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WORLD ENVIRONMENT CENTER

WASTE MINIMIZATION PROJECT

FINAL REPORT

TO

PETROCHEMA

DUBOVA, SLOVAK REPUBLIC

WORLD ENVIRONMENT CENTER
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TABLE OF CONTENTS

		Page
I.	Introduction	1
II.	Executive Summary	2 - 4
III.	Radian Corporation Report	5
IV.	Business Cards of Contacts	6

I. INTRODUCTION

Pursuant to the technical assistance for Central and Eastern European countries funded by the United States Agency for International Development, the World Environment Center (WEC) conducted a Waste Minimization Demonstration Project (WMDP) at the Petrochema White Oil Plant located in Dubova. The participants were:

Thomas J. McGrath	-	Vice President, WEC
B. Bhushan Lodh	-	Project Manager, WEC
Samuel Weiss	-	WEC Specialist
Edward Andrechak	-	Radian Corporation, Consultant
James E. Howes, Jr.	-	Radian Corporation, Consultant

The purpose of the Waste Minimization Demonstration Project included formation of the Waste Minimization Committee, 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. The Petrochema personnel conducted the "Goudron" sludge incineration tests and the data were analyzed by the consultant, Radian Corporation.

This final report issued by Radian Corporation includes the details of the WMDP program and conclusions and recommendations to minimize the sulfur dioxide reduction at the Petrochema White Oil Plant.

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.

- Petrochema staff will conduct the tests as outlined by Radian Corporation to incinerate the "Goudron" sludge wastes and forward the data to Radian for analysis.

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.

Seven incineration tests were conducted by Petrochema personnel using various mixtures of Goudron sludge, wastewater treatment sludge, oily contaminated soil and sewage. The data were transmitted to Radian Corporation for analysis and the results are presented in this report.

The report recommends to neutralize the Goudron sludge wastes by combining with other alkaline wastes prior to incineration. This will achieve the compliance with sulfur dioxide emission limit of 3000 mg/m^3 (1154 ppmv) and save Petrochema from the sulfur dioxide emission penalty of approximately 775,000

Slovak Korunas ($25,000).

Please refer to consultant Radian Corporation report, Section III.

III. RADIAN CORPORATION REPORT

DISCLAIMER

The opinions expressed in the report is the professional opinion of the author and does 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: 27 July 1994

SUBJECT: **Petrochema Waste Minimization Demonstration Program For SO_2 Emissions Reduction--Final Report**

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. This memorandum also documents the results of test data collected by Petrochema in March 1994.

In our initial 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 and the subsequent testing in March 1994 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 and March testing; Section 3.0 discusses the visit and testing logistics; Section 4.0 presents the test program and results for optimizing sulfur trioxide (SO_3) in the White Oil Plant; and Section 5.0 presents the waste minimization program involving the neutralization and incineration of Goudron sludge. Figures and tables 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); sample calculations for the White Oil Plant optimization (Attachment C); test data collected in March 1994 (Attachment D); and sample calculations collected for Goudron sludge neutralization and incineration (Attachment E).

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:

7

- 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.

- 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 appeared to be deactivated, achieving less than 70% conversion. At the same time, the caustic scrubber appeared 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.

- Overall, White Oil Plant optimization tests demonstrated a 75% reduction in SO_2 emissions to the atmosphere from the scrubber. This decrease is equivalent to a reduction of 70 tons of SO_2 annually.

- 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 to conduct Goudron sludge neutralization testing after the WEC/Radian team returned 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.

From the March 1994 tests conducted by Petrochema, the following was accomplished or determined:

- Plant test data were collected to demonstrate the effectiveness of the neutralization of Goudron sludge in reducing SO_2 emissions upon incineration.

- Neutralized Goudron sludge mixtures, when burned, demonstrated SO_2 emissions which were 72% less, on average, than previously burned unneutralized mixtures. This decrease is equivalent to a reduction of 185 metric tons of SO_2 annually.

- Neutralized Goudron sludge mixtures yield average SO_2 emissions upon incineration which comply with the incinerator's emissions permit limit.

3.0 VISIT AND TESTING 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 proposed test plan for the neutralization and incineration of Goudron sludge (this testing was conducted by the Petrochema staff in March 1994). On 6 and 7 December, Jim Howes of Radian conducted classroom and field training for the SO_2 analyzer which was 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.

