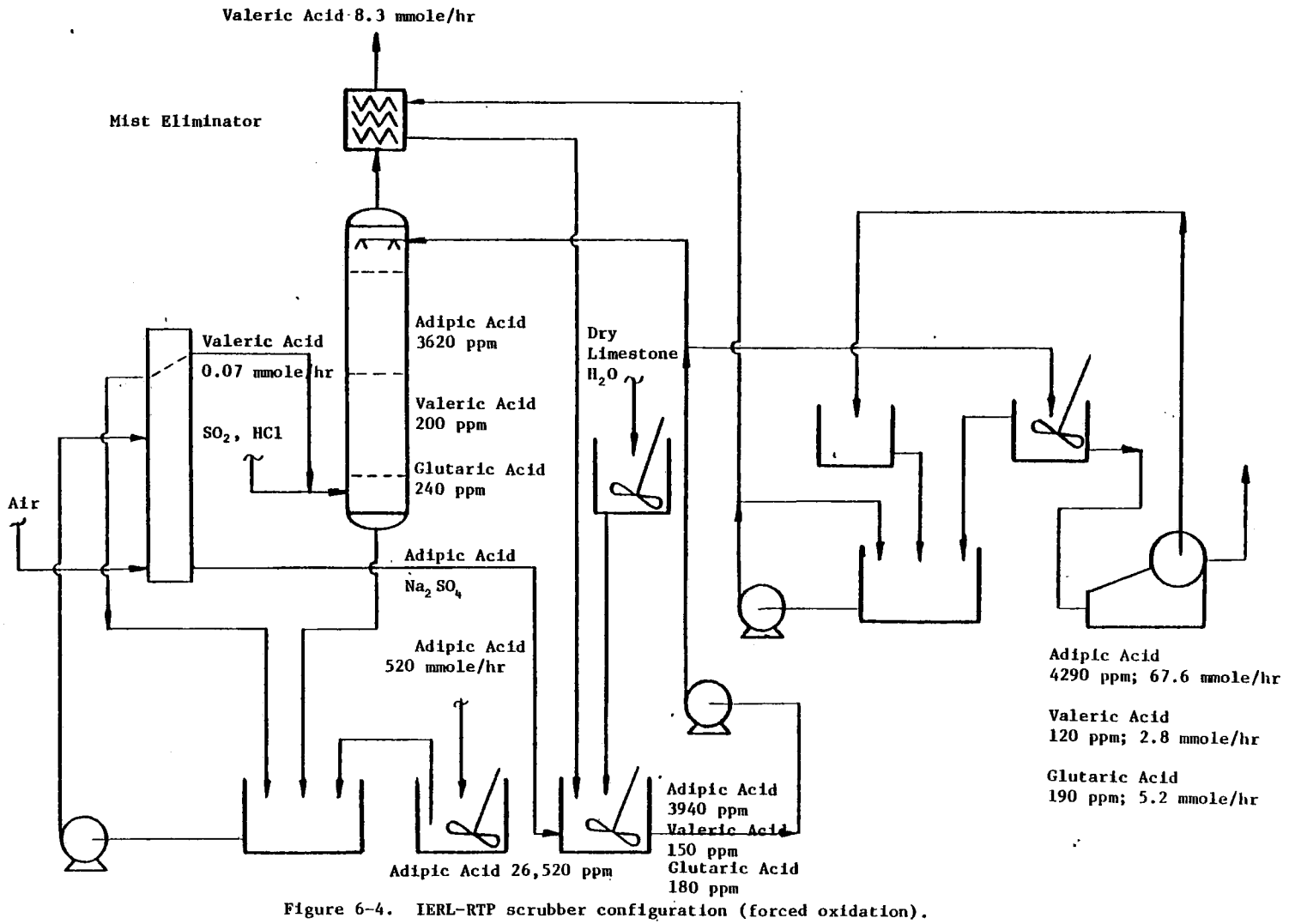


Figure 6-4. IERL-RTP scrubber configuration (forced oxidation).

TABLE 6-9 MATERIAL BALANCE CALCULATIONS; IERL-RTP 12/21/78[1]
(FORCED OXIDATION TESTS)

	Process Stream	Concentrations: Adipic Acid (mmole/ℓ)	Concentrations: Valeric Acid (mmole/ℓ)	Concentrations: Glutaric Acid (mmole/ℓ)	Stream Flow Rate (ℓ/hr)	Species Flow Rate: Adipic Acid (mmole/hr)	Species Flow Rate: Valeric Acid (mmole/hr)	Species Flow Rate: Glutaric Acid (mmole/hr)	Total (mmole/hr)
Inlet	Adipic acid feed	181	--	--	2.9	520	--	--	520
								Total Inlet	520
Outlet	Outlet flue gas	--	1.7×10^{-5}	--	4.8×10^{5}	--	8.3	--	8.3
	Filter cake liquor	29.4	1.2	1.4	2.3	67.6	2.8	3.2	73.6
	Scrubber liquor losses[2]	25.9	1.7	1.6	6.6	171.0	11.2	10.6	192.8
								Total Outlet	275
								Recovery Fraction	53%
								Adipic Acid Degradation[3]	54%

[1]Blowdown data based on IERL-RTP calculations for November 13-17.

[2]Incidental scrubber solution losses other than those associated with the filter cake.

[3]Degradation is defined as the difference between the adipic acid feed rate and the measured discharge rate.

The material balance for adipic acid and its degradation products shown in Table 6-9 closes only within 47%. Approximately 54% of the adipic acid added during this forced oxidation test is degraded. Both valeric acid, which is discharged in the flue gas and liquor, and glutaric acid, which is discharged in the liquor, appear to be major degradation products. In addition, an extract of the filter liquor was analyzed by GC-MS and found to contain small amounts (<10 ppm) of succinic acid. The amount of succinic acid was not great enough, however, to significantly affect the material balance.

6.6 RESULTS OF SHAWNEE MATERIAL BALANCE TEST

Radian personnel conducted a field trip to EPA's Shawnee Test Facility on February 2, 1979 to sample the process streams around the scrubber. The samples taken are summarized in Table 6-10.

TABLE 6-10 SAMPLES OBTAINED AT SHAWNEE

Sampling Point	Type of Sample
1. Venturi Inlet	NaOH impinger Porapak sorbent
2. Venturi Outlet	NaOH impinger Porapak sorbent
3. Oxidizer Air Vent	NaOH impinger Porapak sorbent
4. Venturi Feed	Filtered Slurry Filtered Solids Volatile Organics
5. Spray Tower Feed	Filtered Slurry Filteres Solids Volatile Organics
6. Clarifier Underflow	Filtered Slurry Filtered Solids Volatile Organics
7. Filter Effluent	Filtered Slurry Filtered Solids Volatile Organics
8. Spray Tower Effluent	Filtered Slurry Filtered Solids Volatile Organics

TABLE 6-10 Continued

Sampling Point	Type of Sample
9. Clarifier Overflow	Filtered Slurry Filtered Solids Volatile Organics
10. Venturi Effluent	Filtered Slurry Filtered Solids Volatile Organics

Slurry samples collected at Shawnee were analyzed by GC, IC and TOC. Flue gas samples were analyzed by GC. Results of these analyses are given in Table 6-11.

The configuration of the Shawnee scrubber is shown along with adipic and valeric acid mass flows in Figure 6-5.

The rate of valeric acid loss in the flue gas is 1300 mmole/hr. The adipic acid feed rate is 17,400 mmole/hr. The loss as valeric acid accounts for 7.5% of the adipic acid added.

The material balance for adipic acid and its degradation products shown in Table 6-12 closes only within 17%. Approximately 91% of the adipic acid added during this forced oxidation test is degraded. The major degradation product appears to be valeric acid which is lost from the flue. Valeric and glutaric acid were both found in the liquid phase portion of the recycle slurry samples, but not in the liquid associated with the filter cake. This lack of valeric and glutaric acid in the filter liquor is significant in that it may indicate these species are consumed in the scrubber slurry.

In an attempt to detect low molecular weight hydrocarbons in the flue gas at Shawnee, a sample of the flue gas was drawn through a sorbent trap containing Porapak Q. Earlier work had indicated that trapped hydrocarbons could be thermally de-sorbed from Porapak Q. Subsequent testing however indicated that upon heating Porapak Q bleeds methane, ethane, propane and butane, making identification of components of the flue gas difficult if not impossible.

6.7 SOLIDS CHARACTERIZATION

The presence of many organic compounds during the precipitation of inorganic (ionic) crystals is known to cause changes in the particle shape and/or size. This change in crystal morphology may or may not be associated with an incorporation of the organic species into the crystalline phase. In order to evaluate the effects of adipic acid on the precipitation of calcium sulfite and calcium sulfate solid samples collected during the

TABLE 6-11. RESULTS OF ANALYSIS OF SHAWNEE (2/2/79) SAMPLES (FORCED OXIDATION TESTS)

Stream	GC						IC		TVA[1]	TOC
	Adipic Acid		Valeric Acid		Glutaric Acid		Adipic Acid			Organic Carbon
	(mg/ℓ)	(mmoles C/ℓ)	(mg/ℓ)	(mmoles C/ℓ)	(mg/ℓ)	(mmoles C/ℓ)	(mg/ℓ)	(mmoles C/ℓ)	(mg/ℓ)	(mmoles C/ℓ)
Venturi Feed Slurry 413	1040	43	ND[2]		20	<1	820	34	2288	99
Spray Tower Feed-Slurry 416	960	39	25	1	10	<1	470	19	1544	72
Clarifier Underflow 419	NA						450	18	NA	86
Spray Tower Effluent 424	680	28	250	12	10	<1	690	28	1544	80
Clarifier Overflow 428	NA						950	39	NA	100
Venturi Effluent 431	1180	48	20	1	75	3	900	37	2288	99
Filtrate 425	810	33	ND		ND		620	25	NA	67
Gas										
Venturi Outlet			0.8[3]							
Venturi Oxidizer Vent			ND							

[1]Concentration as analyzed by TVA personnel on site
[2]"Not Detected"
[3]Concentration expressed as ppmv

