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WORLD ENVIRONMENT CENTER

TRIP REPORT #2

TO

PETROCHEMA

DUBOVA, SLOVAK REPUBLIC

DECEMBER 1 - DECEMBER 8, 1993

WORLD ENVIRONMENT CENTER
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I. INTRODUCTION

Pursuant to the technical assistance for Central and Eastern European countries funded by the U.S. Agency for International Development, the World Environment Center (WEC) team conducted a follow-up visit to Petrochema located in Dubova, Slovak Republic from December 1, 1993 to December 8, 1993. The WEC team consisted of:

B. Bhushan Lodh	-	Project Manager
Edward Androchak	-	Radian Corporation, Consultant
James E. Howes, Jr.	-	Radian Corporation, Consultant
Olga Hauskrechtova	-	Special Advisor, Slovak Republic

The purpose of this visit was to implement the Waste Minimization Program, formation of the Waste Minimization Committee (WMC), conducting a demonstration session and hands-on training on the sulfur dioxide analyzer, optimization of the sulfur dioxide converter and caustic scrubber and collection of sampling data at the manufacturing facility.

II. EXECUTIVE SUMMARY

Pursuant to the technical assistance program for Central and East European countries funded by the U.S. Agency for International Development, the World Environment Center (WEC) had organized a reconnaissance trip to Petrochema, Dubova, Slovak Republic, a manufacturer of lubricating oils, located in the western most part of the Slovak Republic during May 9, 1993 to May 13, 1993.

The WEC team and Petrochema management selected the White Oil Plant for the waste minimization demonstration project (WMDP). The consulting engineer and the volunteer expert identified two WMDP projects, namely optimization of sulfur trioxide production and the other neutralization of Goudron sludge to reduce the sulfur dioxide emission thereby complying with the new regulatory permit requirements. The consulting engineer estimated that the regulatory penalty cost savings of $35,000 can be achieved from both the WMDPs between the years 1993 - 1998.

A project implementation trip to Petrochema was organized from December 1 to December 8, 1993. The project team consisted of WEC staff, Dr. Bhushan Lodh and the consultants, Mr. Edward Andrechak and Mr. James E. Howes, Jr., from Radian Corporation.

The following tasks were completed:

- The sulfur dioxide analyzer was assembled, calibrated and tested.
- The sampling probe was installed at the exit duct of the caustic scrubber. Tests were conducted at various sulfur feed rates to the sulfur dioxide generator and caustic feed rates to the scrubber. The corresponding sulfur dioxide concentration was measured at the exit duct of the scrubber. Sulfur dioxide concentration was also measured when caustic scrubber was not in operation.
- Demonstration session and hands-on training were provided to Petrochema personnel to operate the sulfur dioxide analyzer. The Petrochema training personnel included the various department managers, technicians and maintenance employees which also constituted the waste minimization committee (WMC) members.

Based upon the analysis of the test results collected, the following are the conclusions and recommendations:

1. Sulfur dioxide converter appears to be operating at less than 70% conversion efficiency resulting in high concentration of unconverted sulfur dioxide entering the caustic scrubber.

2. The caustic scrubber efficiency is found to be greater than 90%.

3. At the existing plant conditions, by burning liquid sulfur at the rate of 100 kg per hour and maintaining caustic rate in the scrubber between 60-70 liters per hour, the sulfur dioxide concentration in the emission from the scrubber found to be 960 ppmv which complies with the regulatory requirement. Petrochema should operate the White Oil Plant at or near the above mentioned conditions. This will result in a regulatory penalty cost savings of U.S. $10,000 for the period 1993 to 1998.

4. It is recommended that Petrochema should change the catalyst in the sulfur dioxide converter which will result in approximately 120 ppmv sulfur dioxide emission from the White Oil Plant. The plant will save annually U.S. $10,000 in liquid sulfur consumption and U.S. $28,000 to $35,000 in caustic reduction.

   The calculated total annual cost saving for the raw materials is more than US $45,000 annually.

5. The low concentration of sulfur dioxide emission (120 ppmv) from the White Oil Plant due to new catalyst in the converter will enable to preserve the pristine nature of the two national parks in Dubova and a better environment. It will also remove the potential obstacle to the tourism industry.

6. It is recommended that a Brink mist eliminator be installed at the exit section of the scrubber to contain the unabsorbed sulfur trioxide mists.

Please refer to consultant Radian Corporation report, Section V.

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III. MEETINGS

On December 3, 1993 WEC staff, Dr. B. Bhushan Lodh, met with Dr. Peter Vozar, Director and Ms. Valentina Galajdova, Office Manager, Slovak Agency of the Environment and Dr. Otto Tomecek, Prorector, University of Mateja Bela, and briefed them about the Waste Minimization Program (WMP) and the Waste Minimization Impact Program (WMIP). They showed interest and enthusiasm to participate in these programs.

A press conference was held with reporter, Mr. Ivan Karcely of "Smer", a regional newspaper. He was told about the objective of the WMDP at Petrochema which was published in the business and finance section of the newspaper.

On December 9, 1993, the WEC team met with the U.S. AID Mission, the Ministry of Economy and the Chemical Manufacturers Association "CHEMIA" to brief them about the Petrochema WMDP and the results of this visit.

On December 10, 1993, Dr. Bhushan Lodh, WEC staff, met with Ing. Bohuslav Bezuch, Ministry of Environment, and Dr. Magda Korucova, Deputy Director, Research Institute of Chemical Technology, and presented and discussed the Petrochema WMDP and WMIP. They took great interest in the WEC programs. They would like to be kept informed of WEC activities and would like to participate in them.

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IV. ITINERARY

November 30, 1993	-	WEC team arrives in Vienna, Austria. Drive to Banska Bystrica, Slovak Republic. Transportation provided by Petrochema.
December 1 - 8, 1993	-	Conduct WMDP at Petrochema, Dubova.
December 8, 1993	-	Depart Banska Bystrica.
December 9, 1993	-	Meeting with U.S. AID Representative for briefing.
	-	Meeting with CHEMIA and Ministry of the Economy of the Slovak Republic.
December 10, 1993	-	Consulting Engineer returns to U.S.A.
	-	WEC staff meeting with Ministry of Environment of the Slovak Republic.
	-	WEC staff meeting with the Research Institute of Chemical Technology.
	-	WEC staff departs for Vienna.
December 12, 1993	-	WEC staff returns to U.S.A.

V. RADIAN CORPORATION REPORT

DISCLAIMER

The opinions expressed in the report is the professional opinion of the author and do not represent the official position of the Government of the United States or the World Environment Center.

RADIAN
CORPORATION

TECHNICAL MEMORANDUM

TO: Dr. Bhushan Lodh, Project Manager, World Environment Center

FROM: Edward M. Andrechak, Radian Corporation

DATE: 7 February 1994

SUBJECT: **Petrochema Waste Minimization Demonstration Program For SO_2 Emissions Reduction--Second Visit Test Results and Recommendations**

1.0 INTRODUCTION

This technical memorandum summarizes the findings of our December 1993 visit to the Petrochema Dubova Oil Refinery in the Slovak Republic. This was the second visit to Petrochema as part of the World Environment Center's (WEC) Waste Minimization Demonstration Program. In our prior visit in May 1993, we identified two separate waste minimization projects for the reduction of sulfur dioxide (SO_2) emissions. (See the previous technical memorandum, titled Petrochema Site Visit Report and Recommendations [Radian, 8 June 1993], for more detailed background information.) Both projects are associated with the production of white oil. The purpose of this second visit was to perform test measurements to quantify the projected SO_2 emissions reductions and the associated economic savings from the implementation of these two projects.

This document is organized by the following sections: Section 2.0 presents a summary of the findings of the December visit; Section 3.0 discusses the visit logistics; Section 4.0 presents the test program and results for optimizing sulfur trioxide (SO_3) in the White Oil Plant; Section 5.0 presents the waste minimization program involving the neutralization and incineration of Goudron sludge; and Section 6.0 presents a proposed schedule of future activities. Figures referenced in the memorandum are attached. Also attached are photographs of some of the analytical equipment and of the Petrochema/Radian/WEC team members (Attachment A); the test data collected during the December 1993 visit (Attachment B); and sample calculations which were performed on the test data (Attachment C).

2.0 SUMMARY OF FINDINGS

During our eight-day testing and training visit to the Petrochema Refinery in December 1993, the following was accomplished or determined:

- A new SO_2 analyzer was installed in both the White Oil Plant and at Incinerator No. 2. The analyzer worked successfully and provided accurate test data primarily for the optimization of SO_3 production in the White Oil Plant.

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- Plant test data were collected in the White Oil Plant for both the optimization of the SO_2 catalytic converter and the caustic scrubber. From our test results, the catalyst in the converter appears to be deactivated, achieving less than 70% conversion. At the same time, the caustic scrubber appears to be operating well, achieving greater than 90% SO_2 removal efficiency.

- Despite the heavy inlet loading of SO_2 to the caustic scrubber in the White Oil Plant, compliance with the SO_2 scrubber emissions limit can be achieved by significantly increasing the fresh caustic feed rate to the scrubber.

- Changing the SO_2 converter catalyst can reduce the caustic required for SO_2 scrubber emissions compliance and achieve several other economic and pollution benefits. These benefits may pay for the cost of new catalyst.

- Planning discussions were conducted with the Petrochema staff who will conduct Goudron sludge neutralization testing after the WEC/Radian team returns to the United States.

- Radian performed classroom and field training of the Petrochema staff on the operation of the SO_2 analyzer. This training should enable Petrochema's capable staff to conduct their own plant tests in the future.

3.0 VISIT LOGISTICS

The WEC team consisted of four members: Dr. Bhushan Lodh, WEC Project Manager; Mr. Edward Andrechak, Radian Department Head; Mr. Jim Howes, Radian Senior Staff Scientist; and Mrs. Olga Hauskrechtová, Slovak Consultant.

The facility visit took place from Wednesday, 1 December through Wednesday 8 December 1993. During the facility visit and the collection of test data, we worked with various members of the Petrochema staff, including, but not limited to, Mr. Josef Šuráb, Technical and Production Director; Ms. Maria Babiaková, Head of the Department of the Environmental Protection; Mrs. Halajová, Air Emissions Engineer, Department of the Environmental Protection; Mr. Michael Majercik, Head of the White Oil Production Department; Mr. Vagner, Chief Technologist, White Oil Production Department; and Mr. Tibor Duris, Head of Energy Department. Photographs of the Petrochema/Radian/WEC team and some of the analytical equipment are presented in Attachment A.

On 1 December 1993, the analyzer was unpacked and installed in the White Oil Plant in preparation for data collection. From 2 December through 5 December, test data were collected for the optimization of SO_3 production and minimization of SO_2 emissions in the White Oil Plant. On 6 December, the WEC/Radian/Petrochema team reviewed the

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proposed test plan for the neutralization and incineration of Goudron sludge (this testing is to be conducted by the Petrochema staff after the December 1993 visit). On 6 and 7 December, Jim Howes of Radian conducted classroom and field training for the SO_2 analyzer which is being used to collect the waste minimization test data for both projects. On 8 December, we met with Mr. Ján Mataš, General Director, to present our preliminary visit findings.

Returning to Bratislava on Thursday, 9 December, we met with Mr. Ivan Sojka, Chief of Environmental Group, and Mr. Andrej Soltes, Engineer, at the Ministry of Economy to reiterate our findings. We also met with Mr. Ivan Hejda, Head of Chemia, and Mr. Loren Schulze and Mr. Martin Brunovsky, of U.S. Agency for International Development (USAID), to discuss the current status of our project at Petrochema and possible future action.

4.0 WASTE MINIMIZATION TEST PROGRAM NO... OPTIMIZATION OF SO_3 PRODUCTION IN THE WHITE OIL PLANT

The optimization of SO_3 production, and its subsequent usage during white oil production, involved testing the performance of two stages in the production process. The two-step performance test measured the efficiency of 1) the vanadium pentoxide (V_2O_5) conversion catalyst, which converts SO_2 to SO_3, and 2) the caustic scrubber, which captures unconverted SO_2 at the end of the process line. Figure 1 shows a simplified process flow of the overall white oil production process. Figure 2 shows the process flow for the production and consumption of SO_3 in the White Oil Plant.

Step one involved a performance test conducted on the V_2O_5 conversion catalyst. This catalyst converts SO_2 into SO_3 for use in sulphonating white oil feedstock. Unconverted SO_2 passes through the white oil production system and is treated in a caustic scrubber at the tail end of the plant. The objective of this first step was to increase the conversion of SO_3, thereby decreasing the amount of unreacted SO_2 left to pass through the system to the scrubber. Excessive unreacted SO_2 could potentially overwhelm the scrubber's design capability resulting in high SO_2 emissions to the atmosphere.

Parameters which can be varied to optimize SO_3 converter efficiency are: sulfur feed rate, inlet bed catalyst temperature, system pressure, air feed rate, and residence time (by additional catalyst). Only sulfur feed rate and inlet bed catalyst temperature were varied during the December 1993 test program.

Step two of this optimization project involved a performance test conducted on the caustic scrubber, ensuring that unreacted SO_2 emissions do not pass through the scrubber to the atmosphere. The main parameter which can be varied to optimize caustic scrubber performance was the rate of fresh caustic fed to the scrubber.

The test program objectives, test methodology, test results, emissions reductions and economic savings, and conclusions and recommendations associated with the optimization of SO_3 in the White Oil Plant are presented in the following sections.

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4.1 Test Program Objectives

The objectives of this test program were to:

- Optimize the production of SO_3 from SO_2 in the V_2O_5 catalytic converter;
- Optimize the caustic scrubber operation to minimize SO_2 emissions to the atmosphere;
- Demonstrate compliance with the recently received (June 1993) scrubber emissions permit limit for SO_2 of 2500 mg/m^3;
- If successful in optimizing the converter and the scrubber, quantify the following:
  - -- Actual reduction of scrubber SO_2 emissions to the atmosphere;
  - -- Net reduction in liquid sulfur feed volume;
  - -- Net reduction in caustic consumption;
  - -- Cost savings in reduced SO_2 emissions penalties for the period 1993-1998;
  - -- Cost savings for reduction of liquid sulfur usage; and
  - -- Cost savings for reduction in scrubber caustic usage.

4.2 Test Methodology

Based on several discussions with Mr. Majercik and Mr. Vagner on Wednesday, 1 December, we agreed to the following test plan to meet the test program's objectives. The plan reflected what was technically feasible given the limitations of plant equipment and controls in the existing White Oil Plant. Specifically, we agreed to vary the sulfur feed rate to the plant at rates ranging from 86 kg/hr to 120 kg/hr. For each sulfur feed rate condition, the first bed inlet catalyst temperature was set to a reading that was considered "optimal" for that sulfur feed rate based upon the plant operator's judgement. Downstream catalyst bed temperatures could not be varied and were determined by the inlet temperature of the first bed.

At the same time, at each sulfur feed rate condition, the caustic feed rate to the scrubber was varied from 12 l/hr to 120 l/hr. At each caustic rate, the SO_2 concentration was measured at the scrubber outlet to the atmosphere using the SO_2 analyzer provided by WEC. Figure 3 shows the location of the SO_2 measurement in relation to the scrubber. From these

outlet SO_2 measurements, we were able to determine an optimum caustic feed rate at each sulfur feed rate condition.

In addition, the scrubber was shut down at the end of each trial to measure a scrubber inlet concentration. By taking both inlet and outlet SO_2 measurements for the scrubber, the scrubber efficiency could be evaluated for each caustic rate. Using these data, an overall assessment could also be made of the adequacy of the scrubber design to meet the new permit emission limits for SO_2 from the scrubber given the existing converter catalyst performance and resultant SO_2 inlet loading to the scrubber.

Finally, the scrubber inlet SO_2 concentration measurement at each sulfur feed rate could also be used to perform an overall SO_2 balance around the catalytic converter. By performing this material balance, the efficiency of the catalytic converter could be estimated and compared with expected design efficiency (conversion).

Following the test methodology described above, five test trials were performed at sulfur feed rates of 86, 90, 100, 106, and 120 kg/hr; respectively. First bed inlet catalyst temperatures were set at "optimal" conditions based upon operator judgement. Generally, the first bed inlet temperatures and the resultant converter temperature profile were consistent with literature values (400-430° C) for proper reaction kinetics and thermodynamic conversion.

Within each trial, the water rate to the scrubber was held approximately constant in the range of 15-18 l/min. The caustic feed rate, however, was varied from 12 to 120 l/hr, depending on the trial. Scrubber outlet SO_2 concentrations were measured at each new caustic feed rate. At the end of each trial, a scrubber inlet SO_2 concentration was measured. It should be noted that in all cases but one the inlet SO_2 was too high to be read on-scale by the analyzer. For purposes of completing the SO_2 material balance around the catalytic converter and calculating a converter efficiency, we diluted the sample on the fifth trial (90 kg/hr sulfur) with air and obtained an on-scale reading.

4.3 Test Results

The discussion of the test results is focused relative to our test objectives. Test data sheets for each trial and graphs of the individual trials showing scrubber outlet SO_2 concentrations versus caustic feed rate are provided in Attachment B. Sample calculations supporting the following discussion of results are provided in Attachment C.

Catalytic Converter Optimization and Efficiency

For catalytic converter efficiency, we determined that the catalyst in the converter is achieving less than 70% conversion compared with a design conversion of 96 percent. The sample calculation is shown as C-1 in Attachment C. The material balance which supports this converter efficiency calculation was performed for Trial No. 5 at a sulfur feed rate of 90 kg/hr. The off-scale measurements for inlet SO_2 concentrations in Trial Nos.

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1-4 lend further support to the conclusion that the converter is operating well below the design efficiency.

We were able to determine that the catalyst efficiency was generally low after the first four days of testing. It was felt at the time of testing that small gains in converter efficiency (0-3%) could be achieved by continuing the optimization tests. However, based upon such a low efficiency relative to design, it was hypothesized that the catalyst was damaged by either poisoning, aging, or sintering. Given the low efficiency, the tests were terminated pending future resolution of the catalyst issue.

Caustic Scrubber Optimization

While collecting the converter optimization data, we were also collecting data to optimize the caustic scrubber performance. As discussed earlier, we chose to vary fresh caustic feed rate in each trial. Figure 4 shows the correlation between caustic feed rate and outlet SO_2 emissions from the scrubber to the atmosphere. Generally, as liquid sulfur feed rate to the plant increased, the outlet SO_2 emissions from the scrubber also increased at a given caustic feed rate. This observation is most evident on the graph at 40 l/hr caustic. Assuming a fairly constant scrubber efficiency, this suggests that no clear optimum sulfur feed rate was found. The inefficient converter passed more unreacted SO_2 with increasing sulfur feed rate which in turn resulted in a higher outlet concentration of SO_2 from the scrubber.

At each sulfur feed rate, it was observed, without exception, that as caustic feed rate increased outlet scrubber SO_2 emissions decreased. From Figure 4, it appears that the curve has two parts: a steep decline in SO_2 emissions from 0-40 l/hr caustic feed rate. Between 40 and 60 l/hr, depending upon the liquid sulfur feed rate, the curve flattens out. From approximately 50 l/hr to 120 l/hr caustic (maximum caustic feed pump rate), relative SO_2 emissions reductions are smaller per unit increase of caustic.

The caustic scrubber efficiency ranges from an estimated 73% in Trial 5 at 40 l/hr caustic to 90-93% in Trials 1-4. Some sample calculations for scrubber efficiency are provided as calculation C-2 in Attachment C. Therefore, it appears from the data set that the scrubber can achieve good efficiency (>90%). However, it is continuously being heavily loaded with unconverted SO_2 from the catalytic converter.

SO_2 Emissions Compliance

Achieving compliance with the new (June 1993) SO_2 scrubber emissions limit of 2500 mg/m^3 (~960 ppmv) will require that Petrochema generally increase the caustic feed rate from typical levels of 12-20 l/hr to 60-70 l/hr. This represents a 250-400% increase in the amount of caustic the plant will now use to achieve compliance for SO_2 emissions. It also should be noted that at these higher caustic feed levels, Petrochema will achieve compliance, but not by much. Figure 4 can be used as a SO_2 emissions compliance curve for the existing catalyst in the SO_2 converter.

Some preliminary calculations Radian performed (not shown) suggest that at least two to three times the stoichiometric amount of caustic is necessary to achieve compliance. This further suggests that the inefficient SO_2 converter may be overloading the design capability of the caustic scrubber.

4.4 Emissions Reductions and Potential Economic Savings

Despite the low converter efficiency, the scrubber optimization tests demonstrated a reduction of outlet SO_2 emissions to the atmosphere from 10,000 mg/m^3 (3836 ppmv), reported during our May 1993 visit and observed during our December 1993 visit, to ~2500 mg/m^3 (~960 ppmv). This reduction represents a 75% reduction in SO_2 emissions to the atmosphere from the caustic scrubber.

The cost savings in reduced SO_2 emissions penalties from the scrubber should be approximately 300,000 Slovak Korunas, or US$10,000, for the period 1993-1998. However, these cost savings come at the additional expense of increased caustic usage. This increase in caustic is due to the low conversion being achieved by the existing catalyst in the SO_2 converter.

By replacing the existing catalyst with new catalyst, it is projected that improved SO_2 converter performance will decrease:

- SO_2 scrubber outlet emissions;
- The caustic feed rate to the scrubber required for SO_2 permit emissions compliance; and
- The liquid sulfur feed rate to the White Oil Plant required for acceptable sulphonation.

With the addition of new catalyst, SO_2 scrubber outlet emissions to the atmosphere may be reduced to as low as 300 mg/m^3 (~120 ppmv). This level of emissions would represent a 97% reduction in SO_2 emissions from this source based on the 10,000 mg/m^3 SO_2 emissions reported during our May 1993 visit. Supporting calculations are provided as C-3 in Attachment C.

The addition of new catalyst should also provide corresponding reductions in caustic and liquid sulfur consumption. Calculations, provided as C-4 in Attachment C, indicate that caustic savings could total 840,000 to more than 1,000,000 Slovak Korunas (US$28,000-US$35,000) per year if the new SO_2 converter catalyst allowed caustic feed rates to be decreased by 40-50 l/hr. In addition, an improvement in new catalyst efficiency of 26% should result in liquid sulfur feed rate reductions of ~26 kg/hr (100 kg/hr basis). The cost savings associated with this reduction in liquid sulfur consumption are estimated to be 285,000 Slovak Korunas (US$10,000) per year.

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In summary, these total savings of potentially more than 1,285,000 Slovak Korunas (US$45,000) per year may show that converter catalyst replacement both reduces SO_2 emissions and is an economic payout.

4.5 Conclusions and Recommendations

Based upon the test results collected during the December 1993 testing of the White Oil Plant operation, we conclude and recommend the following:

- Based upon an SO_2 system material balance, the SO_2 converter appears to be operating at less than 70% conversion efficiency. This efficiency is significantly less than the design efficiency of 96 percent. The low converter efficiency results in a heavy loading of unreacted SO_2 to pass through the white oil system to the caustic scrubber.

- Despite the heavy loading of SO_2 from the converter, the caustic scrubber is operating well, achieving greater than 90% conversion in most cases. To achieve compliance with the SO_2 scrubber permit limit of 2500 mg/m^3 (~960 ppmv) using the existing converter catalyst, caustic feed rates must be increased to between 60-70 l/hr depending upon the oil and sulfur feed rates. This increase represents a 250-400% increase in current caustic usage.

- Specifically, based on the test data collected and shown in Figure 4, it can be concluded that at the existing plant conditions, by burning liquid sulfur at the rate of 100 kg/hour and using a caustic rate in the scrubber of 60-70 l/hour, the sulfur dioxide emission concentration from the scrubber is found to be 960 ppmv, which satisfies the regulatory requirement. It is recommended that Petrochema operate the White Oil Plant at or near these specific operating conditions. This operation will result in a regulatory penalty cost savings from reduced sulfur dioxide emissions of approximately 300,000 Slovak Korunas, or US$10,000 for the period 1993-1998.

- It is recommended that Petrochema change the catalyst in the SO_2 converter. Changing the SO_2 converter catalyst should significantly reduce scrubber inlet and outlet emissions, scrubber caustic feed rates required for compliance, and liquid sulfur feed rates to the White Oil Plant. By changing the catalyst in the converter, Petrochema will save annually 840,000 to more than 1,000,000 Slovak Korunas (US$28,000-US$35,000) in caustic reduction and 285,000 Slovak Korunas (US$10,000) in liquid sulfur consumption.

  The total cost savings realized may be more than 1,285,000 Slovak Korunas (US$45,000) per year. The economic savings associated with

the process and emissions benefits of new catalyst may pay for the cost of new catalyst.

- SO_2 outlet emissions from the caustic scrubber with new converter catalyst could be as low as 300 mg/m^3 (~120 ppmv). These emissions reductions should result in improving regional air quality and aid in preserving the pristine nature of the two national forests adjacent to Dubova.

- Fine mists of SO_3 are not absorbed and removed in the caustic scrubber, and escape into the atmosphere through the stack in the form of a plume. It is recommended that a Brink mist eliminator be installed at the exit section of the scrubber to contain these SO_3 mists.

5.0 WASTE MINIMIZATION TEST PROGRAM NO.2: GOUDRON SLUDGE NEUTRALIZATION AND INCINERATION

Goudron sludge is a tarry, viscous hydrocarbon pitch which is generated as a waste product from the sulphonation of white oil feedstock. Goudron sludge quality varies but contains components with the following compositions, ranging by weight percent:

- Oil - 10 to 60%;
- Water - 5 to 25%;
- Sulphonic acid - 10 to 45%; and
- Sulfuric acid - 10 to 90 percent.

The main goal of the test program is to measure the effectiveness of the neutralization of Goudron sludge in reducing SO_2 emissions upon incineration. To achieve this goal, we have proposed conducting comparative incinerator trial burns of neutralized and unneutralized sludge of similar composition.

Neutralization of Goudron sludge prior to incineration involves mixing lime [$Ca(OH)_2$] with the acidic Goudron sludge. Additionally, sludge from the wastewater treatment plant (slightly alkaline) and spent clay from the White Oil Plant is added to the neutralization mixture. The neutralization reaction removes sulfur as a precipitate, calcium sulfate ($CaSO_4$). As a result, the SO_2 emissions generated during the incineration of Goudron sludge are reduced by a corresponding amount. Both bench and pilot testing of this neutralization process have been previously conducted with encouraging results.

It should be noted that there are differences in composition, primarily acid content, between "old" Goudron sludge and "fresh" Goudron sludge. Old Goudron sludge is sludge which has been previously generated by White Oil Plant operation and then

subsequently stored at either two off-site landfills or one on-site. Fresh Goudron sludge is sludge which has been more immediately generated by ongoing White Oil Plant operation. Generally, old Goudron sludge is less acidic and easier to neutralize than fresh sludge. Old Goudron sludge has been successfully neutralized. At the same time, Petrochema (and its contractor) are conducting ongoing pilot tests for the potential successful neutralization of fresh Goudron sludge. Some of the difficulties associated with the neutralization of fresh Goudron sludge have been documented previously in Radian's Technical Memorandum titled Petrochema Site Visit Report and Recommendations (8 June 1993).

The test program objectives, test methodology, test results, emissions reductions and economic savings, and conclusions and recommendations associated with the neutralization and incineration of Goudron sludge are presented in the following sections.

5.1 Test Program Objectives

The objectives of this test program are to:

- Demonstrate that the process of neutralizing Goudron sludge with lime will result in a significant reduction in SO_2 emissions when incinerated;
- Demonstrate compliance with the recently-received air permit limit (June 1993) of 3000 mg/m^3; and
- If successful, quantify the following:
  - -- Actual reduction of incinerator SO_2 emissions;
  - -- Usage of wastewater treatment sludge and spent clay in the neutralization process;
  - -- Cost savings in reduced SO_2 emissions penalties for the period 1993- 1998; and
  - -- Cost savings for reduced landfill disposal fees for the usage of wastewater treatment sludge and spent clay in the neutralization process.