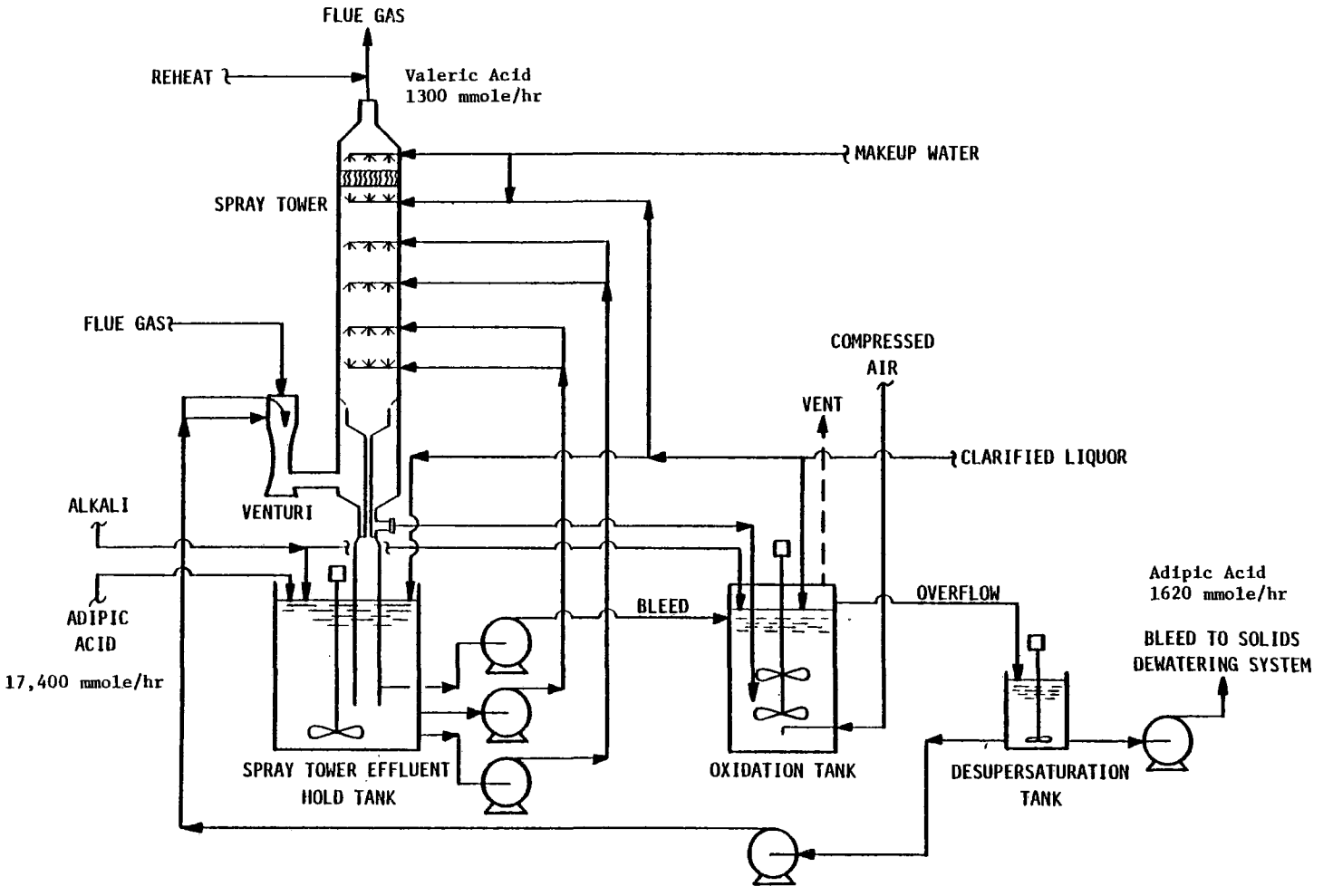


Figure 6-5. Shawnee scrubber configuration.

TABLE 6-12 MATERIAL BALANCE CALCULATIONS - SHAWNEE FACILITY[1]
(FORCED OXIDATION TESTS)

	Process Stream	Concentrations: Adipic Acid (mmole/ℓ)	Concentrations: Valeric Acid (mmole/ℓ)	Concentrations: Glutaric Acid (mmole/ℓ)	Stream Flow Rate (ℓ/hr)	Species Flow Rate: Adipic Acid (mmole/hr)	Species Flow Rate: Valeric Acid (mmole/hr)	Species Flow Rate: Glutaric Acid (mmole/hr)	Total (mmole/hr)
Inlet	Adipic acid feed	--	--	--	--	17,400	--	--	17,400
								Total Inlet	17,400
Outlet	Outlet flue gas	--	3.63×10^{-5}	--	3.58×10^{7}	--	1,300	--	1,300
	Filter cake liquor	7.9	nd	nd	204	1,620	--	--	1,620
	Scrubber liquor losses[2]	--	--	--	--	--	--	--	
								Total Outlet	2,920
								Recovery Fraction	17%
								Adipic Acid Degradation[3]	91%

[1]Blowdown data, adipic acid feed rate and gas flows based on Bechtel calculations for October 10 through November 1.

[2]Incidental scrubber solution losses other than those associated with the filter cake.

[3]Degradation is defined as the difference between the adipic acid feed rate and the measured discharge rate.

adipic acid addition tests were examined using scanning electron microscopy (SEM). Infrared analyses were also performed to semiquantitatively determine the ratios of calcium carbonate ($CaCO_3$), calcium sulfite hemihydrate ($CaSO_3 \cdot \frac{1}{2}H_2O$), coprecipitate ($xCaSO_3 \cdot \frac{1}{2}H_2O$ $(x-1)CaSO_4 \cdot \frac{1}{2}H_2O$), and calcium sulfate dihydrate ($CaSO_4 \cdot 2H_2O$).

The electron micrographs of the solids collected from the IERL-RTP pilot system during natural oxidation tests are shown in Figure 6-7. These are compared to calcium sulfite crystals previously taken from Shawnee during low oxidation conditions, (Figure 6-6) but with no adipic acid present. The crystals grown in the presence of adipic acid appear to be much more layered than usual. This appears to correlate with a small change in filterability of the solids as measured during RTP tests. The weight percent solids dropped to 49% at adipic acid concentrations near 2000 ppm from a normal value of 55% (1).

The calcium sulfate dihydrate crystals produced during forced oxidation runs using adipic acid seem to show a decrease in average size as the concentration of adipic acid increases. This effect can be seen in the electron micrographs shown in Figure 6-8 to 6-11..

Infrared spectral analyses were performed to characterize the general composition of the scrubber solids. Samples from both natural and forced oxidation tests were analyzed. No organic compounds could be detected in these samples (detection limit is approximately 1000 ppm). The inorganic compositions as determined by infrared spectroscopy are shown in Table 6-13 along with average compositions of the solids analyzed by on-site personnel during the appropriate test periods.

TABLE 6-13 COMPOSITIONAL ANALYSIS OF SCRUBBER SOLIDS

Technique	Sample Period	Limestone Utilization (%)	Oxidation Fraction (%)
Chemical Analysis (RTP)	10/23-27/78	92-103	30
Infrared Spectroscopy	10/25/78 (am)	>95	20
Infrared Spectroscopy	10/25/78 (pm)	>95	69
Chemical Analysis (RTP)	11/13-17/78	79-82	97
Infrared Spectroscopy	11/15/78	80	75
Infrared Spectroscopy	11/16/78	75%	>95

Figure 6-6. Calcium sulfite hemihydrate crystals taken from EPA's Shawnee Test Facility, no additives (x500).

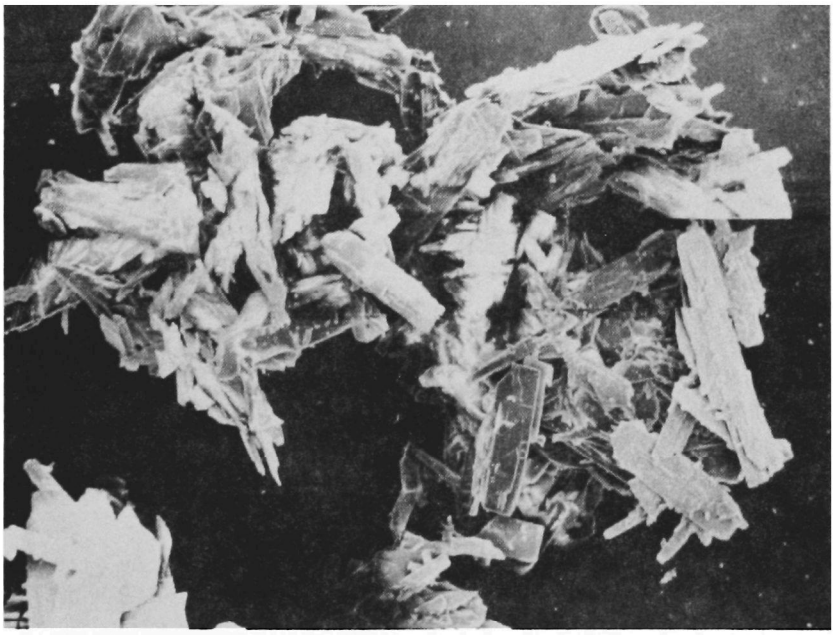


Figure 6-7. Calcium sulfite hemihydrate crystals from natural oxidation tests at RTP, 2500 ppm adipic acid (x590).

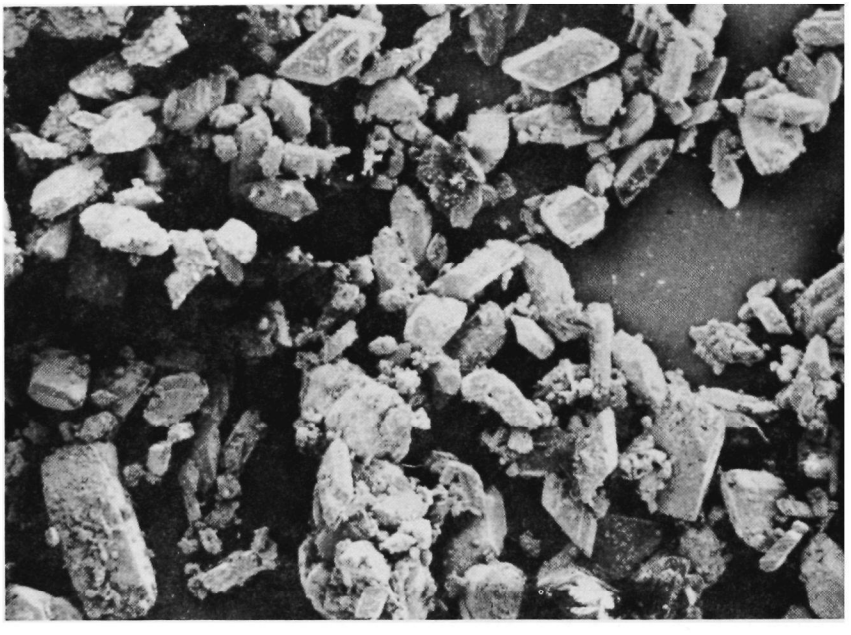


Figure 6-8. Calcium sulfate dihydrate crystals from forced oxidation tests at RTP, 600 ppm adipic acid (x200).

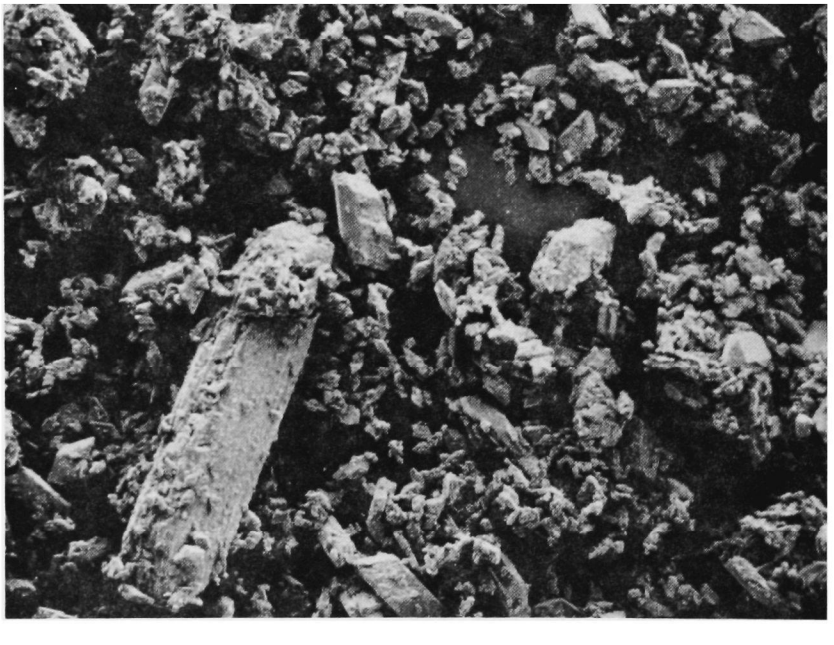


Figure 6-9. Calcium sulfate dihydrate crystals from forced oxidation tests at RTP, 4000 ppm adipic acid (x200).