5.2 Test Methodology

For each trial two batches of sludge should be burned:

- An unneutralized mixture of Goudron sludge, wastewater treatment (WWT) plant sludge, and spent clay from the white oil plant; and
- A neutralized mixture, using lime, of the same three components.

Ultimately, comparative trials should be performed for both old and fresh Goudron sludge mixtures.

Initially, the tests should be performed on the one incinerator which is currently in operation, Incinerator No. 2. Later, the test program may be expanded at Petrochema's prerogative to include Incinerator No. 1 (now undergoing repairs). Figures 5 and 6 show the stack location where the SO_2 analyzer will be placed during the testing of Incinerator No. 1 and No. 2, respectively.

If the initial comparative trials are successful in significantly reducing SO_2 emissions from the incinerator, then future tests could include varying the composition of the individual components in the Goudron sludge mixture. The goal of this subsequent testing would be to determine an optimal sludge mixture which minimizes incinerator SO_2 emissions. Depending upon the timeframe required to collect this "optimization" data set, it may not be considered within the scope of WEC's activities and funding. However, Petrochema will have all the analytical tools and technical expertise to collect this kind of data by themselves in the future.

Figure 7 is a Test Plan Data Collection Form and shows the key data which should be collected for the neutralization of Goudron sludge testing. Two critical measurements, in addition to the measurement of SO_2 concentration in the flue gas, are the amount of excess oxygen (O_2) and the flue gas velocity in the stack. During our December visit, the Petrochema/WEC team discussed how these two important parameters would be measured. It was agreed that a source test contractor could be used to measure stack velocity (and temperature). At the same time, excess oxygen could be measured by making a manual measurement using an inexpensive test apparatus known as a Bacharach Fyrite Gas O_2 Analyzer. In Radian's memorandum titled, Supplier and Service Representative Information (21 December 1993), ordering details for the Fyrite analyzer were provided.

Finally, the team agreed that Petrochema staff would collect the test data for this program after the departure of WEC/Radian team from Slovakia on 10 December 1993.

5.3 Test Results

[Test results will be collected by Petrochema staff during the first quarter of 1994. After the results have been forwarded to Radian for analysis, they will be documented as a revision to this report.]

5.4 Emissions Reductions and Potential Economic Savings

If the neutralization of Goudron sludge is successful, the following waste reduction and economic benefits should be realized:

- SO_2 emissions from the facility's incinerator when burning Goudron sludge may be reduced from 10,000 mg/m^3 (3836 ppmv) to at least the

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new air permit limit of 3000 mg/m^3 (1150 ppmv). Assuming one metric ton of Goudron sludge per hour is burned in the incinerator on average and 24 hour/day operation, 365 days per year, a reduction of 180 metric tons/year of SO_2 emissions could be achieved.

[Actual reductions may be significantly greater and will be verified during the test program.]

- Both sludge from the wastewater treatment plant and spent clay from the white oil plant can be mixed with Goudron sludge and incinerated, reducing the volume of these two waste materials requiring land disposal.

  [Actual cost savings due to sludge reduction will be calculated based on the data collected during the test program.]

- For the period 1993-1998, the cost savings in reduced SO_2 emissions penalties is estimated to be approximately 775,000 Slovak Korunas, or about US$25,000.

  [Actual cost savings may be significantly greater and will be recalculated based on the data collected during the test program.]

5.5 Conclusions and Recommendations

[To be developed after incineration SO_2 emissions test results have been collected and analyzed.]

6.0 SCHEDULE OF PROPOSED STEPS

As agreed upon in our team meeting on Monday, 6 December, the Petrochema staff will be responsible for collecting the test data for the neutralization of Goudron sludge. Once the data is collected, it will be forwarded to Radian for analysis.

In order to keep the project moving forward, we propose the following schedule. Of course, the actual implementation of this schedule will be determined by Petrochema.

March 15	Petrochema to Collect Goudron Sludge Incineration Test Data & Fax to Radian
March 31	Radian to Analyze Data with Petrochema Assistance
April 15	Radian to complete Goudron Sludge Section of Final Report

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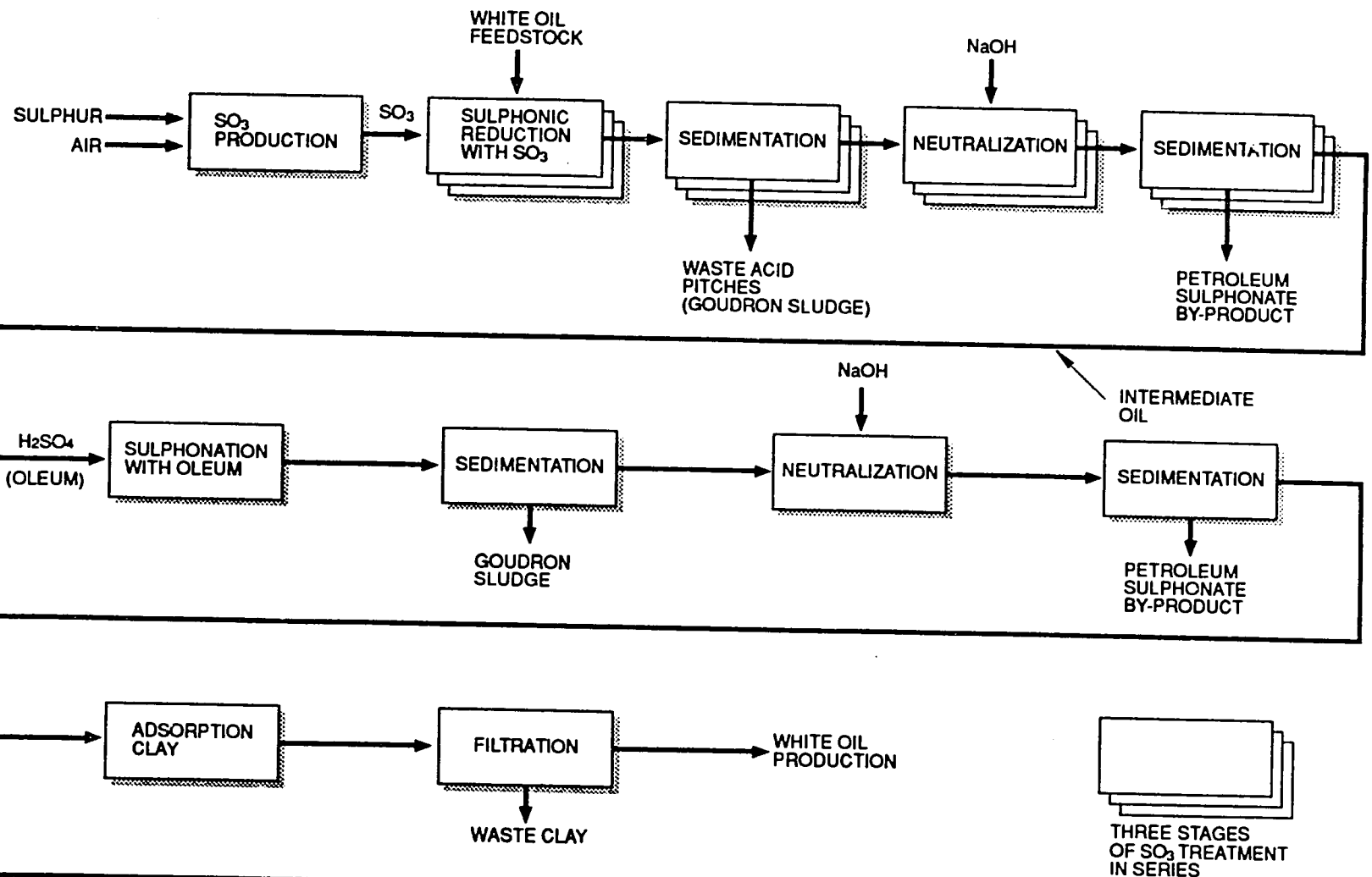

Figure 1. Process Flow Digram - White Oil Production

ELS700-101-01-01/05-93-59-01

RADIAN CORPORATION

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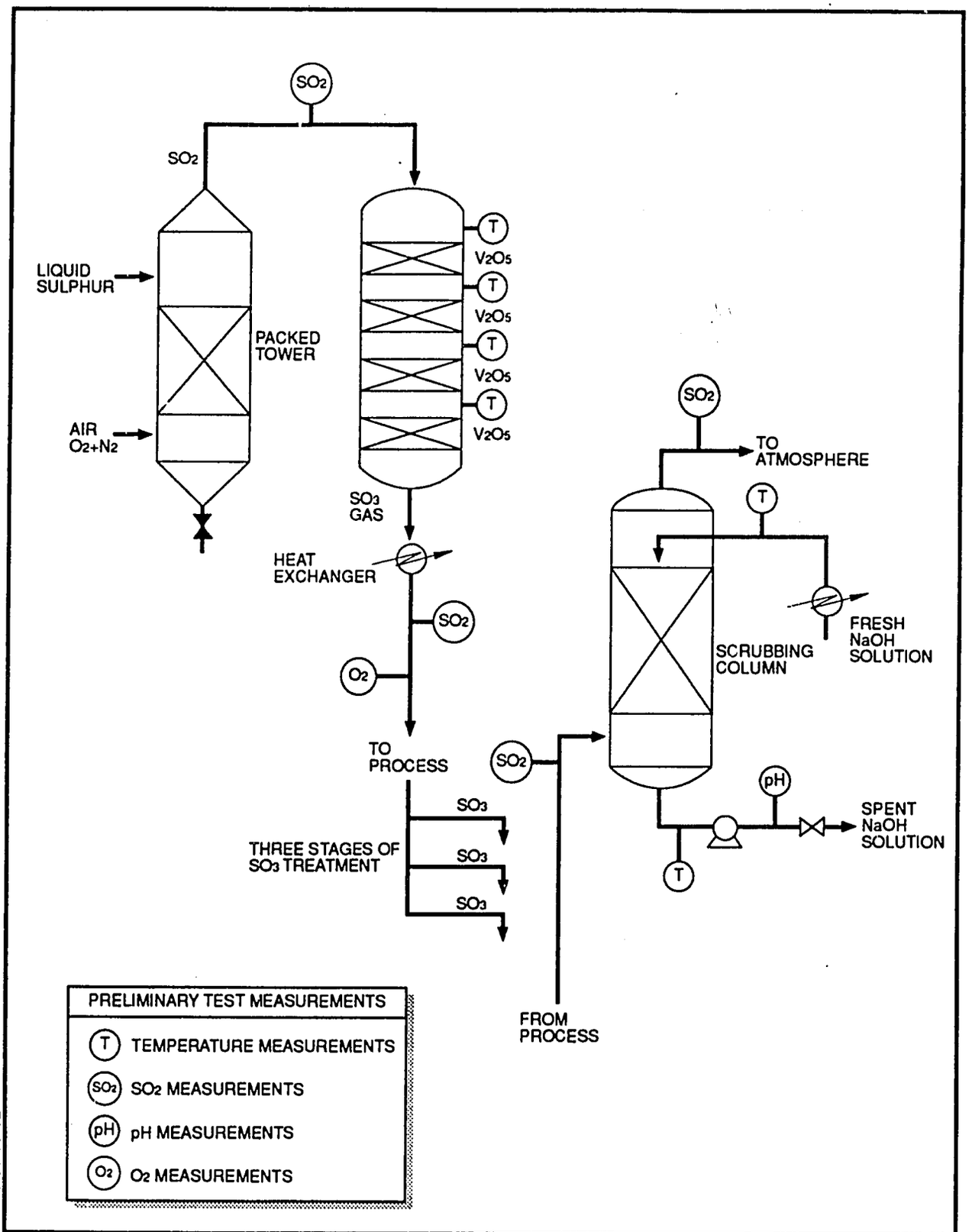