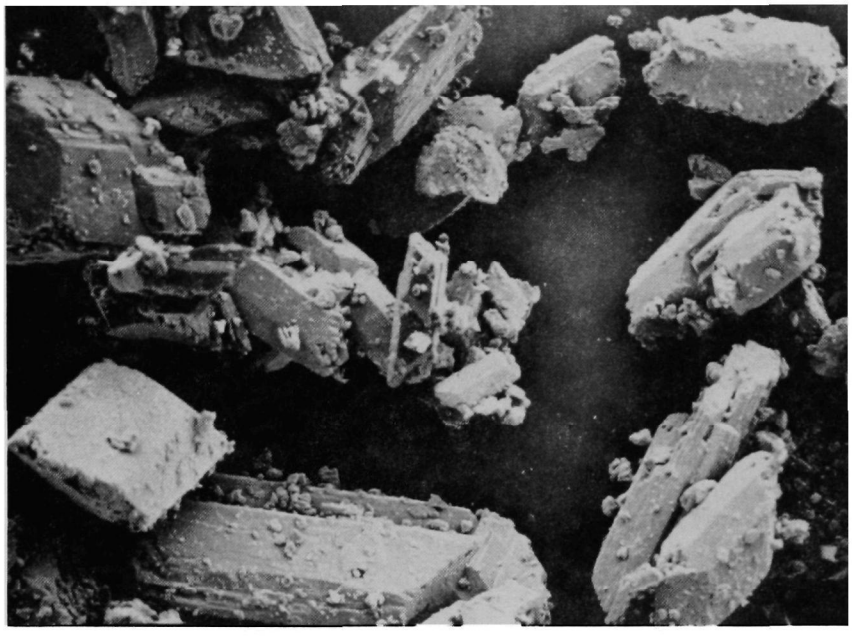


Figure 6-10. Calcium sulfate hemihydrate crystals from forced oxidation tests at RTP, 600 ppm adipic acid (x460).

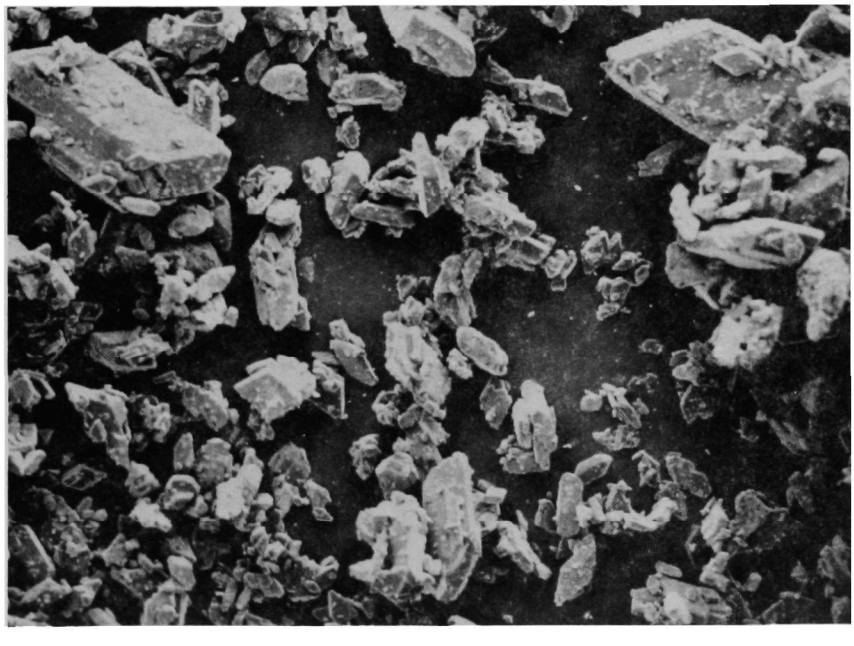


Figure 6-11. Calcium sulfate hemihydrate crystals from forced oxidation tests at RTP, 4000 ppm adipic acid (x460).

6.8 FIELD DATA CORRELATION

The adipic acid degradation observed at RTP and Shawnee was correlated with the sulfite oxidation rate and the adipic acid concentration in solution to determine the influence of these parameters. The test data used in this correlation are presented in Table 6-14. The graphical relationship is shown in Figure 6-12. Although there is substantial scatter in the data, it does appear that increases in both the sulfite oxidation rate and the adipic acid concentration will produce an increase in the degradation rate. Therefore, for control purposes, the adipic acid concentration should be maintained at a value just needed to accomplish the desired increase in removal efficiency. Since the use of organic acids for increased mass transfer purposes will be most desirable in forced oxidation solutions, the oxidation rate will be set by the amount of SO_2 absorbed across the scrubber. The stoichiometry of excess air to sulfite may have some effect on the degradation mechanism.

TABLE 6-14 ADIPATE DECOMPOSITION DATA FROM RTP AND SHAWNEE

Date	Location	Run Type	Adipate Conc. (ppm)	Adipate Degradation Rate (lb/hr)	Sulfite Oxidation Rate (lb SO_2/hr)
9/14-18/78	RTP	For. Ox.	1650	.0300	5.1
10/16-20/78	RTP	Nat. Ox.	2050	.0142	0.90
10/23-27/78	RTP	Nat. Ox.	2090	.0143	0.94
10/30-11/3/78	RTP	Nat. Ox.	1630	.0144	1.2
11/6-10/78	RTP	For. Ox	709	.0255	4.9
11/13-17/78	RTP	For. Ox.	760	.0238	5.4
11/27-12/1/78	RTP	For. Ox.	633	.0243	5.5
10/8-30/78	Shawnee	For. Ox.	2350/1550	4.9	490
10/10-30/78	Shawnee	Nat. Ox.	1620	2.3	110

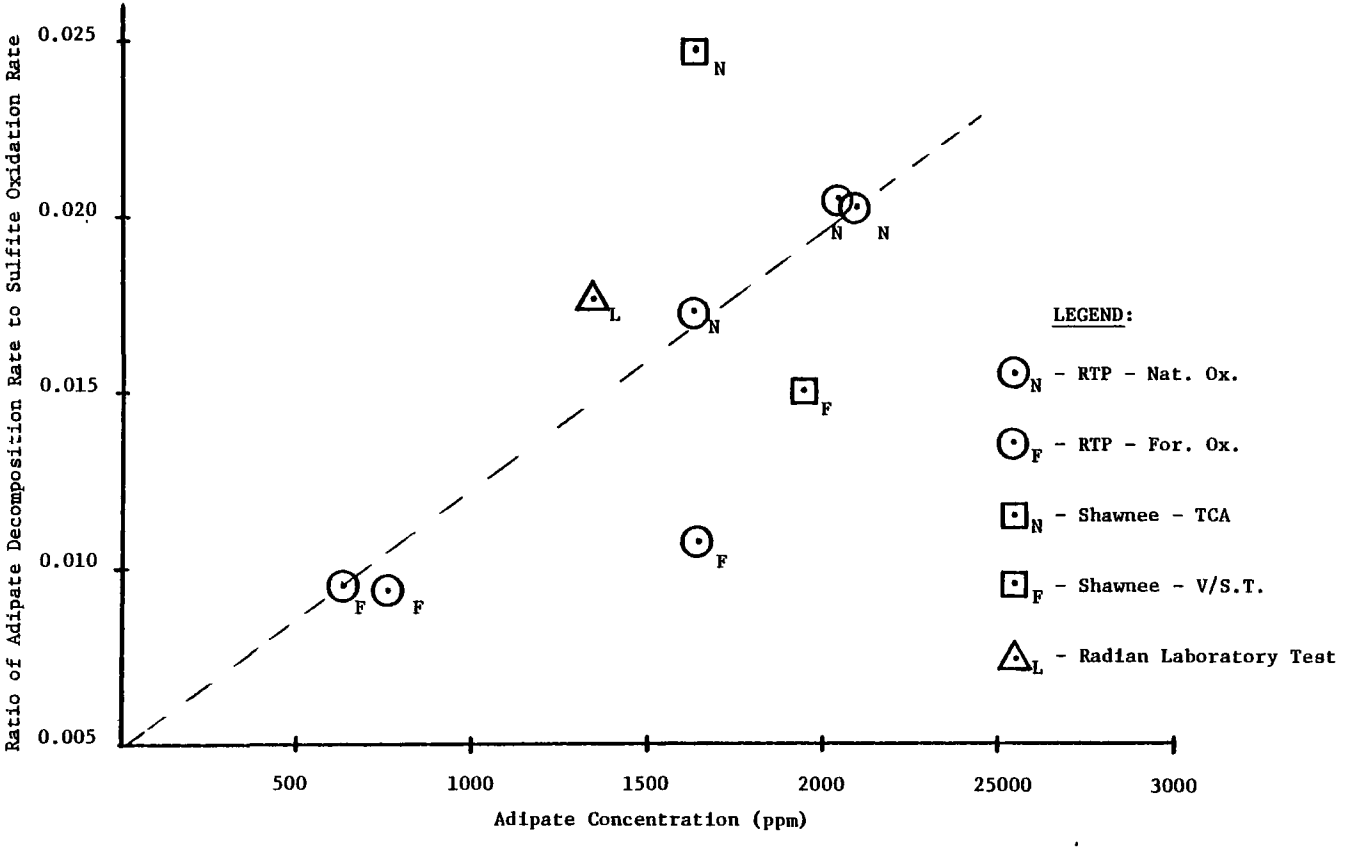


Figure 6-12. Adipate decomposition as a function of sulfite oxidation and adipate concentration.

REFERENCES

1. Limestone Scrubbing of SO_2 at EPA/RTP Pilot Plant - Progress Report 37 - November 1978, Mr. Robert H. Borgwardt.

SECTION 7

LABORATORY TESTS

A series of laboratory tests was conducted to study adipic acid degradation under conditions simulating those found in FGD systems. The lab tests were designed to maintain scrubber-like conditions while allowing for a broad range of experimental flexibility. The tests were primarily aimed at providing the necessary data for characterizing the conditions under which degradation occurs, and the mechanism responsible for the degradation process.

7.1 SCREENING TESTS

Initial bench scale testing consisted of a series of screening tests designed to narrow the scope of subsequent testing. The first priority in the screening tests was to establish a set of conditions sufficient for degradation to occur, and then to demonstrate the degradation process in the laboratory. Once degradation was induced under laboratory conditions, subsequent tests were designed to define the essential elements in the degradation process. Manipulation of these elements was then used to yield data pertaining to the nature of this mechanism.

Slurry samples collected by Radian personnel at IERL-RTP during a natural oxidation material balance run on October 25, 1978 were composited for use in the initial screening tests. The composite was divided into five portions for the test, 01-05. An additional slurry sample, collected November 15, 1978 during a forced oxidation run, was designated as 06. All samples had been refrigerated in sealed plastic bottles since they were collected.

Samples 02 and 04 were filtered through 1 μm membrane filters, and the filtrate was used for the test. Samples 01, 03, 05 and 06 were left unfiltered. Sample 05 was sterilized by boiling for ∿2 hours. Samples 03, 04, 05, and 06 were placed in fritted glass impingers and 01 and 02 were placed in Erlenmeyer flasks. All six vessels were suspended in water baths maintained at ∿50°C. Samples 03, 04, 05 and 06 were supplied with air at ∿120 ml/min. The air for the purged samples was saturated with water by first passing through an impinger of DI water maintained at the same temperature as the samples. This was done to minimize the concentrating effect due to evaporation. Samples 01 and 02 were not purged with air, but were stirred in an open flask. The appratus used for samples 03-06 is diagrammed in Figure 7-1.