ELS700-101-01-01/05-93-59-02

Figure 2. Process Flow Diagram - SO_3 Production in the White Oil Plant

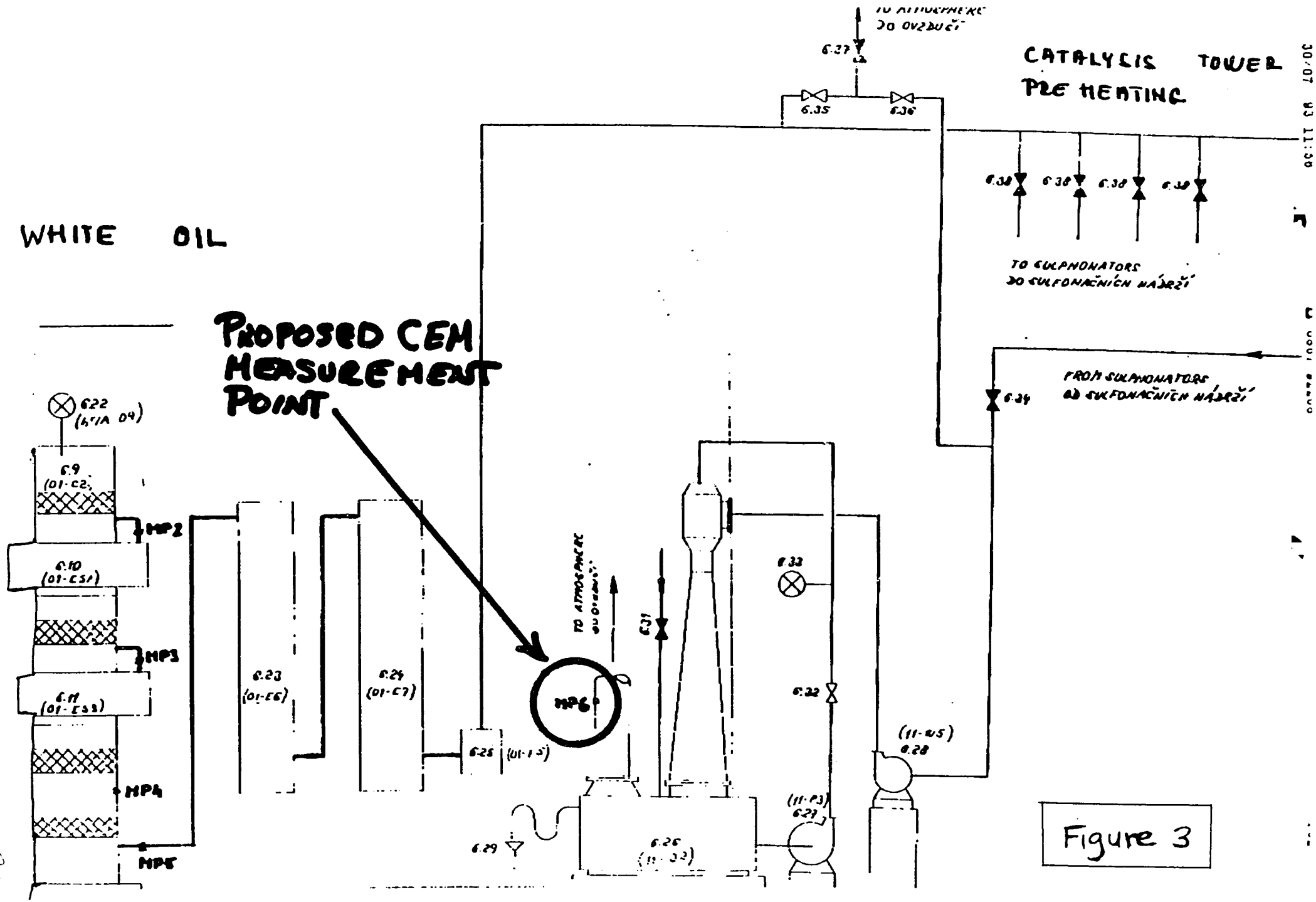

CATALYSIS TOWER
PRE HEATING
WHITE OIL
PROPOSED CEM MEASUREMENT POINT
TO ATMOSPHERE
DO OVZDUŠÍ
TO SULPHONATORS
DO SULFONAČNÍCH NÁDRŽÍ
FROM SULPHONATORS
OD SULFONAČNÍCH NÁDRŽÍ
6.27
6.35
6.36
6.38
6.39
6.34
6.22
6.9
6.10
6.11
6.23
6.24
6.25
6.26
6.29
6.31
6.32
6.33
6.28
MP2
MP3
MP4
MP5
MP6

Figure 3

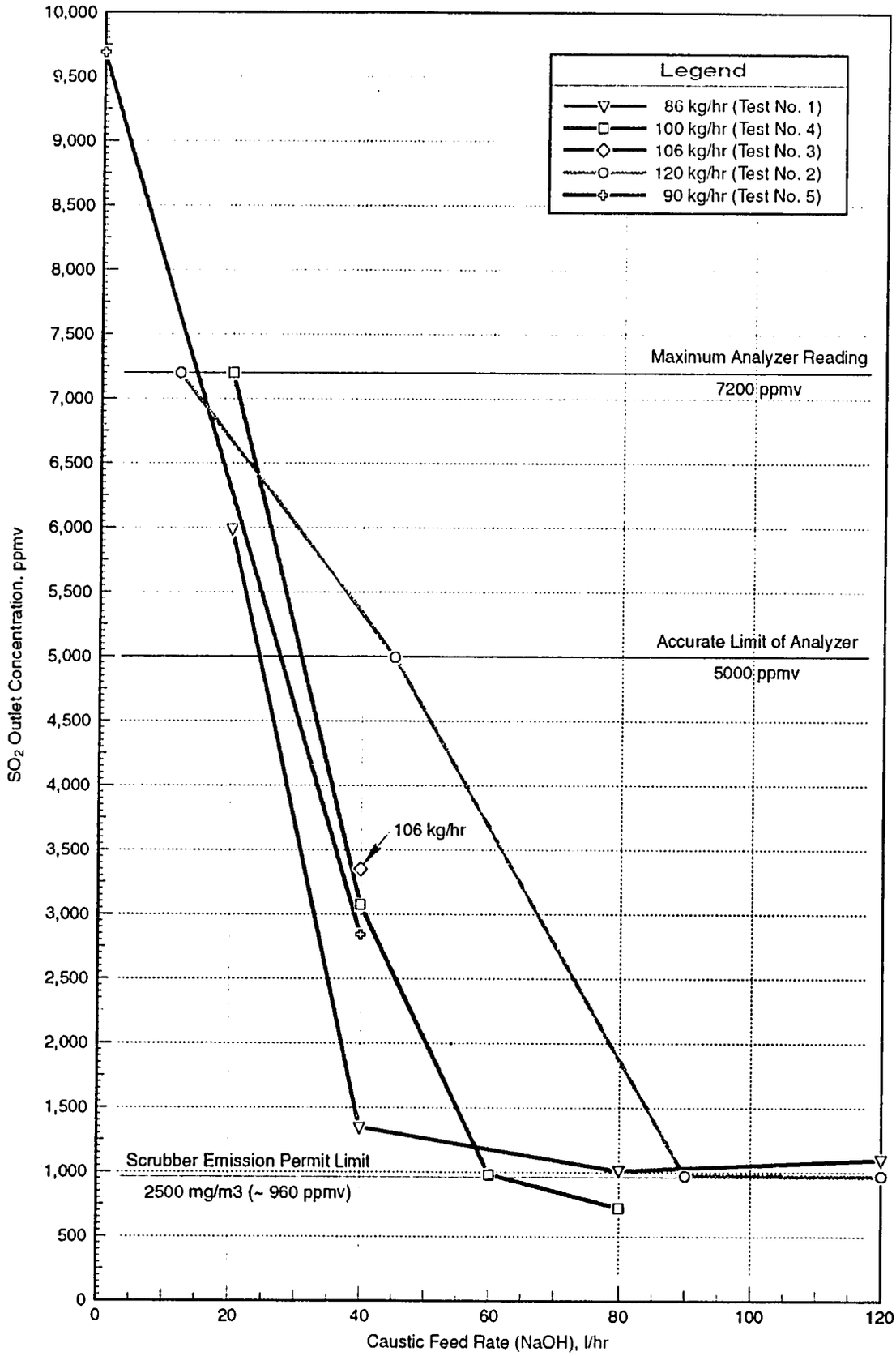


Figure 4. Scrubber Outlet SO_2 Concentration vs. Caustic Feed Rate

INCINERATOR 1.

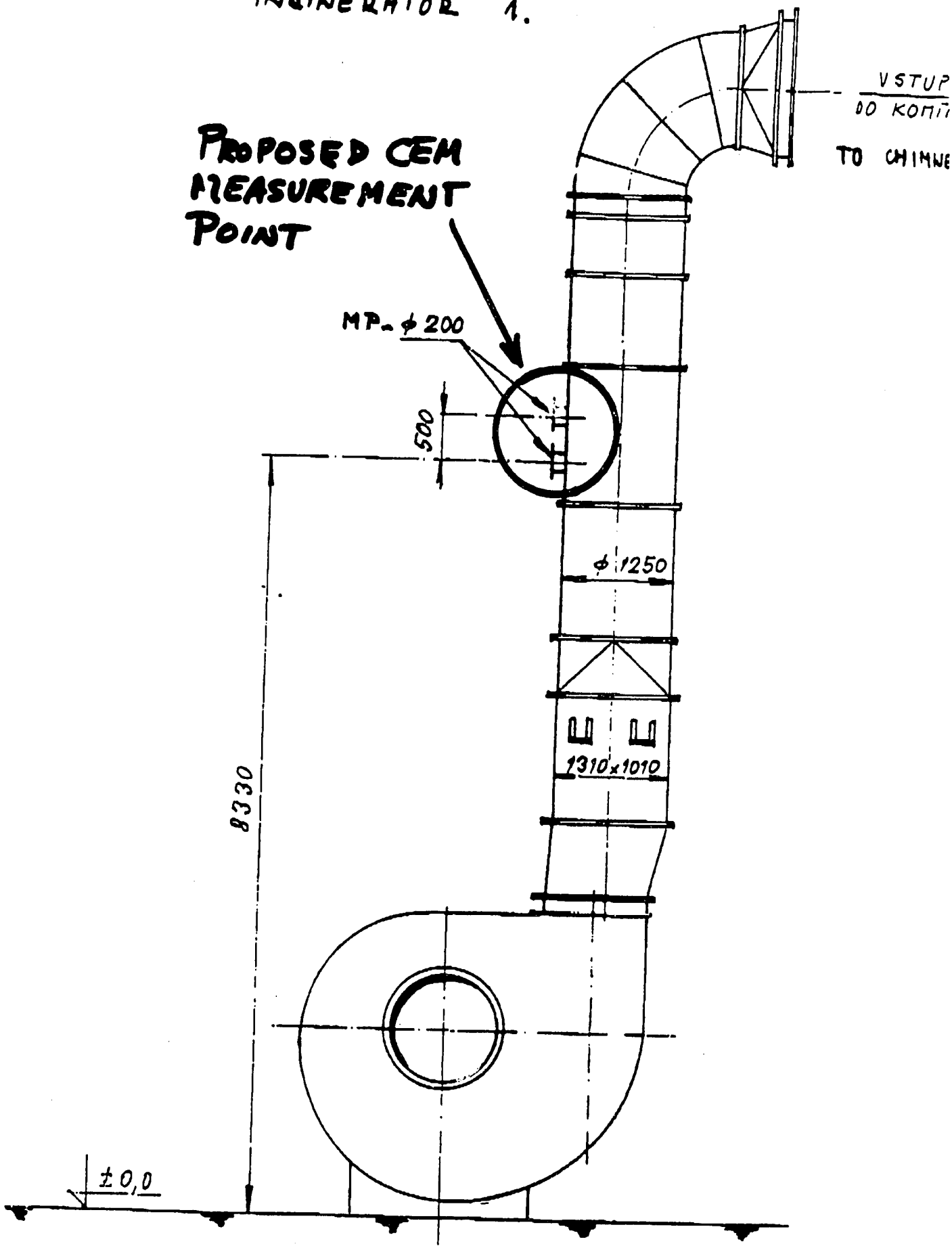


Figure 5

MP - MEASURING PLACES OF SO_2

INCINERATOR 2.

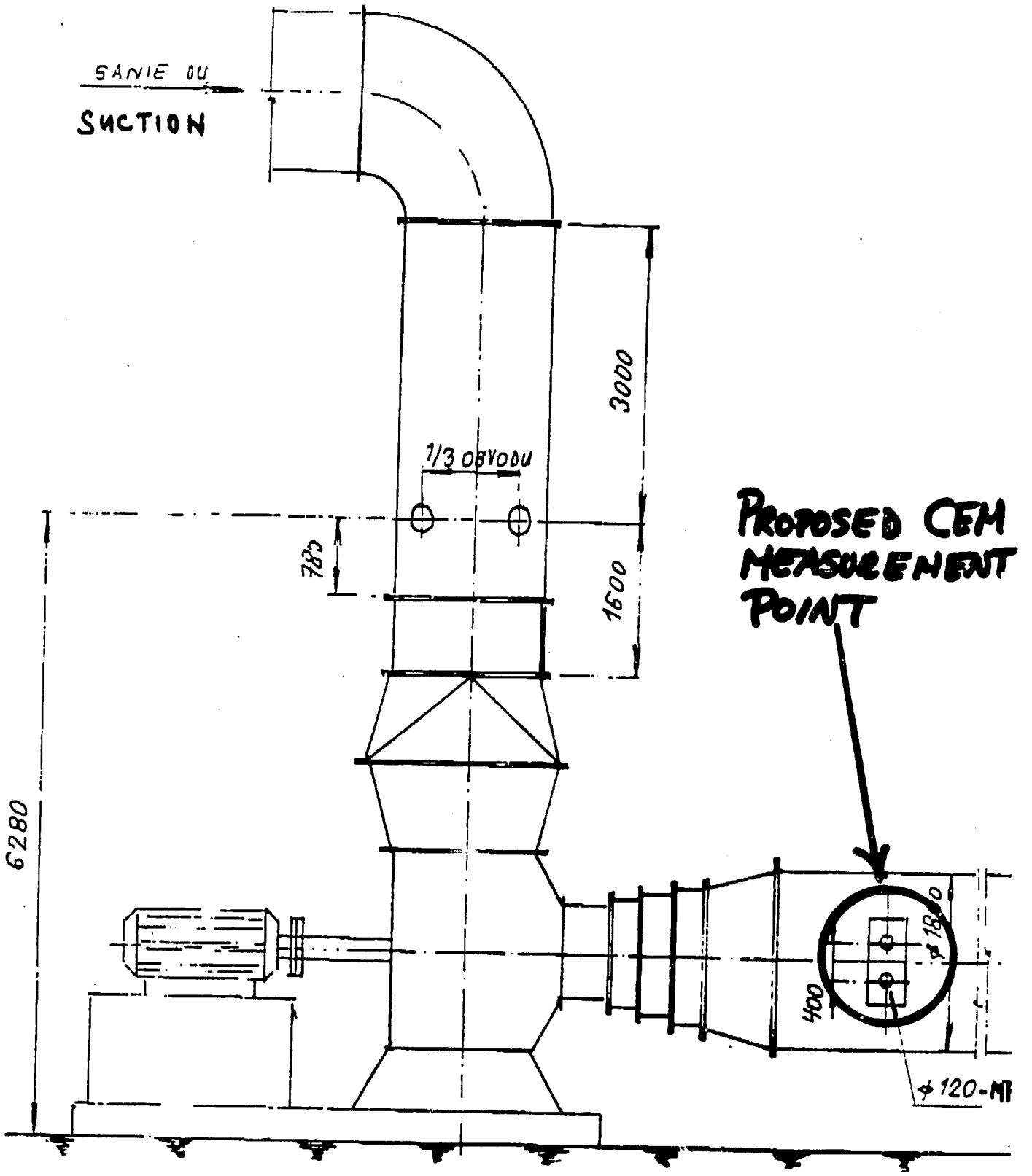


Figure 6 MP- MEASURING PLACES OF SO_2

TEST PLAN DATA COLLECTION FORM

Formulár pre zozbieranie hodnôt testovania

GENERAL INFORMATION Všeobecné informácie	GUDRON SLUDGE QUALITY/BURN MIXTURE Kvalita gudrónových smôl/spaľovacia zmes
TRIAL No. Číslo pokusu	GUDRON SLUDGE COMPOSITION (%) (PRIOR TO NEUTRALIZATION) Zloženie gudrónových smôl (%) (Pred neutralizáciou)
DATE Dátum	
TEST START TIME Čas začiatku pokusu	GUDRON TYPE Druh gudrónu
TEST END TIME Čas ukončenia pokusu	OIL Olej
TEST DURATION Trvanie pokusu	WATER Voda
INCINERATOR TYPE Typ spaľovne	SULPHONIC ACID Sulfokyselina
OTHER GENERAL INFORMATION: Iné všeobecné informácie	SULFURIC ACID Kyselina sírová
	SPENT CLAY Použitá hlinka (IF MEASURED) (Ak je namiešaná)
BURN CONDITIONS Podmienky spaľovania	SULFUR CONTENT Obsah síry
SLUDGE FEED RATE Nástrek smôl	SLUDGE MIXTURE VOLUME (OR MASS) Množstvo zmesi gudrónov
INCINERATOR TEMPERATURE Teplota spaľovania	GUDRON SLUDGE Gudrónové smoly
INCIN. EXCESS O2 Prebytok O2 na spaľ.	WWT SLUDGE Kaly z ČOV
FLUE GAS FLOW RATE Prietok dymu	SPENT CLAY Použitá hlinka
SO2 STACK EMISSIONS Emisie SO2 do komína	LIME Ca(OH)2
OTHER Iné	TOTAL VOLUME (OR MASS) OF SLUDGE MIXTURE INCINERATED Celkové spálené hmotové množstvo zmesi smôl
	OTHER Iné

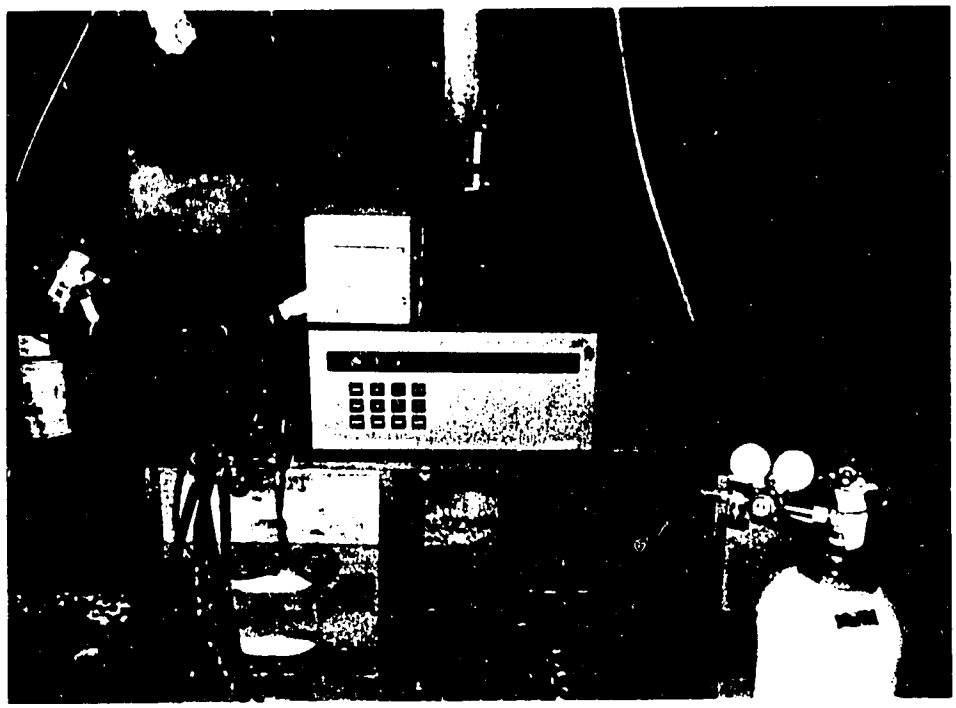
OTHER KEY TEST MEASURMENTS/TEST RUN COMMENTS:
Iné kľúčové merania testu/Poznámky k priebehu testu

FIGURE 7

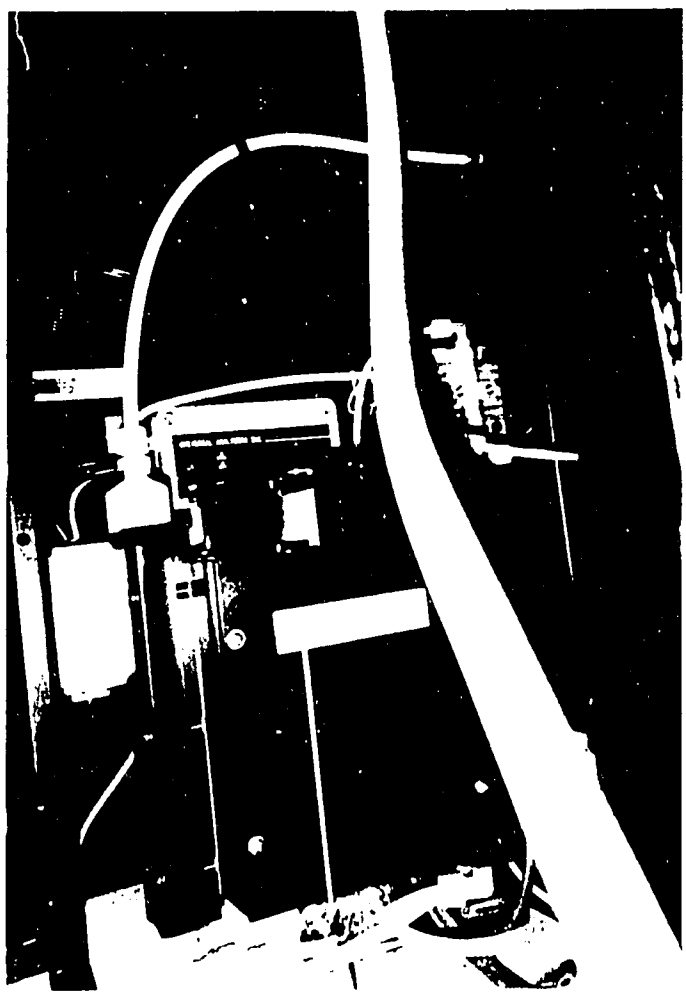
RADIAN
CORPORATION

ATTACHMENT A

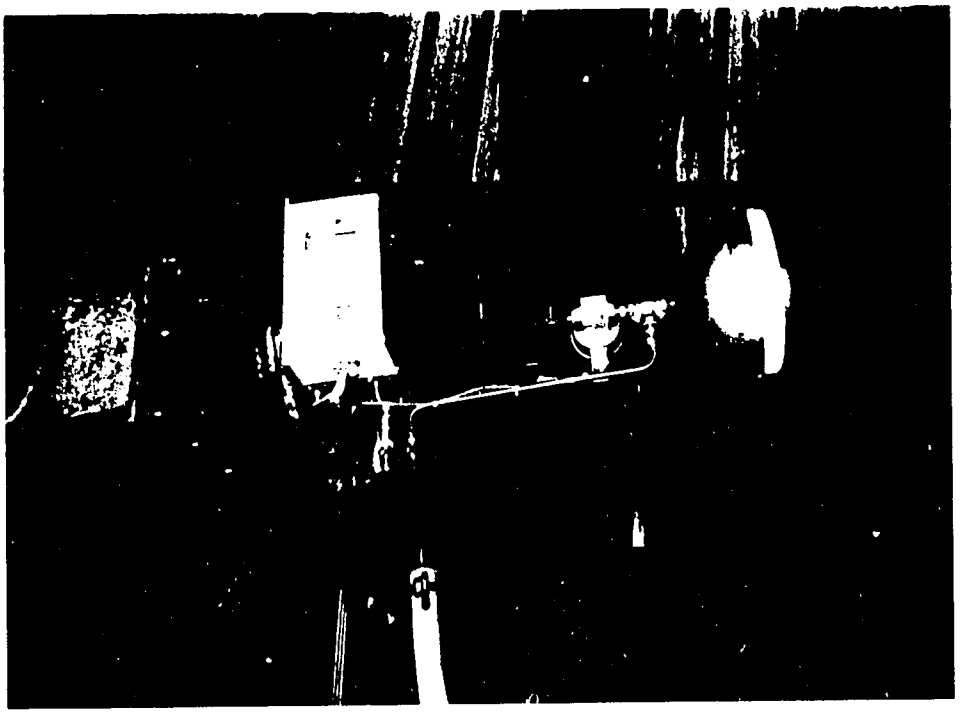
DECEMBER 1993 VISIT PHOTOGRAPHS



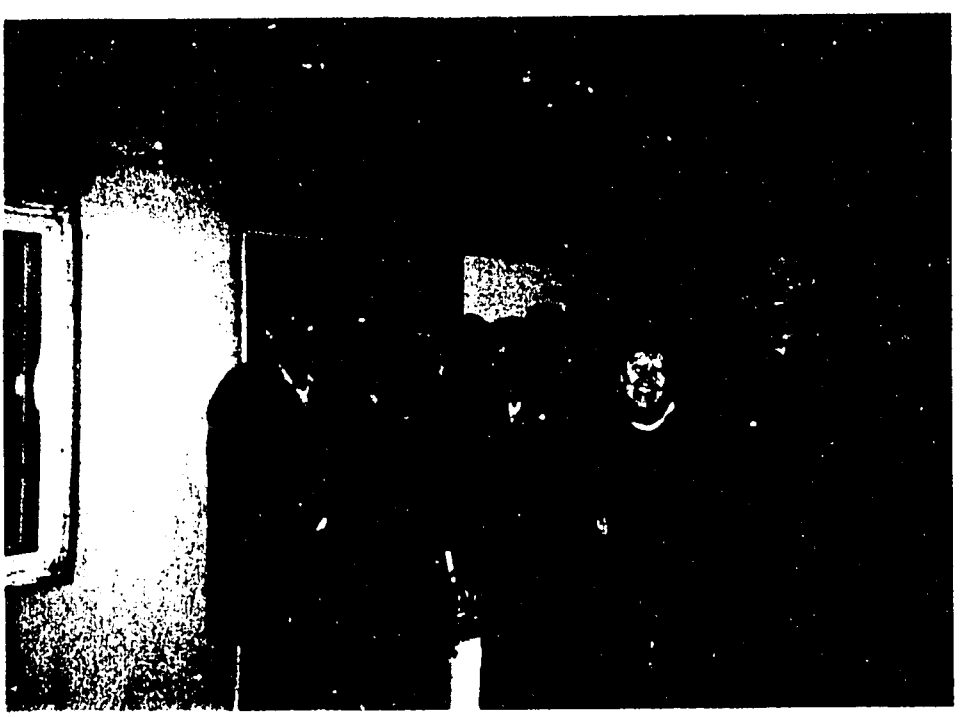
ROSEMOUNT ANALYTICAL MODEL 890 SO_2 ANALYZER



UNIVERSAL ANALYZERS SAMPLE CONDITIONING SYSTEM



UNIVERSAL ANALYZERS SO_2 SAMPLE COLLECTION PROBE



PROJECT TEAM MEMBERS

ATTACHMENT B

TEST DATA
DECEMBER 1993 VISIT

PETROCHEMA - WHITE OIL PLANT
Petrochema - Biele oleje

CAUSTIC SCRUBBER OPTIMIZATION
Optimalizácia lúhovej pračky plynov

DATA SHEET
List pre zber dát

GENERAL INFORMATION Všeobecné informácie	
TEST DATE Dátum skúšky	12/2/93
SCRUBBER CONFIGURATION Konfigurácia práčky	NEW SCRUBBER ONLY
LIQUID SULFUR FEED RATE Nástrek kvapalnej síry	86 kg/hr
OIL FEED RATE (2) Nástrek oleja	1440 l/hr OR 1238 kg/hr
WATER FLOW RATE TO SCRUBBER Nástrek vody do pračky	18 l/MIN
AIR FLOW RATE (3) Nástrek vzduchu	736 m³/hr (46 %)
SO2/IN AT TEST END ppmv Vstup SO2 pri ukončení skúšky	> 7178 ppmv (4)

TRIAL No. 1 Č. pokusu	1 5:20 pm	2 5:05 pm	3 4:30 pm	4 3:40 pm	5 —
CAUSTIC FEED RATE l/hour Nástrek NaOH l/hod.	20	40	80	120	Ø
pH OF CAUSTIC OUTLET pH NaOH na výstupe	6.0	7.0	6.5	6.5	6.5
SO2/OUT (1) ppmv SO2 na výstupe	~6000	1350	1009	1100	>7178 (5)

NOTE:
Poznámka WAIT ~ 1/2 HOUR BETWEEN CHANGES IN CAUSTIC FEED RATE TO SCRUBBER TO ACHIEVE STEADY STATE.

TEST COMMENTS:
Pripomienky k testu (1) ANALYZER CALIBRATION CHECKS WERE 3991 & 3928 ppm (VS. 4000 ppmv) AT 1:30 & 3:30 pm — OK; SYSTEM CHECK WAS > 3800 ppmV AT 4:55 pm (±2%) — OK.