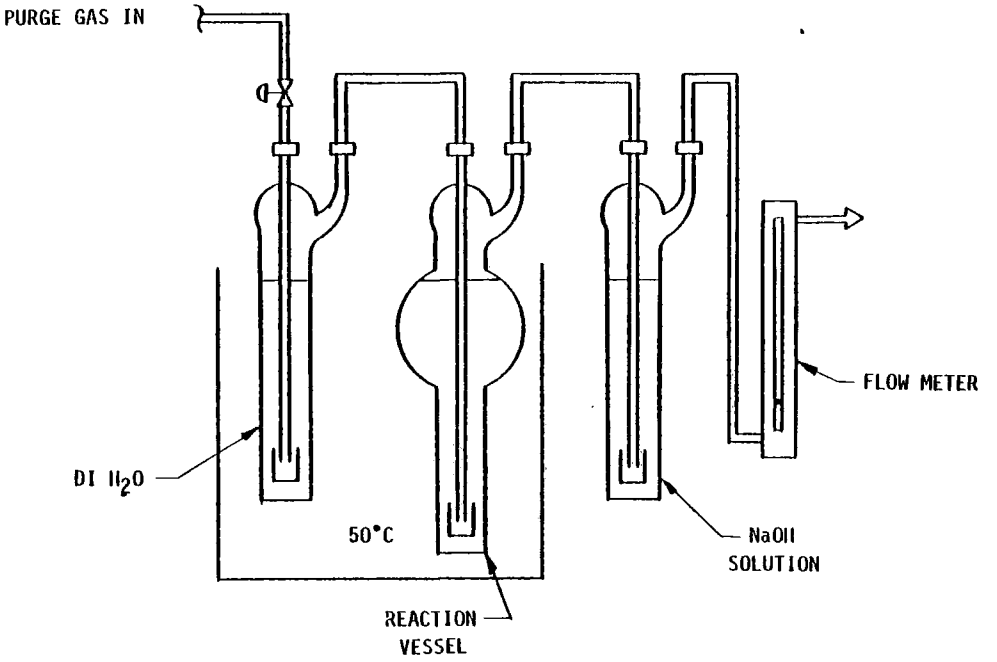


Figure 7-1. Laboratory apparatus for screening tests (construction consisted of glass vessels with teflon tubing and connections)

Under these conditions, the test was expected to reveal the following:

- the effect, if any, of an air purge on the adipic acid concentration in the raw slurry as compared to slurry which was not purged with air (03 vs 01),
- the effect, if any, of an air purge on the adipic acid concentration in slurry filtrate as compared to filtrate which was not purged with air (04 vs 02),
- the difference, if any, in effect of an air purge on the adipic acid concentration in natural oxidation slurry as compared with forced oxidation slurry (03 vs 06), and
- the ability of microbial activity to account for changes in adipic acid concentration in scrubber slurry (03 vs 05).

The initial adipic acid concentration of samples 01-05 was determined by analysis of the composite slurry sample by ion chromatography(IC). The initial concentration of sample 06 was determined by the same method. After 36 hours each of the six samples was again analyzed to determine the percent loss of adipic acid. The results are shown in Table 7-1.

TABLE 7-1. RESULTS OF PHASE ONE LAB SCREENING TESTS

Sample	Description	Initial (mg/ℓ)	Final (mg/ℓ)	Loss (%)
01	Slurry, no air purge	2780	2190	21
02	Filtrate, no air purge	2780	2700	3
03	Slurry, air purge	2780	2050	26
04	Filtrate, air purge	2780	3070	-10
05	Boiled slurry, air purge	2780	2120	24
06	Forced oxy. slurry, air purge	730	730	<1

Several implications can be drawn from the data in Table 7-1. First, degradation of adipic acid occurs to a significant extent only in solutions which contain solids. If degradation occurs at all in the filtrate, it is at a much slower rate. The apparent 3% loss indicated in Sample 02 is more likely due to analytical error. The increase in adipic acid concentration in 04 is most probably due to evaporation, since none of the values reported were corrected for evaporation. Samples 01, 03 and 05 all showed substantial losses of adipic acid. The differences between the three are not considered significant when analytical error is taken into account. This would seem to indicate that an air purge is not necessary for degradation to occur in the raw slurry. If air is necessary, the amount available to Sample 01 by stirring in an open flask was sufficient, and Samples 03 and 05 were simply provided with a large excess which did not significantly affect the net

result. The analytical data also indicate that biological acitvity does not play a significant role in the degradation process since Sample 05 showed a loss of adipic acid comparable to that seen in 01 and 03.

Of the four samples in this test which contained solids, only 06 showed no degradation of adipic acid. This sample differed from the other three slurry samples in two major ways. First, its initial adipic acid concentration was approximately one fourth that of the other three. Second, it was obtained during a forced oxidation run in which sulfite oxidation was about 98 mole percent while the other three were collected during a natural oxidation run in which oxidation was about 30 mole percent. Therefore, Sample 06 contained virtually no sulfite while Samples 01, 03 and 05 had relatively high sulfite concentrations in the solids. Since degradation has been observed at RTP with adipic acid concentrations as low as those in Sample 06, this is probably not a significant factor. That would imply a link between adipic acid decomposition and the oxidation of sulfite.

The second phase of the screening tests was designed to confirm the apparent link between sulfite oxidation and adipic acid degradation, and to yield qualitative data pertaining to pH dependence. The following comparisons were made in this series of tests:

- unpurged solution vs nitrogen purged solution vs air purged solution,
- initial pH 4 vs pH 5 vs pH 6 with an air purge and $CaSO_3 \cdot \frac{1}{2}H_2O$ solids (no attempts to control pH during test were made), and
- $CaSO_3 \cdot \frac{1}{2}H_2O$ added (50 grams/ℓ) vs no $CaSO_3 \cdot \frac{1}{2}H_2O$ added.

This phase of the screening tests differed from the first in several important ways. The primary difference was in the nature of the solutions tested. Synthetic "slurry" solutions were used in these tests rather than actual samples of real scrubber slurry. A solution of approximately 1700 mg/ℓ of adipic acid was used to simulate slurry filtrate. Unfiltered slurry was simulated by adding calcium sulfite solids to the adipic acid solution. Another difference in these tests was the use of bottled purge gases. The initial set of tests relied on a purge of room air via a peristaltic pump. The third major difference was in the samples which were not purged. In the initial tests, the two samples which were not purged (01 and 02) were stirred in an open flask. In these tests the unpurged samples (07 and 08) were stirred in sealed flasks so that the only oxygen available was that which was in the relatively small headspace of the flask at the start of the run. All tests were run with the reaction vessels suspended in a water bath maintained at 50°C. Tests 09-19 were conducted using a series of fritted glass impingers, as before (Figure 7-2). In each

test, the initial and final adipic acid concentrations were determined by ion chromatography. The results of this series of tests are presented in Table 7-2.

TABLE 7-2. SUMMARY OF PHASE TWO - LAB SCREENING TESTS

	Test Designation	Initial Adipic Acid Conc.	Initial pH	Purge	Loss of Adipic Acid	Test Duration
07	Adipate Solution	.1640	5	(sealed)	2%	24 hr
08	Adipate/$CaSO_3 \cdot \frac{1}{2}H_2O$	1640	5	(sealed)	1%	24 hr
09	Adipate/$CaSO_3 \cdot \frac{1}{2}H_2O$	1640	5	N_2	<1%	24 hr
10	Adipate Solution	1640	5	N_2	8%	24 hr
11	Adipate/$CaSO_3 \cdot \frac{1}{2}H_2O$	1640	5	Air	38%	24 hr
12	Adipate Solution	1640	5	Air	7%	24 hr
13	Adipate/$CaSO_3 \cdot \frac{1}{2}H_2O$	1770	4	Air	24%	24 hr
14	Adipate/$CaSO_3 \cdot \frac{1}{2}H_2O$	1770	6	Air	36%	24 hr

As indicated in the table above, a significant amount of degradation occurred only when sulfite was available and oxidizing conditions prevailed (Tests 11, 13 and 14). The degradation values for the other tests are low enough to be considered insignificant and are most likely due to analytical error. Although the data do not conclusively prove that degradation does not occur in the absence of sulfite and/or oxygen, they do indicate that sulfite oxidation is sufficient to cause the degradation of adipic acid. The adipic acid losses in Tests 11, 13 and 14 are of the same order as that measured in the initial tests. Comparing Tests 13 and 14, the data show that the net loss was 50% greater in Test 14 than in Test 13 over the same period of time. This would seem to indicate that the rate of degradation is slightly higher at pH 6 than at pH 4. However, the glass frit on the air sparge tube in the reaction vessel used in Test 13 became clogged with gypsum twice during the test causing the air flow to cease. The total amount of time during which there was no flow is not known, but could have been as much as eight hours. Therefore, this test cannot be regarded as conclusive evidence of pH effect, but may simply reflect the dependence of degradation rate on sulfite oxidation.

The conclusions that can be drawn from the screening studies are outlined in the following list:

- adipic acid degradation occurs in the presence of sulfite oxidation,
- sterilization of slurry didn't prevent adipic acid degradation indicating that bacterial degradation is not important,

- contact of adipic acid solutions with oxygen doesn't result in degradation,
- adipic acid is not stripped (volatilized from solutions at 50°C),
- adipic acid is apparently not adsorbed by either $CaSO_3 \cdot \frac{1}{2}H_2O$ or $CaSO_4 \cdot 2H_2O$, and
- dependence of degradation on pH was not established.

The third phase of the screening tests was specifically aimed at detecting any low molecular weight hydrocarbons which might be generated in the degradation process. Such compounds would not have been detected in the field sampling efforts conducted prior to these tests due to the nature of the methods employed. However, the oxidative decarboxylation of adipic acid would be expected to yield such products to some extent.

Tests conducted during this phase of the laboratory studies used sealed 500 ml flasks as reaction vessels to facilitate trapping and concentration of gaseous products. Since an air purge was not possible with this type of apparatus, vigorous stirring provided the necessary gas-liquid contact. A 10:1 gas-liquid ratio (volume) was used to provide sufficient oxygen for the reaction to proceed to a measurable extent. Three reaction vessels were set up for the first part of this test. One contained a 1500 ppm solution of adipic acid, another contained 1880 ppm solution of valeric acid, and the third contained an equivalent volume of deionized water. Calcium sulfite solids were added to each vessel in the ratio of 0.05 grams of solids per milliliter of solution. All three were sealed, then stirred at 50°C for 36 hours. At the conclusion of the run, the headspace of each flask was analyzed by GC. The results are presented in Table 7-3.

TABLE 7-3. RESULTS OF SEALED FLASK EXPERIMENTS

Sample Description	Initial Concentration Adipic Acid (ppm)	Initial Concentration Valeric Acid (ppm)	Headspace Butane (ppm)	Gas
Deionized H_2O $+CaSO_3 \cdot \frac{1}{2}H_2O$	0	0	0	Air
Valeric Acid Solution + $CaSO_3 \cdot \frac{1}{2}H_2O$	0	1880	1280	Air
Adipic Acid Solution + $CaSO_3 \cdot \frac{1}{2}H_2O$	1500	0	20	Air

The data from these three tests confirm that butane can be generated in the degradation process. The amount of oxygen available in these tests would be expected to be the limiting factor in the degradation reaction. Since the solutions were not analyzed at the conclusion of the run, the amount of butane generated in these tests cannot be correlated with the amount of adipic acid or valeric acid which was decomposed.