(2) SPECIFIC GRAVITY OF OIL IS 0.86; SO OIL FEED RATE IN l/hr x 0.86 = OIL FEED RATE IN kg/hr

(3) AIR FEED RATE IS CALCULATED AS A % OF COMPRESSOR MANUFACTURER'S MAXIMUM RATING OF 1600 m³/Hr

(4) INLET SO_2 CONCENTRATION WAS GREATER THAN THE MAXIMUM READING OF THE ANALYZER

(5) ESTIMATE ONLY — NOT ACTUALLY MEASURED

PETROCHEMA - WHITE OIL PLANT
Petrochema - Biele oleje

CAUSTIC SCRUBBER OPTIMIZATION
Optimalizácia lúhovej pračky plynov

DATA SHEET
List pre zber dát

GENERAL INFORMATION Všeobecné informácie	
TEST DATE Dátum skúšky	12/3/93
SCRUBBER CONFIGURATION Konfigurácia práčky	NEW SCRUBBER ONLY
LIQUID SULFUR FEED RATE Nástrek kvapalnej síry	120 kg/hr
OIL FEED RATE Nástrek oleja	1000 l/hr OR 1548 kg/hr
WATER FLOW RATE TO SCRUBBER Nástrek vody do pračky	15 l/MIN
AIR FLOW RATE Nástrek vzduchu	800 m³/hr (50%)
SO2/IN AT TEST END ppmv Vstup SO2 pri ukončení skúšky	> 7178 ppmv (2)

TRIAL No. 2 Č. pokusu	1 8:20 am	2 10:45 am	3 10:15 am	4 9:10 am	5 —
CAUSTIC FEED RATE l/hour Nástrek NaOH l/hod.	12	45	90	120	C
pH OF CAUSTIC OUTLET pH NaOH na výstupe	6	6-7	6-7	6-7	—
SO2/OUT ppmv SO2 na výstupe	>7178	4762 (4) (~5000)	962	987	>>7178 (3)

NOTE:
Poznámka

TEST COMMENTS: (1)
Pripomienky k testu

(1) SEE TEST COMMENTS (2) & (3) FROM TRIAL NO. 1

(2) INLET SO_2 CONCENTRATION WAS GREATER THAN THE MAXIMUM READING OF THE ANALYZER

(3) ESTIMATE ONLY — NOT ACTUALLY MEASURED

(4) CONCENTRATION [illegible] INCREASE [illegible] AFTER IT WAS RECORDED TO BE 4762 ppmv — ESTIMATED TO BE [illegible] ppmv

2/2

PETROCHEMA - WHITE OIL PLANT
Petrochema - Biele oleje

CAUSTIC SCRUBBER OPTIMIZATION
Optimalizácia lúhovej pračky plynov

DATA SHEET
List pre zber dát

GENERAL INFORMATION Všeobecné informácie	
TEST DATE Dátum skúšky	12/3/93
SCRUBBER CONFIGURATION Konfigurácia práčky	NEW SCRUBBER ONLY
LIQUID SULFUR FEED RATE Nástrek kvapalnej síry	106 kg/hr
OIL FEED RATE Nástrek oleja	1902 l/hr OR 1636 kg/hr
WATER FLOW RATE TO SCRUBBER Nástrek vody do pračky	15 l/MIN
AIR FLOW RATE Nástrek vzduchu	896 m³/hr (56%)
SO2/IN AT TEST END ppmv Vstup SO2 pri ukončení skúšky	> 7178 ppmv (2)

TRIAL No. 3 Č. pokusu	1 1:15 pm	2	3	4	5
CAUSTIC FEED RATE l/hour Nástrek NaOH l/hod.	40				
pH OF CAUSTIC OUTLET pH NaOH na výstupe	6-7				
SO2/OUT (3) ppmv SO2 na výstupe	3352				

NOTE: WAIT BETWEEN 1/2 HOUR TO 1 HOUR BETWEEN
Poznámka CHANGES IN CAUSTIC FEED RATE TO ACHIEVE STEADY STATE (DEPENDING ON CAUSTIC FEED RATE

TEST COMMENTS: (1)
Pripomienky k testu

(1) SEE TEST COMMENTS (2) + (3) FROM TRIAL NO. 1

(2) INLET SO_2 CONCENTRATION WAS GREATER THAN THE MAXIMUM READING OF THE ANALYZER

(3) CALIBRATED SO_2 ANALYZER AT 1:00 pm WITH 4000 ppmv CALIBRATION GAS; ANALYZER READING = 3997 ppmv - OKV

PETROCHEMA - WHITE OIL PLANT
Petrochema - Biele oleje

CAUSTIC SCRUBBER OPTIMIZATION
Optimalizácia lúhovej pračky plynov

DATA SHEET
List pre zber dát

GENERAL INFORMATION Všeobecné informácie	
TEST DATE Dátum skúšky	12/3/93
SCRUBBER CONFIGURATION Konfigurácia práčky	NEW SCRUBBER ONLY
LIQUID SULFUR FEED RATE Nástrek kvapalnej síry	100 kg/hr
OIL FEED RATE Nástrek oleja	1902 l/hr or 1636 kg/hr
WATER FLOW RATE TO SCRUBBER Nástrek vody do pračky	15 l/MIN
AIR FLOW RATE Nástrek vzduchu	832 m³/hr (52%)
SO2/IN AT TEST END ppmV Vstup SO2 pri ukončení skúšky	> 7373 (2)

TRIAL No. 4 Č. pokusu	1	2	3	4	5
CAUSTIC FEED RATE l/hour Nástrek NaOH l/hod.	20	40	60	80	
pH OF CAUSTIC OUTLET pH NaOH na výstupe	6-7	7	6.5	6	
SO2/OUT ppmV SO2 na výstupe	>7373 (3)	3080	990	720 (4)	

NOTE:
Poznámka

TEST COMMENTS: (1)
Pripomienky k testu

(1) SEE TEST COMMENTS (2) & (3) FROM TRIAL NO. 1

(2) INLET SO_2 CONCENTRATION WAS GREATER THAN THE MAXIMUM READING OF THE ANALYZER

(3) ESTIMATE ONLY – NOT ACTUALLY MEASURED

(4) FIRST COMPLIANCE MEASUREMENT – COMPARE 720 ppmV WITH EMISSION LIMIT OF 960 ppmV (2500 mg/m³)

PETROCHEMA - WHITE OIL PLANT
Petrochema - Biele oleje

CAUSTIC SCRUBBER OPTIMIZATION
Optimalizácia lúhovej pračky plynov

DATA SHEET
List pre zber dát

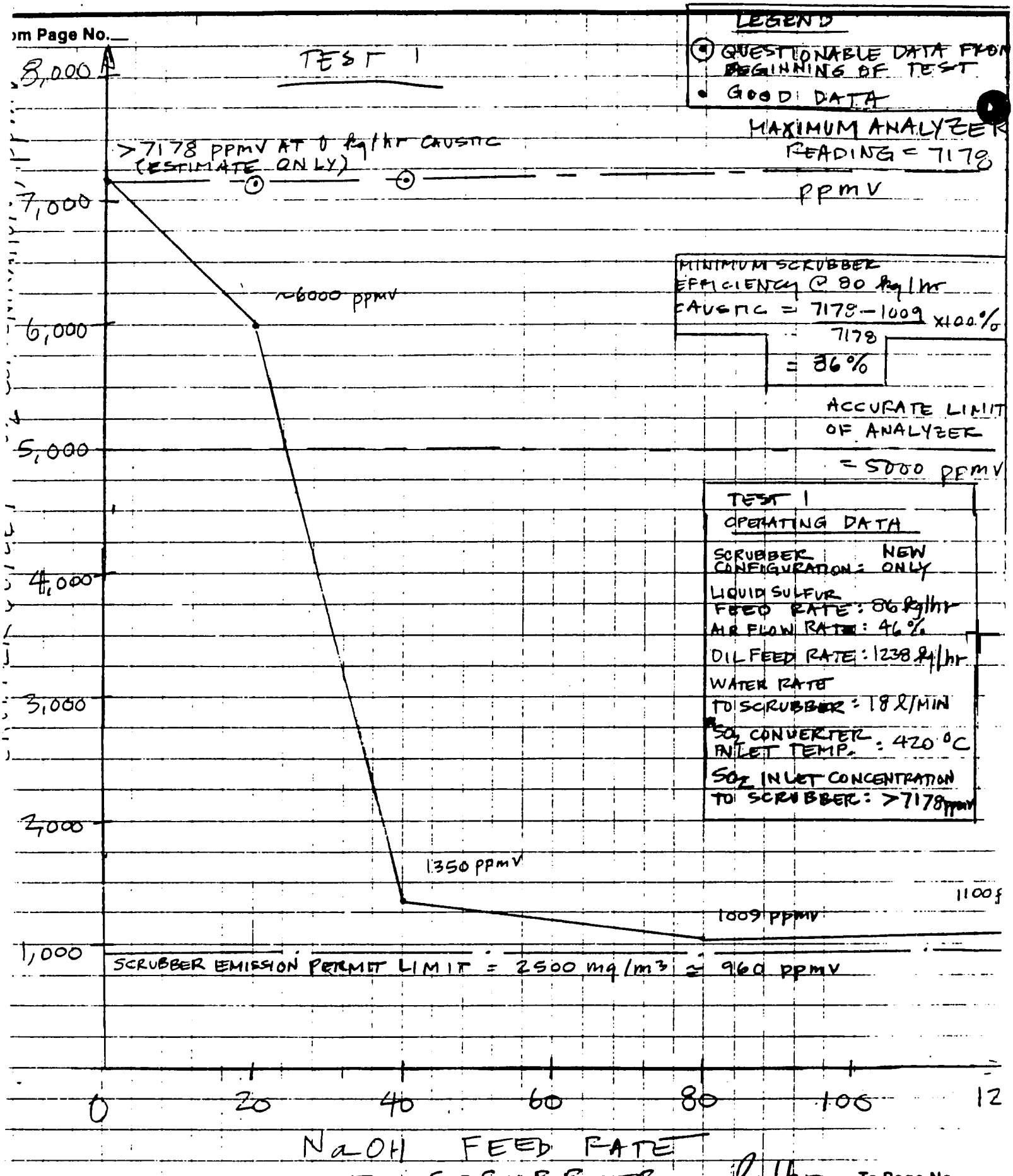
GENERAL INFORMATION Všeobecné informácie	
TEST DATE Dátum skúšky	12/5/93
SCRUBBER CONFIGURATION Konfigurácia práčky	NEW SCRUBBER ONLY
LIQUID SULFUR FEED RATE Nástrek kvapalnej síry	90 kg/hr
OIL FEED RATE Nástrek oleja	1900 l/hr OR 1634 kg/hr
WATER FLOW RATE TO SCRUBBER Nástrek vody do pračky	16 l/MIN
AIR FLOW RATE Nástrek vzduchu	7560 m³/hr (45%)
SO2/IN AT TEST END ppmv Vstup SO2 pri ukončení skúšky	10,386 ppmv (2)

TRIAL No. 5 Č. pokusu	1 12 NOON	2 12:45 pm	3	4	5
CAUSTIC FEED RATE l/hour Nástrek NaOH l/hod.	Ø	40			
pH OF CAUSTIC OUTLET pH NaOH na výstupe	6-7	6-7			
SO2/OUT SO2 na výstupe	9698	2840			

NOTE:
Poznámka

TEST COMMENTS: (1)
Pripomienky k testu

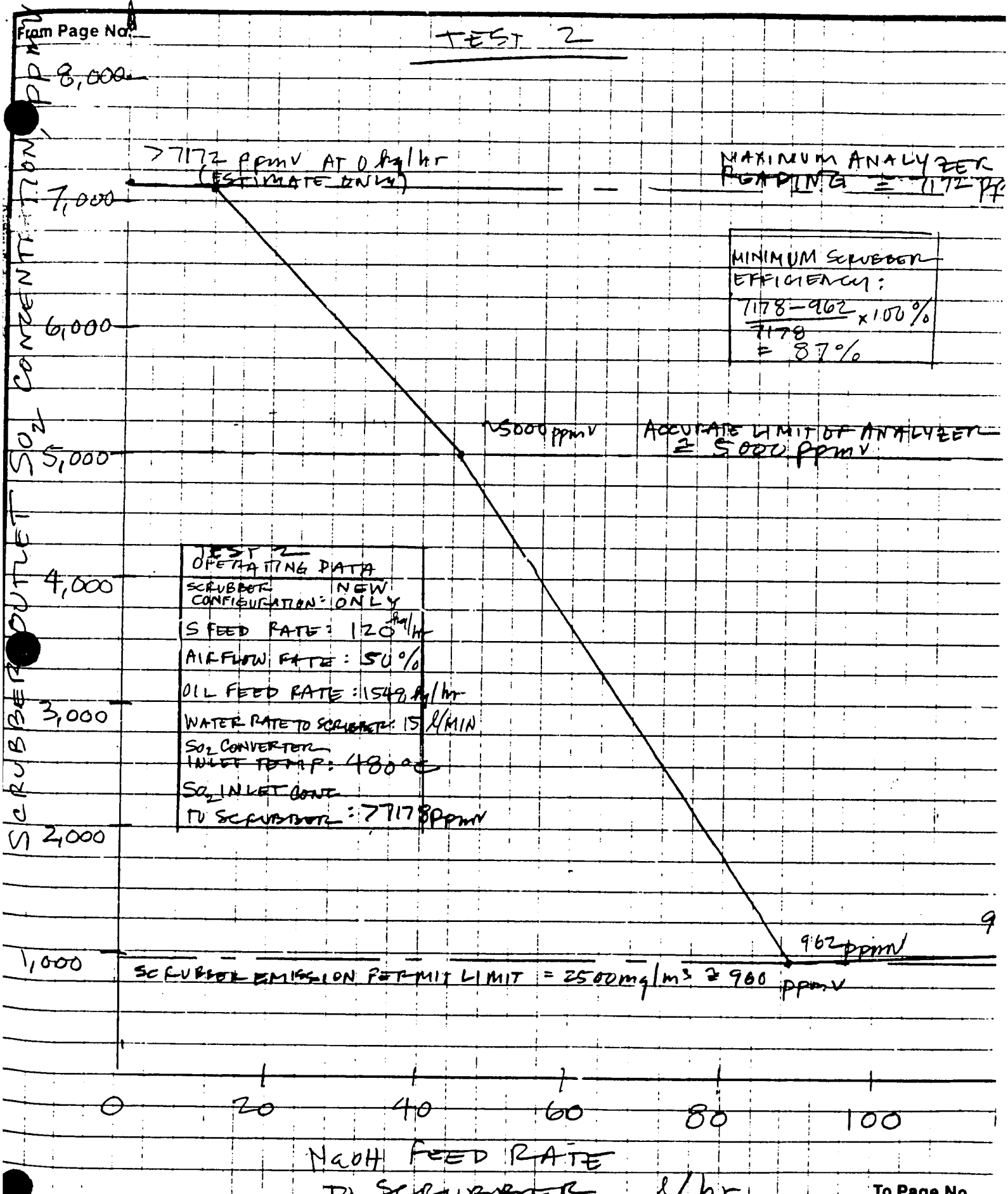
(1) SEE TEST COMMENTS (2) + (3) FROM TRIAL NO. 1
(2) INLET SO_2 CONCENTRATION WAS MEASURED ON-SCALE USING ABOUT ~3.7 DILUTION FACTOR OF AIR TO SAMPLE.