A fourth test of this type was run to measure actual degradation as well as quantify the products. This test was essentially the same as the adipic acid version of the first three, with a few modifications. The main difference was the use of pure oxygen as the headspace gas rather than air. Thus, five times as much oxygen was available for reaction with the sulfite. In addition, air was allowed to enter the reaction vessel through a water bubbler to replace the oxygen consumed in the reaction and maintain the pressure within the vessel as near as possible to atmospheric pressure. At the conclusion of the test run, again 35 hours at 50°C, the solution was analyzed by IC for adipic acid, then extracted and analyzed by GC. Analysis of the headspace gas was done in the same manner as in the previous tests. A material balance for this test is presented in Table 7-4. Butane is apparently not a favored product under the conditions encountered in this test and represents only a small fraction of the products of the decomposition reaction. In addition to detection by GC analysis, however, its presence was confirmed by GC-MS analysis of the head space gas.

TABLE 7-4. RESULTS OF SEALED FLASK EXPERIMENT WITH MATERIAL BALANCE

Sample	Adipic Acid (Initial)	Adipic Acid (Final)	Valeric Acid (Final)	Butane (Final)	Final Total	% Initial[1]	Gas
Adipic Acid (ppm)	1400	1140	120	30	--	--	O_2
Solution + $CaSO_3 \cdot \frac{1}{2}H_2O$ (mmole)	0.48	0.39	0.06	5.6×10^{-4}	0.45	94%	O_2

[1] Percent of original material accounted for by analyses at conclusion of test.

7.2 MECHANISMS TESTS

The screening tests described in the previous section were designed to yield information pertaining to specific aspects of the degradation process. Based on this information, a series of mechanism tests was conducted, aimed at providing data for evaluation of the interaction of the various parameters and their relationship to one another. The tests were designed to reflect actual scrubber conditions and to allow a material balance to be done on a flow through system.

The apparatus used in the first flow-through laboratory test incorporated a sorbent trap for collection of butane and other low molecular weight hydrocarbons, preceded by a sodium hydroxide impinger for collection of CO_2 generated in the decarboxylation reaction and any valeric acid which might be in the gas phase. The reaction vessel was preceded by an impinger of deionized water for saturation of the oxygen stream with moisture to mini-

mize evaporation of the adipic solution, and both were immersed in a water bath maintained at 50°C. The reaction vessel was magnetically stirred, and contained 15 grams of $CaSO_3 \cdot \frac{1}{2}H_2O$ in 300 ml of adipic acid solution. After addition of the calcium sulfite, the solution pH was adjusted to 6.0. The apparatus is diagrammed in Figure 7-2.

The sorbent trap consisted of a 2' x 3/8" i.d. stainless steel tube packed with Porapak Q 100/120. The trap was cooled to 7°C during the run and was de-sorbed in the following manner: A two liter flask was evacuated and attached to the inlet of the trap. A bag of nitrogen was attached to the outlet of the trap. The flask was opened and the trap was back-flushed with about two volumes of nitrogen to remove entrained oxygen. The trap was then heated to 180°C and desorbed into the flask at a rate of about 50 ml/min until the flask was full. The gas in the flask was then analyzed on the GC. At least 28 liters of purge gas was necessary in order to reduce the concentrations of the compounds being desorbed from the column to 10% of their concentration in the first two liters of purge gas. Calculations had indicated that two liters of purge gas would be sufficient to desorb the sample that had been trapped. Subsequent testing indicated that this sorbant material bleeds low molecular weight hydrocarbons when heated. This problem is possibly due to reaction of the column material with residual oxygen that cannot be efficiently flushed from the trap.

Samples of the solids and liquid in the reaction vessel were obtained at intervals during the test run, as well as at the start and conclusion of the run. Initial, intermediate and final adipate concentrations were determined by IC analysis. The adipic acid solution was extracted and analyzed by GC at the conclusion of the test, as was the NaOH solution preceding the sorbent trap. Samples of the NaOH solution were also analyzed for CO_2. The analytical results for this test are presented in Table 7-5.

Carbon balance calculations carried out using the data in Table 7-5 are shown below:

TABLE 7-6. CARBON BALANCE FOR MECHANISM TESTS USING PORAPAK Q TRAP

INITIAL	FINAL					
Adipic Acid (mmoles C)	Adipic Acid (mmoles C)	Carbon Dioxide (mmoles C)	Valeric Acid (mmoles C)	Hydrocarbons (mmoles C)	Total (mmoles C)	% Initial
18.7	11.4	1.4	3.7	3.2	19.7	105%

If the hydrocarbon values are rejected and the actual amount of carbon as butane, propane, ethane and methane is assumed to be negligible the carbon balance looks like this:

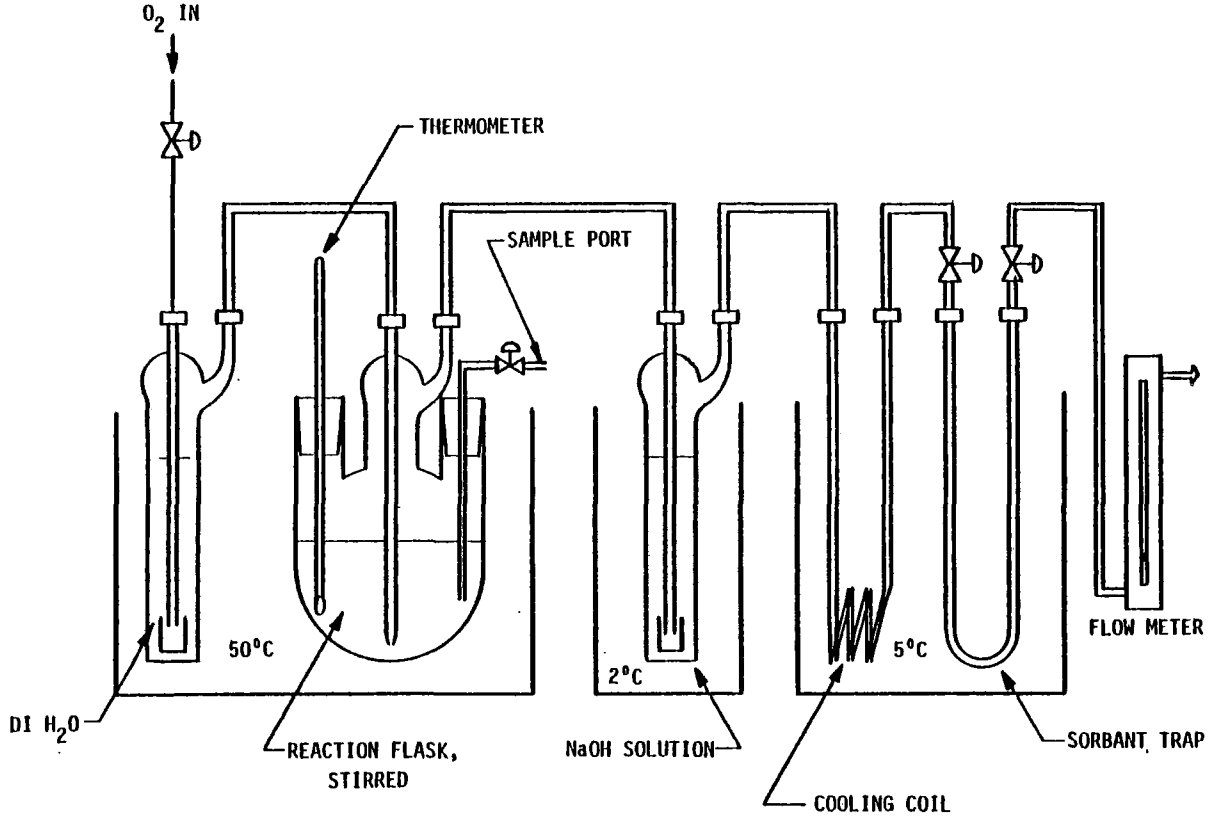


Figure 7-2. Laboratory apparatus for mechanism test with Porapak Q sorbent trap.

TABLE 7-5. RESULTS OF MECHANISM TEST WITH PORAPAK Q SORBENT TRAP

Sample	ppm Adipic Acid	mmoles Adipic Acid	Δmmoles from start	Δ%	Solids % $SO_3^=$	mmoles $SO_3^=$	Δmmoles $SO_3^=$ from start*	mmoles Valeric Acid	mmoles Hydrocarbons	mmoles CO_2	$\frac{\partial Ad^-/\partial t}{\partial SO_3^=/\partial t}$
Initial	1520	3.12			79	92					
6 hrs	1200	2.46	.66	21.0	34.8	39	53				0.012
24 hrs	980	2.00	1.12	35.5	17.3	19	73				0.023
40 hrs	930	1.90	1.13	38.8	4.7	5	87	0.74	[1] $C_4$0.23 $C_3$0.07 $C_2$0.20 $C_1$1.65	1.4	0.001
											0.013

* Subsequent work indicates these values are in error due to hydrocarbon bleed from sorbent material.

TABLE 7-7. CARBON BALANCE FOR MECHANISM TEST USING PORAPAK Q TRAP; HYDROCARBON VALUES NEGLECTED

INITIAL	FINAL					
Adipic Acid (mmoles C)	Adipic Acid (mmoles C)	Carbon Dioxide (mmoles C)	Valeric Acid (mmoles C)	Hydrocarbons (mmoles C)	Total (mmoles C)	% Initial
18.7	11.4	1.4	3.7	--	16.5	88%

Since the use of the Porapak sorbant trap failed to provide a reliable means of trapping and concentrating hydrocarbon byproducts of the degradation process, a second flow through test was done without the sorbant trap. In order to concentrate the gas phase reaction products, a closed loop system was used whereby the sparge gas was recirculated by a peristaltic pump. The system was flushed with oxygen initially and additional oxygen was bled into the system periodically. Two NaOH bubblers were used in series to assure complete trapping of all CO_2. A gas mixing flask was placed in line prior to the reaction vessel to provide a point for obtaining a homogeneous gas sample. Two identical systems were set up and run simultaneously with the only difference being the initial adipic acid concentrations. The reaction vessel in system 01 contained 300 ml of 1550 ppm adipic acid solution and 17.25 grams of calcium sulfite while that in system 02 contained 300 ml of 770 ppm solution with 17.25 grams of calcium sulfite. The initial pH was adjusted to 6.0 as in the previous test. The apparatus is diagrammed in Figure 7-3 . A TOC analysis was done on the adipic acid solutions at the conclusion of the test, in addition to the analyses described for the previous test. The test results are presented in Table 7-8.