* SEE ATTACHED DATA SHEET FOR CONVERTER BED TEMPERATURES DURING TEST

TITLE _____ Project No. Book No. 28332 **RADIAN CORPORATION**

From Page No. _____



To Page No. _____

Witnessed & Understood by me,	Date	Invented by	Date
		Recorded by	

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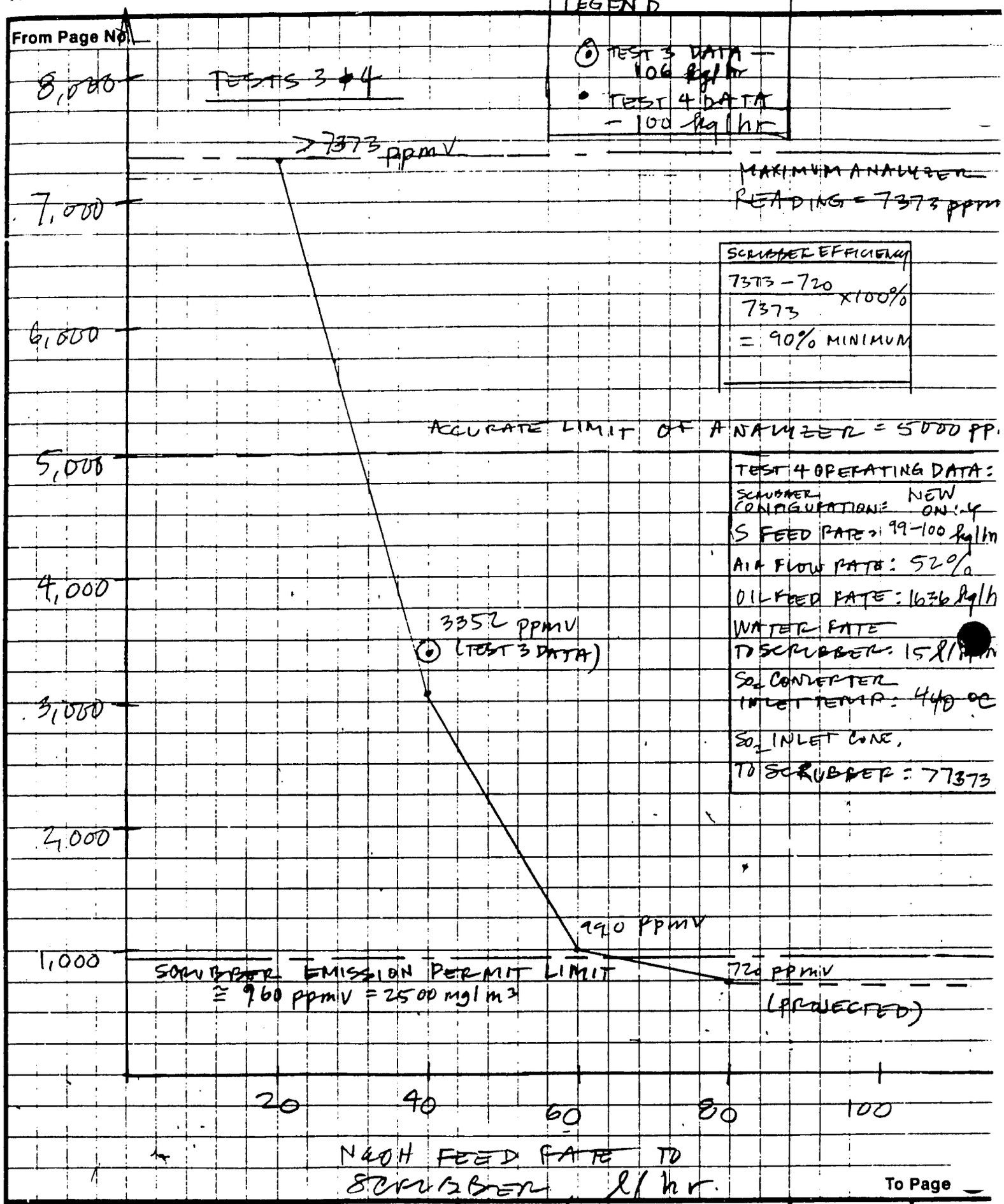
Project No. 28332
Book No.

TITLE

RADIAN CORPORATION

From Page No.



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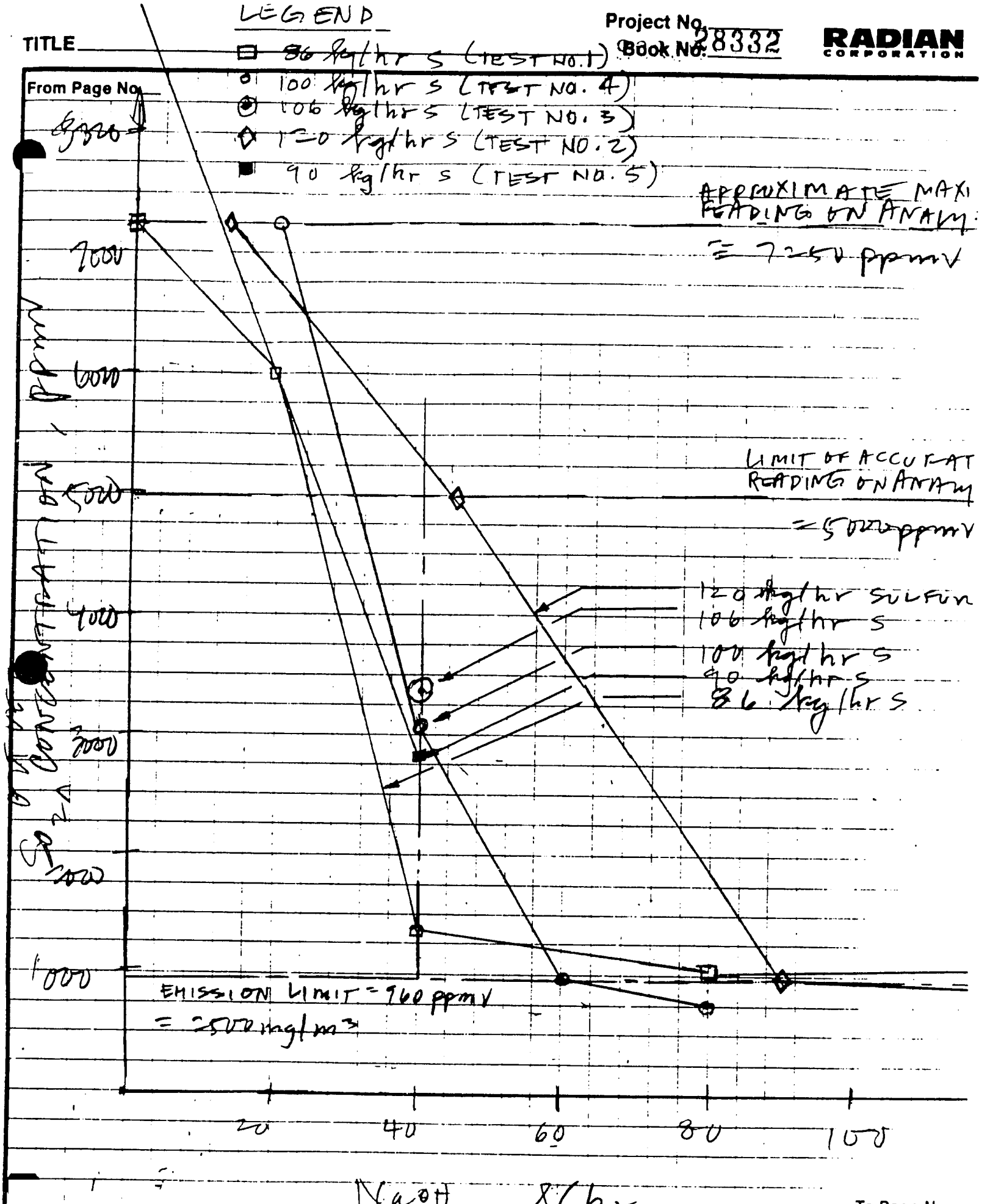
		Recorded by	

TITLE

Project No. 28332
Book No.

RADIAN CORPORATION

From Page No.



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		Recorded by	

RADIAN CORPORATION

CALCULATION SHEET

CALC. NO. —

SIGNATURE [illegible] DATE 12/2/93 CHECKED [illegible] DATE 12/3/93

PROJECT SO_3 OPTIMIZATION - WHITE OIL PLANT JOB NO. PETROCHEMICAL INDUSTRY MINIMIZATION DEMONSTRATION

SUBJECT TEST DATA — TEMPERATURE PROFILES SHEET 1 OF 1 SHEETS

	TIME	INLET TO CONVERTER	BED 1 OUTLET	BED 2 OUTLET	BED 3 OUTLET	BED 4 OUTLET
12/2	6:00	425°C	445	370		330
	7	425	440	370		325
	8	SHUT DOWN TO INSTALL PROBE				
	9					
TEST 1	10	340	320	220		210
	11	400	320	250		220
	12 NOON	420	380	280		240
	13	420	410	320		260
	14	420	420	330		280
	15	425	425	340		300
	16	430	440	350		300
	17	430	445	370		320
	18					
12/3	6:00	455°C	490	425		375
TEST 2	7	470	485	420		375
	8	480	505	435		375
	9	480	510	440		380
	10	480	510	445		390
	11	480	510	445		395
TEST 3	12 NOON	470	510	445		395
TEST 4	13	455	490	430		380
	14	440	480	420		380
	15	435	475	420		375
	16	440	470	415		370

10-88-30702 40

TEST 5 —

Hodiny	Teplota v °C: Síra 01 V1	Síra T 228	Pec 01 H1	Sili.sušič 01 E4	01 vrch	01 Sp.	Výstup	Konverzná veža: hla Hesd	I.	II.	III.	IV.	Výstup SO_2	Prosadenie: 01 Síra	01 K1	NaOH 11 E4		11 J-2	PH	Tlak: 01 H1 Hod.	para	Činnosť 01 -V2
6	143		580					440	470	405		355		17	44							
7	143		590					440	470	405		360		17	46							
8	142		595					440	470	405		360		17	46							
9	143		580					445	475	405		360		17	46							
10	143		585					440	470	405		360		17	46							
11	143		590					440	470	405		360		17	46							
12	143		585					440	470	405		355		17	46							
13	143		585					440	470	405		355		17	46							
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ATTACHMENT C

SAMPLE CALCULATIONS

RADIAN CORPORATION

CALCULATION SHEET

CALC. NO. C-1

SIGNATURE [illegible] DATE 12/27/93 CHECKED _____ DATE _____

PROJECT SO_3 OPTIMIZATION - WHITE OIL PLANT JOB NO. PETROCHEMA WASTE MINIMIZATION DEMONSTRATION

SUBJECT CONVERTER EFFICIENCY CALCULATION / SO_2 MATERIAL BALANCE SHEET 1 OF 3 SHEETS

SO_2 MATERIAL BALANCE - 90 kg/hr LIQUID SULFUR FEED RATE (TRIAL NO. 5)

ASSUMPTIONS:
1) 100% OF SULFUR BURNED IS CONVERTED TO SO_2
2) SCRUBBER ID FAN RATE ~ 2070 m^3/hr (DATA PROVIDED BY MR. MAJERCIK)
3) SO_2 IS NOT ABSORBED BY OIL & IT PASSES THROUGH SYSTEM UNREACTED. CONSERVATIVE ASSUMPTION - WE ARE CALCULATING MAXIMUM CONVERSION.

BASIS: 90 kg/hr; 10,386 ppmv SO_2 INLET TO SCRUBBER; 2070 m^3/hr SCRUBBER EXHAUST RATE

OVERALL WHITE OIL PLANT SYSTEM BALANCE FOR SO_2 (SEE ATTACHED PROCESS FLOW DIAGRAM - FIGURE C-1)

$$SO_2 \text{ INTO THE SYSTEM} = \frac{90\ kg\ S}{Hr} \left| \frac{kg\text{-}MOLE\ S}{32\ kg\ S} \right| \frac{1\ kg\text{-}MOLE\ SO_2}{1\ kg\text{-}MOLE\ S} \left| \frac{64\ kg\ SO_2}{kg\text{-}MOLE\ SO_2} \right.$$

$$= 180\ kg\ SO_2\ IN$$

$$SO_2 \text{ OUT OF SYSTEM} = \frac{10{,}386\ ppmv\ SO_2}{} \left| \frac{2.61\ mg/m^3}{ppmv} \right| \frac{2070\ m^3}{hr} \left| \frac{kg\ SO_2}{10^6\ mg\ SO_2} \right.$$

$$= 56.1\ kg\ SO_2\ OUT$$

10-88-30702

RADIAN CORPORATION

CALCULATION SHEET

CALC. NO. C-1

SIGNATURE [illegible] DATE 12/27/93 CHECKED _____ DATE _____

PROJECT [illegible] JOB NO. [illegible]

SUBJECT [illegible] SHEET 2 OF 3 SHEETS

CONVERTER EFFICIENCY (MAXIMUM - SEE ASSUMPTION NO. 3) $= \frac{(180 - 56.1)\ \text{kg } SO_2 \text{ REMOVED}}{180\ \text{kg } SO_2 \text{ IN}} \times 100\%$