Carbon balance calculations carried out using the data in Table 7-8 are presented below:

TABLE 7-9. CARBON BALANCE FOR MECHANISM TEST USING RECIRCULATED GASES

Initial Adipic Acid (mmoles C)	Final Adipic Acid (mmoles C)	Carbon Dioxide (mmoles C)	Valeric Acid (mmoles C)	Hydrocarbons (mmoles C)	Total (mmoles C)	% Initial
19.0	11.5	3.2	0.5	<0.1	15.2	80%
9.5	4.1	1.1	nd	nd	5.2	55%

nd - not detected

The small amount of butane detected in 01 followed by its disappearance, coupled with the poor recovery and lack of degradation products in 02 suggest several possibilities:

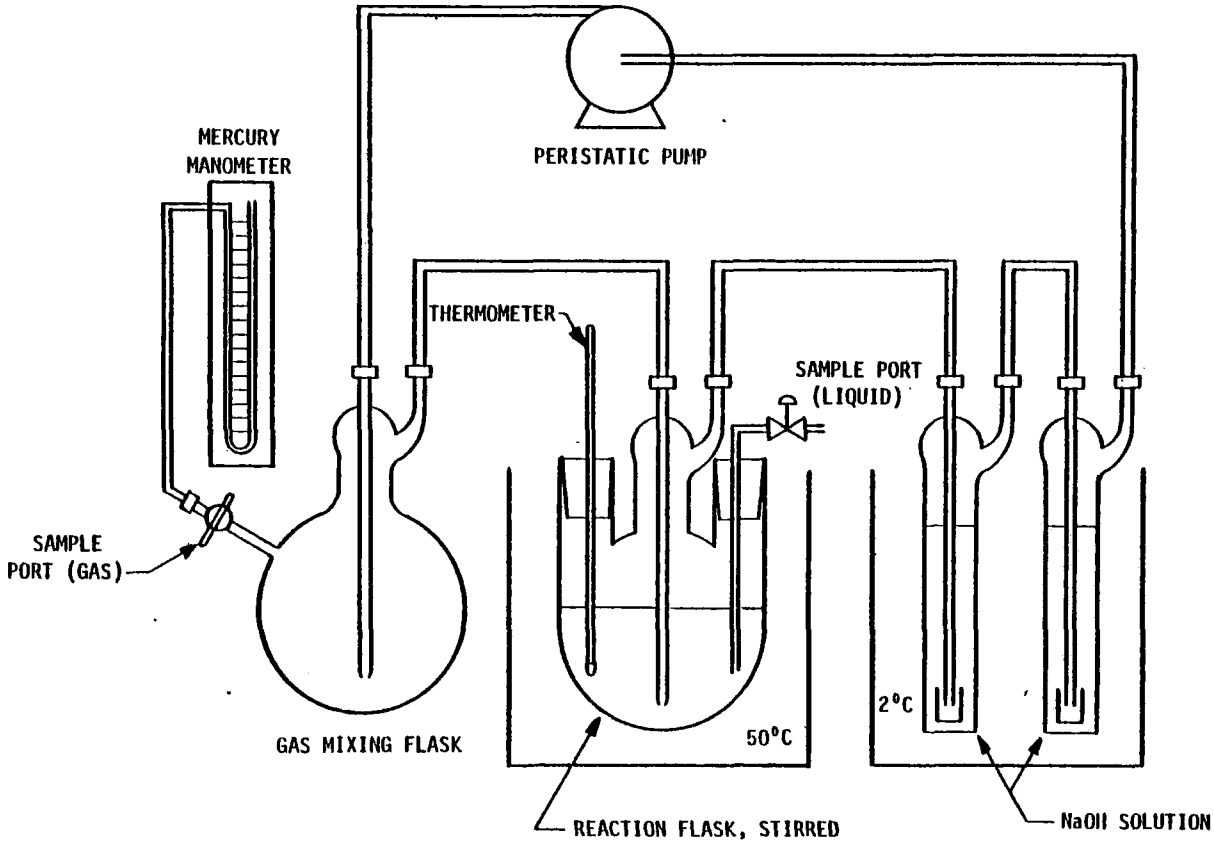


Figure 7-3. Laboratory apparatus for mechanism test with recirculated gases.

TABLE 7-8. RESULTS OF MECHANISM TEST WITH RECIRCULATED GASES

Sample	ppm Adipic Acid	mmoles Adipic Acid	Δ mmoles from start	Δ%	Solids % $SO_3^=$	mmoles $SO_3^=$	Δmmoles $SO_3^=$ from start	mmoles Valeric Acid	μmoles hydrocarbons	mmoles CO_2	mmoles Carbon By TOC	$\frac{\partial Ad^-/\partial t}{\partial SO_3^=/\partial t}$
01												
Initial	1550	3.17			94.9	129			0			
5 hrs	1300	2.66	0.51	16.1	84.8	111	18		0.17			0.028
17 hrs	1190	2.45	0.72	23.2	81.0	103	26		0.17			0.026
24 hrs	1080	2.21	0.96	30.3	72.0	90	39		0.22			0.018
90 hrs	930	1.91	1.26	40.0	59.0	73	56	0.49	0.00	3.16	19.58	0.018
											TOTAL	0.022
02												
Initial	770	1.58			94.7	127						
5 hrs	490	1.01	0.57	35.7	86.9	113	14					0.041
17 hrs	400	0.83	0.75	47.6	76.3	97	30					0.011
24 hrs	580	1.19	0.39	24.7	67.0	84	43					-0.028
90 hrs	340	0.69	0.89	56.2	60.0	74	53	nd	nd	1.10	9.00	0.05
											TOTAL	0.012

- the hydrocarbon products were further degraded by the reaction,
- the test set-up leaked, or
- the hydrocarbons were adsorbed by the tubing and pump.

Since no significant amounts of low molecular weight hydrocarbons were detected in the closed loop system, a return to the flow through system was indicated. A diagram of this system can be seen in Figure 7-4.

The conditions of this test were identical to those in the first flow through mechanism test with the following modifications:

- two NaOH impingers were used in series in order to more efficiently trap CO_2, and
- two sorbent traps were used in series, one containing silia gel and the other activated carbon.

The sorbent traps in this test consisted of 2' by 3/8" stainless steel tubes, one packed with 35-60 mesh silica gel and the other packed with activated carbon. Laboratory tests indicated that the silica gel trap was efficient at trapping n-butane but would not retain methane or ethane well. The trap was cooled to 7°C during the run and then desorbed in the same manner as the Porapak Q trap. A single two liter purge was found to be sufficient to desorb all of the n-butane trapped on the silica gel trap. Desorption of the carbon trap failed to yield any hydrocarbons.

The samples were obtained and analyzed in a manner identical to those in the first flow-through mechanism test. The results of this test are tabulated in Table 7-10. A carbon balance is shown below.

TABLE 7-11. CARBON BALANCE FOR MECHANISM TEST USING SILICA GEL AND ACTIVATED CARBON TRAPS

Initial Adipic Acid (mmoles C)	Final Adipic Acid (mmoles C)	Carbon Dioxide (mmoles C)	Valeric Acid (mmoles C)	Hydrocarbons (mmoles C)	Total (mmoles C)	% Initial
19.2	12.6	1.0	0.3	<0.1	13.9	72%

This large discrepancy in the carbon balance indicates the possibility that a degradation product that is not detectable by the sampling and analytical techniques employed is being formed.

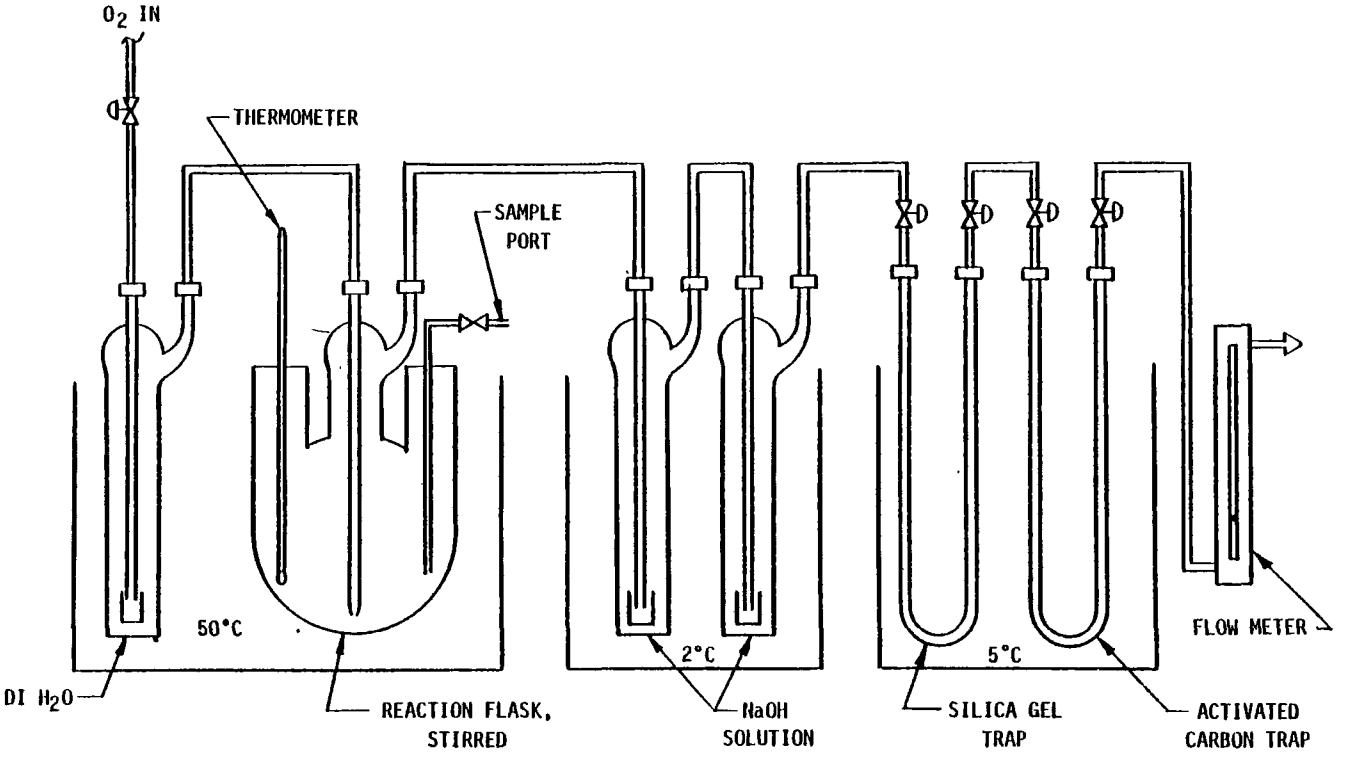


Figure 7-4. Laboratory apparatus for mechanism test with silica gel and carbon traps.

TABLE 7-10. RESULTS OF MECHANISM TEST WITH SILICA GEL AND ACTIVATED CARBON TRAPS

Sample	ppm Adipic Acid	mmoles Adipic Acid	Δ mmoles from start	Δ%	Solids % $SO_3^=$	mmoles $SO_3^=$	Δmmoles $SO_3^=$ from start	mmoles Valeric Acid	μ moles hydrocarbons	mmoles CO_2	mmoles Carbon By TOC	$\frac{\partial Ad^-/\partial t}{\partial SO_3^=/\partial t}$
Initial	1650	3.2	--	--	92.3	120	--	--	--	--		--
6 hrs	1320	2.7	0.5	15.5	78.8	100	20	--	0.83 n-butane 0.4 methane	0.61		0.025
24 hrs	1020	2.1	1.1	34.2	61.6	77	43	0.3	4.17 n-butane 0.6 methane total n-butane = 5.0 total methane = 1.0	0.95 1.56 total	16.25	0.026

BIBLIOGRAPHY

Anderson, J. M. and J. K. Kochi. 1970. J. Am. Chem. Soc., 92:2450.

Berezin, I. V., E. T. Denisov, and N. M. Emanuel. 1964. The Oxidation of Cyclohexane. Pergamon, New York.

Borgwardt, Robert H. November 1978 Progress Report. Limestone Scrubbing of SO_2 at EPA/RTP Pilot Plant - Progress Report 37.

Bunce, N. J. 1972. J. Org. Chem., 37:664, 1972.

Chen, T., and C. H. Barron. 1972. Ind. Eng. Chem. Fundam., 11:466.

Christensen, Herbert E. and Edward J. Fairchild, eds. 1976. Registry of Toxic Effects of Chemical Substances. NIOSH, Public Health Service, Rockville, Maryland.

Clifford, A. A. and W. A. Waters. 1965. J. Chem. Soc., 2796.

Denisov, E. T., N. I. Mitskevich, and V. E. Agabekov. 1977. Liquid-phase Oxidation of Oxygen-containing Compounds. Consultants Bureau, New York.

Dias, F. F. and M. Alexander. 1971. Appl. Microbiol., 22:1114

Grula, M. M.; Grula, E. A. 1976. BERC-RI-76-6, 61 pp.

Hammersma, Warren J. 20 October 1978. Personal communication to Mr. Ronald A. Venezia, EPA.

Hammond, M. W.; Alexander, M. 1972. Environ. Sci. Technol., 6(8):732-735.

International Technical Information Institute. 1976. Toxic and Hazardous Industrial Chemicals Safety Manual for Handling and Disposal with Toxicity and Hazard Data. Tokyo.

Keith, C. L., et al. 1978. Arch Microbiol., 118 (2):173-176.

Kiseleva, R. A. and M. S. Dudkin. 1967. Zh. Prik, Khim., 40:2513.

Kraeutler, B.; Bard, A. J. 1978. J. Am. Chem. Soc., 100(19):598-2-92.

Kuhnle, J. A., R. E. Lundin, and A. C. Waiss. 1972. J.C.S. Che. Com., 287.

BIBLIOGRAPHY (continued)

Leavitt, C., et al. 1978. Environmental Assessment of Coal- and Oil-Firing in a Controlled Industrial Boiler; Volume III. Comprehensive Assessment and Appendices. EPA-600/7-78-164c. Environmental Protection Agency, Research Triangle Park, North Carolina.

Messier, F.; DeJongh, D. C. 1977. Can. J. Chem., 55:2732-2740.

Potai, S. 1969. The Chemistry of Carboxylic Acids and Esters. Interscience New York.

Rochelle, G. 1977. The Effect of Additives on Mass Transfer in $CaCO_3$ and CaO Slurry Scrubbing of SO_2 from Waste Gases, Ind. Eng., 16:67-75.

Sax, N. Irving. 1975. Dangerous Properties of Industrial Materials, 4th ed. Van Nostrand-Reinhold, New York, New York.

Sheldon, R. A., and J. K. Kochi. 1972. In: Organic Reactions, W. G. Danben, ed.

Tinker, H. B. 1970. J. Catalysis, 19:237.

APPENDIX A

ANALYTICAL METHODS

GAS CHROMATOGRAPHY

Samples were analyzed for adipic, valeric and glutaric acids on a Tracor Model 560 gas chromatograph equipped with a flame ionization detector. Peak areas were integrated with either a Hewlett-Packard Model 3380 A Integrator or a Spectra Physics Model 4000.

Conditions for the analysis are listed below:

Column: 6' x 2mm i.d. glass, packed with Tenax GC, 60/80 mesh
Carrier Gas, Flow: N_2, 25 ml/min
Oven Program:
  Initial: 100°C, hold 3 minutes
  Rate: 10°C/min
  Final: 300°C, hold 5 minutes
Injector Temperature: 250°C
Detector Temperature: 300°C

Samples were analyzed for low molecular weight hydrocarbons on an Analytical Instrument Development Inc. Model 511 Gas Chromatograph. Peaks were recorded on a strip chart recorder and concentrations were determined by peak height. Conditions for the analyses are listed below.

Column: 6' x 1/8" i.d. stainless steel, packed with Chromosorb 102, 80/100 mesh
Carrier Gas, Flow = N_2, 20 ml/min
Oven Temperature: 125°C isothermal

ANALYSIS FOR ADIPIC ACID BY ION CHROMATOGRAPHY

A Dionex Model 14 Ion Chromatograph was used for adipic acid analyses.

INSTRUMENT CONDITIONS

Standard Dionex anion separator (3 x 500 mm) and suppressor columns were used. The eluent (see below) was 2.0 mm $NaHCO_3$ and 1.6 mM Na_2CO_3 for most analyses. It was made up in 3 liter batches from stock solutions as needed. The flow rate was set at 30%. Chloride, adipic acid, sulfite, and sulfate may all be resolved and quantified under these conditions. Table A-1 details the response characteristics of these four species with the most commonly used eluent.

TABLE A-1. RESPONSE CHARACTERISTICS OF SPECIES ANALYZED BY DIONEX

Anion	Retention Time	Relative Response	Working Range
Cl^-	3.2 min.	15 µmho/mMole	0.005-5mM
Adipate	6.8 min.	1 µmho/mM	0.01-2mM
$SO_3^=$	8.4 min.	4.5 µmho/mM	0.03-6mM
$SO_4^=$	14.3 min.	3.8 µmho/mM	0.03-6mM

TABLE A-2. IC ELUENTS

Eluent #	mM $NaHCO_3$	mM Na_2CO_3
1	3.60	3.00
2	3.00	2.40
3	2.40	1.80
4	1.90	1.50
5	2.40	1.90
6	2.00	1.60

PREPARATION OF REAGENTS AND STANDARDS

A. Eluent Stock Solution

Weigh Out
25.4g of Na_2CO_3 and 25.2g of $NaHCO_3$ and dissolve in 500 ml of deionized water in a volumetric flask.

B. Eluent Solution (2mM $NaHCO_3$, 1.6 mM Na_2CO_3)

Pipette 10 mls. of eluent stock solution into a standard Dionex deflatable eluent container and dilute to 3 liters.

C. Adipic Acid Stock Solution

Weigh 1.46 g of desicated adipic acid to the nearest .01 mg. Place in a 1 liter volumetric flask and add 700 mls of deionized water. Allow the solid to dissolve. Mild heating and swirling may be necessary. Allow the flask to cool to room temperature and dilute to the mark.

Working standards may be prepared by suitably diluting this stock solution.

PROCEDURE

1. The ion chromatograph is initially allowed to stabilize under the analysis conditions (30% flow, with analytical eluent, etc.) until a stable base line is obtained.

2. Several standards over the range of interest are analyzed and a calibration curve obtained, (plotting peak height vs. concentration.) In practice, 0.1 mM to 0.6 mM adipic acid is a convenient range.

3. Samples are analyzed for 2½ to 3½ hours.

4. One or two "check" standards and a quality control check are analyzed to see that the machine response is not drifting, and is still functioning properly.

5. Samples are again analyzed for several hours.

6. Standards are again run and a calibration curve obtained at the end of the day.

LABORATORY GENERATION OF $CaSO_3 \cdot \frac{1}{2}H_2O$

$CaSO_3 \cdot \frac{1}{2}H_2O$ solids, used to simulate scrubber solids, were synthesized by titrating a 0.77 M $CaCl_2$ solution with a 0.77 M solution of Na_2SO_3. Na_2SO_3 was used as the titrant to minimize oxidation of sulfite solids to a fulfate phase. Following the titration, the solution was vacuum filtered and dried at 50°C. The resulting solids were then pulverized with a mortar and pestle and stored in a sealed container until used in the bench scale tests. Using this technique, approximately 90% ±5% pure $CaSO_3 \cdot \frac{1}{2}H_2O$ solids could be generated.

SULFITE ANALYSES

Equipment

1. 50 ml buret
2. Magnetic stirrer
3. Pipets (10ml); bulb pipet fillers; and 100 ml graduated cylinder
4. 150 ml beakers
5. 4-ounce small mouth glass bottles
6. microammeter apparatus:
   a. 2 1-cm square platinum-sheet electrodes mounted about 1 cm apart
   b. 1.5 volt dry cell battery
   c. electrometer or microammeter 0-25 μamp
   d. voltage divider
7. Laboratory analytical balance accurate to 0.05 mg

REAGENTS & SOLUTIONS

1. Sodium Arsenite Stock Solution (∿0.010 mole/ℓ)

Dissolve 1.3 grams of $NaAsO_2$ into one liter of D.I. water. Standardize this solution using reagent grade 0.1 N standard iodine.

$$(\text{molarity of } NaAsO_2) = \frac{(\text{ml } I_2)\ (\text{normality of } I_2)}{2\ (\text{ml } NaAsO_2)}$$

2. Preparation of a 0.1 Normal Iodine Solution

Dissolve 25 grams of potassium iodide (KI) in as little D.I. water as possible. Accurately weigh 12.69 grams of resublimed iodine and dissolve it completely in the saturated potassium iodide solution. When the dissolution of

of the iodine is completed, dilute with D.I. water accurately to one liter. A larger solution can be made up at one time, if desired. Iodine should be kept in a well stoppered, dark colored bottle, in a cool place. It need not be standardized if only used for the sulfite analysis since a blank is also run.

3. pH 6 Buffer

This solution contains 1 mole/ℓ NaAc and 0.05 mole/ℓ HAc. Pipet 2.9 ml of glacial acetic acid into 500 ml of D.I. water. Stir in 82 grams of NaAc and when completely dissolved make up to one liter. It is convenient to prepare several liters of this solution at a time since 50 ml is used for each analysis.

PROCEDURE

1. Weigh 50 mg of dry solid sample to the nearest 0.1 mg.
2. Pour 100 ml of pH 6 buffer solution into a 4 oz glass bottle with cap, and and stirring bar.
3. Pipet 10 ml of 0.1 N standard iodine solution into the bottle, cap, and begin stirring.
4. Add the weighed solid sample and recap.
5. Stir for 15 minutes.
6. Empty bottle quantitatively into a 150 ml beaker.
7. Place the platinum electrodes in the solution, stir and connect the microammeter. The current should be 30-50 microamps.
8. Begin the titration with the 0.11 mole/liter sodium arsenite solution using the 50 ml buret. The color of the solution serves as a rough indicator of the state of the titration. The iodine color (red) changes to yellow 5 ml before the endpoint is reached. When the solution turns light yellow, the titration should be carried out dropwise. The solution will become colorless one to two drops before the endpoint. The titration is completed when the current reaches 3-4 microamp.
9. After the titration is completed, record the volume of sodium arsenite used and rinse the electrodes with with D.I. water after removing them from the solution.
10. Blanks are to be run each day using the above procedure without the addition of sample.