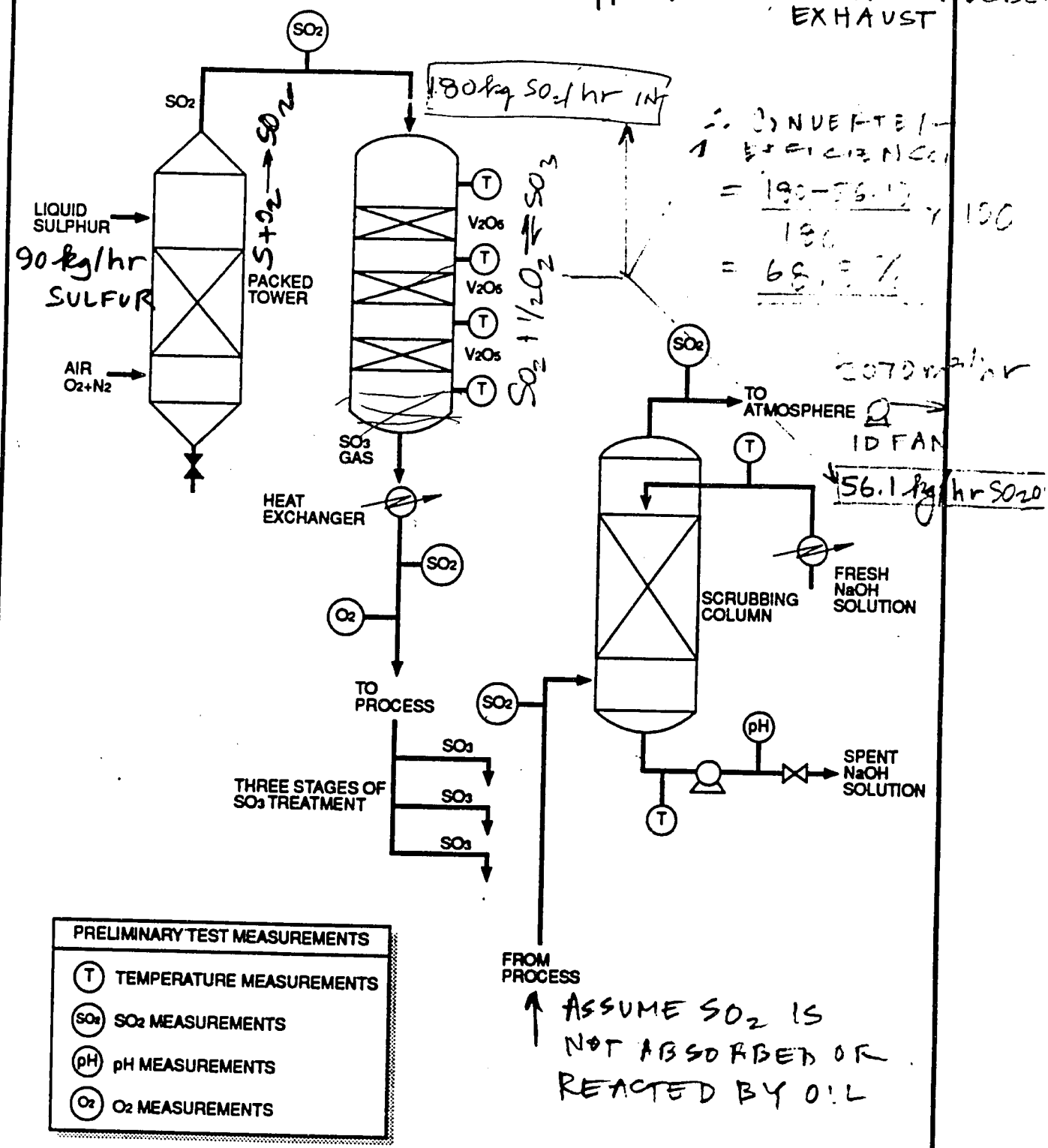
$= \boxed{68.8\%}$ — MAXIMUM CATALYTIC CONVERTER EFFICIENCY

$\Downarrow$

VS. $\boxed{96\%\ \text{DESIGN}}$ EFFICIENCY

<u>CONCLUSION</u>: CATALYST IS OPERATING WELL BELOW ITS DESIGN EFFICIENCY.

BASIS: 90 kg/hr SULFUR; 10,386 ppmV; 2070 m³/hr SCRUBBER EXHAUST



∴ CONVERTED EFFICIENCY = (180 − 56.1)/180 × 100 = 68.9%

2070 m³/hr

ASSUME SO2 IS NOT ABSORBED OR REACTED BY OIL

ELS700-101-01-01/05-93-59-02

Figure C-1. Process Flow Diagram - SO3 Production in the White Oil Plant

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CALCULATION SHEET

CALC. NO. C-2

SIGNATURE [illegible] DATE [illegible] CHECKED _____ DATE _____

PROJECT [illegible] JOB NO. [illegible]

SUBJECT CAUSTIC SCRUBBER [illegible] SHEET 1 OF 1 SHEETS

CAUSTIC SCRUBBER EFFICIENCIES

1) TRIAL 5 @ 40 ℓ/hr CAUSTIC, 90 kg/hr SULFUR

$$\text{SCRUBBER EFFICIENCY} = \frac{(10{,}386 - 28.40)\ \text{ppmv}}{10{,}386\ \text{ppmv}} \times 100$$

$$= \underline{\underline{72.7\%}}$$

2) TRIAL 4 @ 60 ℓ/hr CAUSTIC, 100 kg/hr SULFUR

$$\text{SCRUBBER EFFICIENCY} = \frac{(10{,}500 - 720)\ \text{ppmv}}{10{,}500\ \text{ppmv}} \times 100$$

ASSUMED VALUE (READING WAS OFF-SCALE > 7373 ppmv)

$$= \underline{\underline{93\%}}$$

3) TRIAL 2 @ 90 ℓ/hr CAUSTIC, 120 kg/hr

$$\text{SCRUBBER EFFICIENCY} = \frac{(12{,}000 - 962)\ \text{ppmv}}{962\ \text{ppm}} \times 100 = \underline{\underline{92\%}}$$

ASSUMED VALUE DUE TO OFF-SCALE READING

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CALCULATION SHEET

CALC. NO. C-3

SIGNATURE [illegible] DATE 1/29/94 CHECKED _____ DATE _____

PROJECT SO_2 OPTIMIZATION - WHITE OIL PLANT JOB NO. PETROCHEMA WASTE MINIMIZATION DEMONSTRATION

SUBJECT SO_2 SCRUBBER OUTLET EMISSIONS WITH ADDITION OF NEW CATALYST SHEET 1 OF 1 SHEETS

SO_2 SCRUBBER OUTLET EMISSIONS — ADDITION OF NEW CATALYST

ASSUME
- 100 kg/hr SULFUR FEED (NOTE: THIS IS A VERY CONSERVATIVE ASSUMPTION BECAUSE NEW, ACTIVE CATALYST SHOULD ALLOW FOR < 100 kg/hr TO ACHIEVE ACCEPTABLE SULPHONATION);
- 96 % EFFIENCY OF CONVERTER CATALYST (ie., 4% UNREACTED SO_2 PASSES TO SCRUBBER);
- 92 % SCRUBBER EFFICIENCY

$$\frac{100\ kg\ S}{hr} \cdot \frac{kg\text{-}MOLES\ S}{32\ kg\ S} \cdot \frac{1\ kg\text{-}MOLES\ SO_2\ IN}{1\ kg\text{-}MOLES\ S} \cdot \frac{0.04\ kg\text{-}MOLES\ SO_2\ OUT\ OF\ CONVERTER}{1\ kg\text{-}MOLES\ SO_2\ IN}$$

96% CONVERTER EFFICIENCY

92% SCRUBBER EFFICIENCY

$$\times \frac{0.08\ kg\text{-}MOLES\ SO_2\ OUT\ OF\ SCRUBBER}{kg\text{-}MOLE\ SO_2\ OUT\ OF\ CONVERTER} \cdot \frac{64\ kg\ SO_2\ OUT\ OF\ SCRUBBER}{kg\text{-}MOLE\ SO_2}$$

$$\times \frac{10^6\ mg\ SO_2}{kg\ SO_2\ OUT\ OF\ SCRUBBER} \cdot \frac{hr}{2070\ m^3\ SCRUBBER\ EXHAUST}$$

$$= \boxed{309\ mg/m^3\ SO_2\ IN\ SCRUBBER\ EXHAUST}$$

$$= \boxed{118\ ppmv\ SO_2}$$

POTENTIAL SO_2 OUTLET EMISSIONS FROM SCRUBBER WITH ADDITION OF NEW CATALYST

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CALCULATION SHEET

CALC. NO. C-4

SIGNATURE [illegible] DATE 1/29/94 CHECKED _____ DATE _____

PROJECT SO_2 OPTIMIZATION - WHITE OIL PLANT JOB NO. PETROCHEMA WASTE MINIMIZATION DEMONSTRATION

SUBJECT CAUSTIC & LIQUID SULFUR SAVINGS WITH ADDITION OF NEW CATALYST SHEET 1 OF 3 SHEETS

CAUSTIC & LIQUID SULFUR SAVINGS - ADDITION OF NEW CATALYST

CAUSTIC SAVINGS

NEW CATALYST WOULD ALLOW FOR CAUSTIC REDUCTION FROM 50-70 ℓ/hr TO 10-20 ℓ/hr

CHECK STOICHIOMETRIC CAUSTIC REQUIRED (BASIS 100 kg/hr S)

96% CONVERSION ASSUMED

$$\frac{100\ kg\ S}{hr} \left| \frac{kg\text{-}MOLE\ S}{32\ kg\ S} \right| \frac{1\ kg\text{-}MOLE\ SO_2\ TO\ CONVERTER}{1\ kg\text{-}MOLE\ S} \left| \frac{0.04\ kg\text{-}MOLE\ SO_2\ TO\ SCRUBBER}{kg\text{-}MOLE\ SO_2\ TO\ CONVERTER} \right.$$

$= 0.125$ kg-MOLES SO_2 TO SCRUBBER/hr

NEUTRALIZATION REACTION IN SCRUBBER IS:

$$NaOH + SO_2 \longrightarrow NaHSO_3$$

∴ 0.125 kg-MOLES NaOH/hr ARE NEEDED

$$\frac{0.125\ kg\text{-}MOLES\ NaOH}{HR} \left| \frac{40\ kg\ NaOH}{kg\text{-}MOLE\ NaOH} \right| \frac{\ell}{1.45\ kg\ SOLUTION} \left| \frac{kg\ NaOH\ SOLUTION}{0.45\ kg\ NaOH} \right.$$

$= \boxed{7.7\ \ell/hr}$ ← STOICHIOMETRIC AMOUNT OF 45 WT% CAUSTIC SOLUTION REQUIRED

SPECIFIC GRAVITY OF 45 WT% NaOH SOLUTION

∴ CONCLUSION - CAUSTIC RATE TO SCRUBBER COULD BE REDUCED TO 10-20 ℓ/hr (> 7.5 ℓ/hr).

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CALCULATION SHEET

CALC. NO. C-4

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PROJECT SO_3 OPTIMIZATION – WHITE OIL PLANT JOB NO. PETROCHEMIA WASTE MINIMIZATION DEMONSTRATION

SUBJECT CAUSTIC & LIQUID SULFUR SAVINGS WITH ADDITION OF NEW CATALYST SHEET 2 OF 3 SHEETS

CAUSTIC SAVINGS

REDUCED FROM 60–70 ℓ/hr (REQUIRED FOR SO_2 EMISSIONS COMPLIANCE)

TO 10–20 ℓ/hr (∴ REDUCTION = 40–50 ℓ/hr

ECONOMIC SAVINGS:

ASSUMES 50% WHITE OIL PLANT OPERATING FACTOR

$$\frac{40\ \ell\ \text{NaOH SOL'N}}{\text{hr}} \cdot \frac{24\ \text{hr}}{\text{DAY}} \cdot \frac{180\ \text{DAYS}}{\text{YR}} = \frac{172{,}800\ \ell/\text{yr}}{45\ \text{wt\%}\ \text{CAUSTIC SOLUTION}}$$

$$\frac{172{,}800\ \ell\ \text{NaOH SOLUTION}}{\text{yr}} \cdot \frac{7440\ \text{SLOVAK kr}}{1000\ \text{kg NaOH}} \cdot \frac{1.45\ \text{kg NaOH SOLUTION}}{\ell\ \text{SOLUTION}} \cdot \frac{0.45\ \text{kg NaOH}}{\text{kg NaOH SOLUTION}}$$

100 WT%

SPECIFIC GRAVITY – 45 WT% SOLUTION

$$\boxed{\begin{aligned} &= 839{,}000\ \text{SLOVAK kr/YR} \\ &= \sim \text{US\$}28{,}000/\text{YR} \end{aligned}}$$

ANNUAL CAUSTIC SAVINGS OF 40 ℓ/hr WITH NEW CATALYST

50 ℓ/hr SAVINGS = 1.2 × 839,000 S kr = ~1,000,000 S kr

= 1.2 × 28,000 US$ = ~35,000 US$

ANNUAL CAUSTIC SAVINGS OF 50 ℓ/hr WITH NEW CATALYST

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CALCULATION SHEET

CALC. NO. C-4

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PROJECT SO_3 OPTIMIZATION - WHITE OIL PLANT JOB NO. PETROCHEMA

SUBJECT CAUSTIC & LIQUID SULFUR SAVINGS WITH ADDITION OF NEW CATALYST SHEET 3 OF 3 SHEETS

LIQUID SULFUR SAVINGS

ASSUME CONVERSION EFFICIENCY INCREASES FROM ~70% (CURRENT CONVERSION WITH EXISTING CATALYST) TO ~96% (DESIGN CONVERSION WITH NEW CATALYST)

BASIS: 100 kg/hr USING OLD CATALYST

THEN (96 − 70)% = 26% IMPROVEMENT IN CATALYST EFFICIENCY

$0.26 \times \frac{100\ kg\ S}{hr}$ = 26 kg S/hr LESS SHOULD BE REQUIRED TO ACHIEVE ACCEPTABLE SULPHONATION.

ECONOMIC SAVINGS ARE:

50% OPERATING FACTOR — WHITE OIL PLANT

26 kg S / hr	24 hr / Day	180 DAYS / yr	2540 SLOVAK kr / 1000 kg S

= 285,000 Slovak kr

= 10,000 US $

LIQUID SULFUR SAVINGS WITH NEW CATALYST

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