CALCULATIONS

The concentration (mmole/gram) of sulfite present in the solid sample can be determined by use of the following equation:

$$C = \frac{(B-S)M}{W}$$

where,

C = concentration of sulfite(in mmoles/g)
B = volume of arsenite used to titrate the blank, in ml
S = Volume of arsenite used to titrate the sample in ml
M = concentration of the sodium arsenite (moles/ℓ)
W = weight of sample used, in grams

APPENDIX B

SAMPLE CHROMATOGRAMS

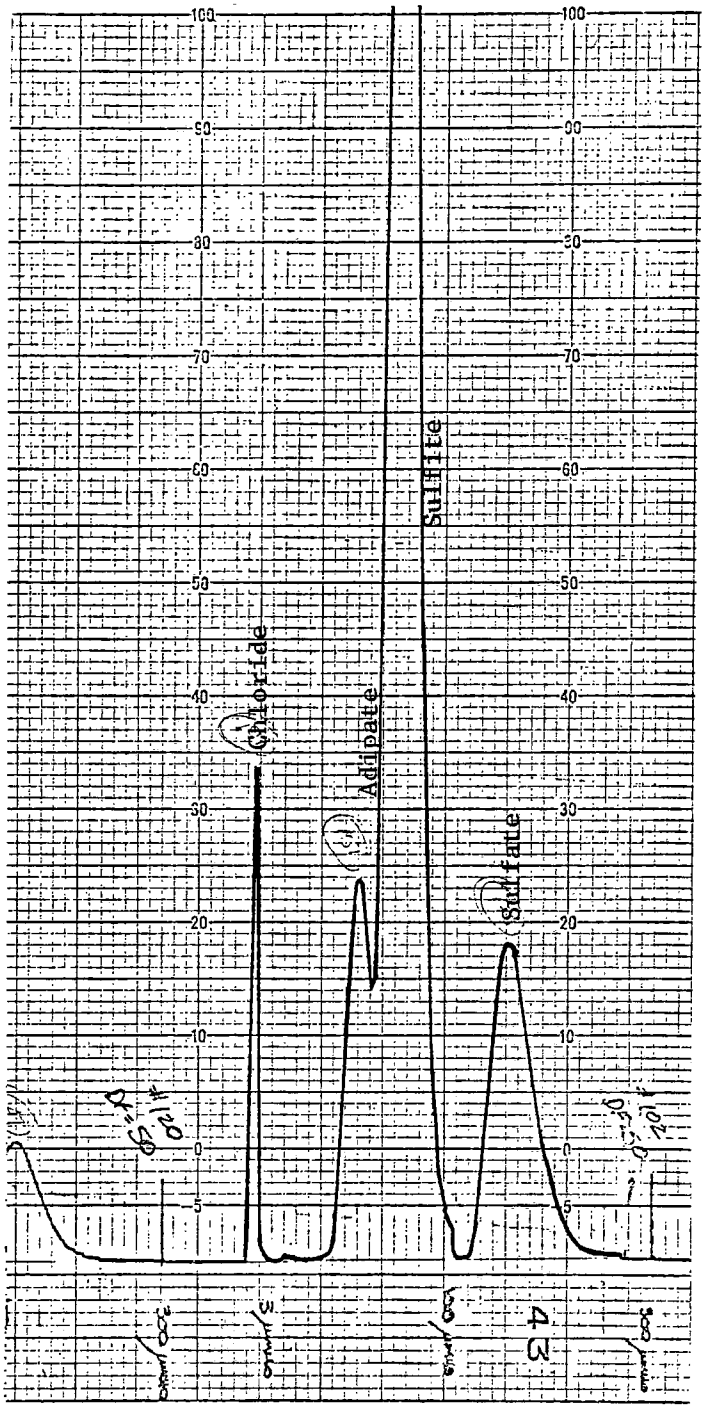


Figure B-1. Sample IC chromatogram with high sulfite.

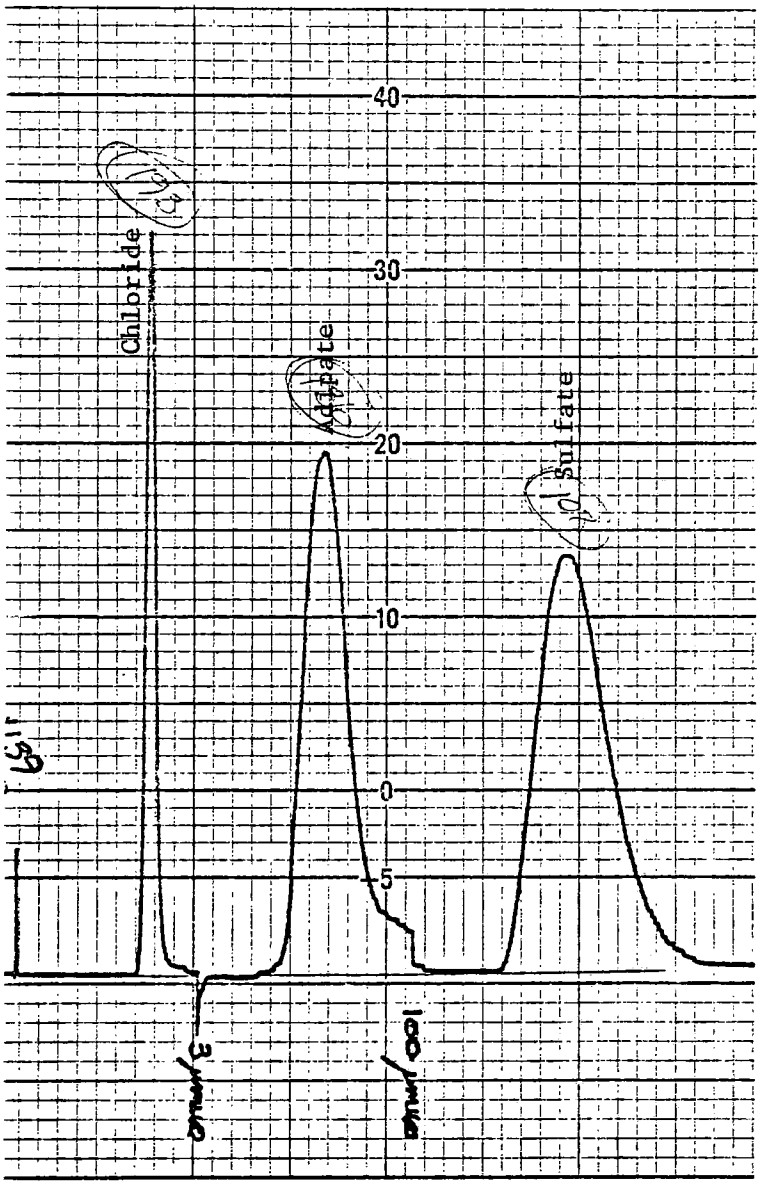
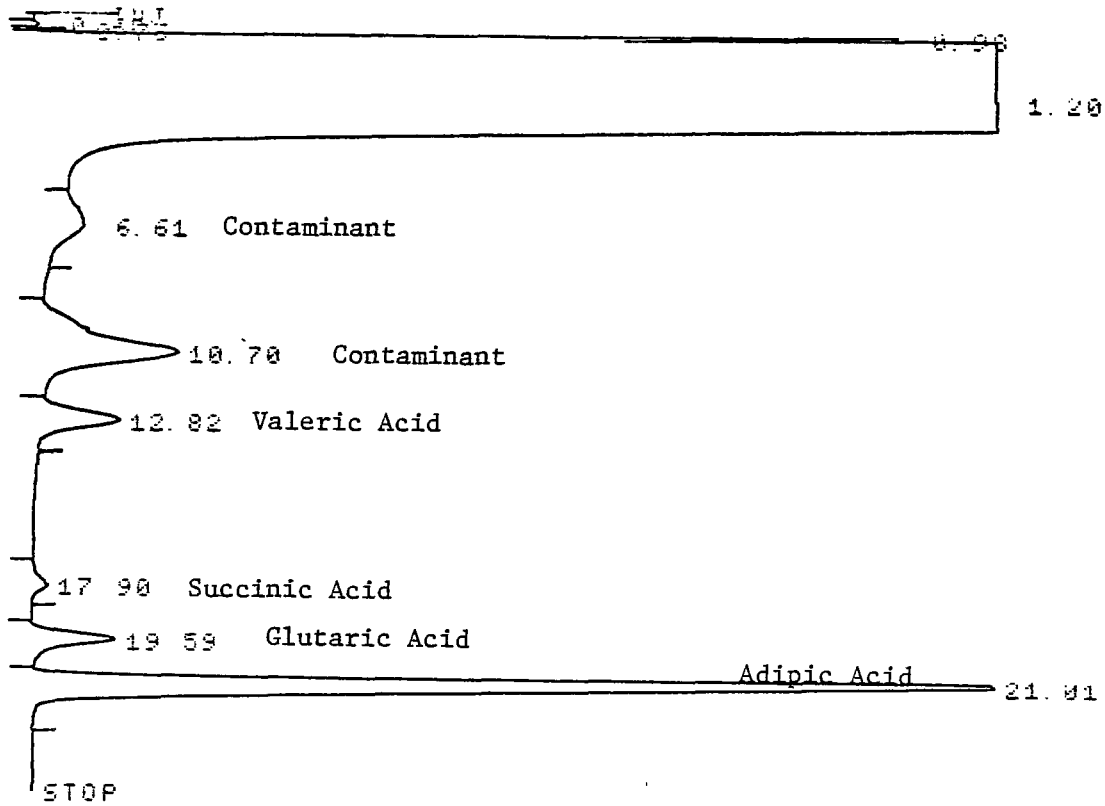


Figure B-2. Sample IC chromatogram with no sulfite.



RT	TYPE	AREA	AREA %
60		1311	.001 291
76	M	1559	001 535
98	M	195995	193
1.20	*M	99999999	98.49
6 61	T	57779	056 9
10 70	T	269351	265 3
12.82	TM	94324	092 9
17 90		15941	.015 7
19.59		73995	.072 87
21.01	M	827002	814 5

HP 3380A
DLY OFF STOP 45 REJECT 1000
AV/M 20 ATTN 32

Figure B-3. Sample GC chromatogram.

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO. EPA-600/7-79-224	2.	3. RECIPIENT'S ACCESSION NO.
4. TITLE AND SUBTITLE Adipic Acid Degradation Mechanism in Aqueous FGD Systems		5. REPORT DATE September 1979
		6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) F.B. Meserole, D.L. Lewis, A.W. Nichols, and G. Rochelle		8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS Radian Corporation 8500 Shoal Creek Blvd. Austin, TX 78766		10. PROGRAM ELEMENT NO. EHE624
		11. CONTRACT/GRANT NO. 68-02-2608, Task 58
12. SPONSORING AGENCY NAME AND ADDRESS **EPA, Office of Research and Development Industrial Environmental Research Laboratory Research Triangle Park, NC 27711**		13. TYPE OF REPORT AND PERIOD COVERED Final; 10/78 - 4/79
		14. SPONSORING AGENCY CODE **EPA/600/13**

15. SUPPLEMENTARY NOTES IERL-RTP project officer is Robert H. Borgwardt, Mail Drop 65, 919/541-2336.

16. ABSTRACT

The report gives results of a field and laboratory study of the adipic acid degradation mechanism in aqueous flue gas desulfurization (FGD) systems. (Adding adipic acid to limestone-based, SO2 wet scrubbers increases SO2 removal and limestone utilization. However, as much as 80% of the adipic acid added to some systems is lost, supposedly through degradation.) The degradation is associated with the oxidation of sulfite, possibly through a free radical mechanism. At least one mechanism is an oxidative decarboxylation yielding valeric acid, butyric acid, glutaric acid, and CO2. The quantities of products measured during laboratory testing only account for approximately 30% of the adipic acid degraded.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS		b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group	
Air Pollution	Sulfur Dioxide	Air Pollution Control	13B	07B
Adipic Acid	Organic Acids	Stationary Sources	07C	
Degradation	Buffers (Chemistry)	Buffer Additives	14B	
Limestone	Additives		08G	11G
Flue Gases			21B	
Scrubbers			07A	
Desulfurization			07D	

18. DISTRIBUTION STATEMENT **Release to Public**	19. SECURITY CLASS *(This Report)* Unclassified	21. NO. OF PAGES 93
	20. SECURITY CLASS *(This page)* Unclassified	22. PRICE

EPA Form 2220-1 (9-73)