As agreed during our December visit, Petrochema staff completed a series of incineration tests in March 1994. The purpose of these subsequent tests was to determine the effectiveness of the neutralization of Goudron sludge in reducing SO_2 emissions upon incineration. Petrochema forwarded the March test results to Radian for analysis in May 1994.

4.0 WASTE MINIMIZATION TEST PROGRAM NO.1: 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 could be varied to optimize SO_3 converter efficiency were: 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 could 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.

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. 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. On a mass basis, this decrease is equivalent to a reduction of 70 metric tons of SO_2 annually.

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 further;
- 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.

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 further 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:

14

- 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.

- The White Oil Plant optimization tests demonstrated a 75% reduction in SO_2 emissions to the atmosphere from the scrubber. This decrease is equivalent to a reduction of 70 metric tons of SO_2 annually.

- 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 incremental cost savings realized by changing catalyst may be more than 1,285,000 Slovak Korunas (US$45,000) per year. The economic savings associated with the process 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 was 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 alkaline wastewater treatment sludge (WTS) with the acidic Goudron sludge. The neutralization reaction removes sulfur as a sulfate salt precipitate. 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 had been previously conducted with encouraging results.

Alternatively, lime [$Ca(OH)_2$] may be used as a neutralizing agent. Some of the previous bench and pilot tests included the successful use of lime. For purposes of this waste minimization demonstration project, lime was *not* used in any of the test trials.

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 that is located 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 and was used during the performance of this waste minimization test. 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 were to:

- Demonstrate that the process of neutralizing Goudron sludge with wastewater treatment sludge 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

Seven incineration trials were conducted using various mixtures of Goudron sludge, wastewater treatment sludge (WTS), oily-contaminated soil (CS), and sewage (SEW). The Goudron sludge component in the test trials was either water acid *emulsion* (WAE) from the dump (i.e., landfill) or actual *sludge* from the dump (SD). None of the trials used *fresh* Goudron sludge directly produced from the White Oil Plant.

17

Three of the trials (Test Nos. 2, 3, and 4) utilized alkaline WTS as a neutralizing agent and represent partially *neutralized* test mixtures. The four remaining trials (Test Nos. 1, 5, 6, and 7) represent *unneutralized* test mixtures.

Figure 7 is a Test Data Plan Collection Form and generally summarizes the key data (with some deviations) which were collected for the neutralization and incineration of Goudron sludge testing.

Table 1 details the waste feed type and characteristics. Specifically, pre-test measurements of the waste feed components and the resultant mixtures included:

- Total Feed Mass, kg;
- Feed Type (WAE, SD, WTS, CS, & SEW);
- Proportion of Each Waste Type in Burn Mixture;
- Percentage Water, %;
- Acid Number;
- Percentage Sulfuric Acid, %;
- Percentage Oil, %; and
- Total Sulfur, %.

The acid numbers measured for the individual feed components and the resultant mixtures in Tests 2, 3, and 4 were used to determine if the wastewater treatment sludge (WTS) was effective in neutralizing the acidic components of the Goudron sludge (WAE and SD).

The key data collected during the incineration portion of the trial were:

- Test Start & End Time;
- Incinerator Temperature, °C;
- Excess Oxygen, % O_2;
- Incinerator Flow, m^3/hr; and
- Incinerator SO_2 Emissions, ppm (measured by SO_2 analyzer).

The SO_2 emissions data collected during the trials were used to determine if neutralized batches of Goudron sludge achieved lower SO_2 emissions than corresponding unneutralized

batches. We also performed a sulfur balance using the pre-test waste sulfur measurements (sulfur in) versus the sulfur emitted as SO_2 from the incinerator (sulfur out) to confirm that the lower emissions represented a true reduction in waste SO_2 emissions (i.e., waste minimization).

The incinerator SO_2 emissions data were also used to determine if Petrochema could attain compliance with the permit limit of 3000 mg/m^3 ($\sim$1150 ppmv).

5.3 Test Results

The discussion of the test data is focused relative to our test objectives. The neutralization and incineration test data collected in March 1994 are provided in Attachment D. Sample calculations supporting the following discussion of results are provided in Attachment E.

Evidence of Neutralization

A review of the acid number data in Appendix D and in Table 1 for Test Nos. 2, 3, and 4 suggests that some neutralization may be occurring. Specifically, in Test No. 2, the acidic SD initially had an acid number of 53.4 mg KOH/g. Mixing the alkaline WTS with the SD reduced the acid number of the resultant mixture to 1.6 mg NaOH/g. A similar reduction was achieved in Test No. 4. In that trial, the resultant mixture after neutralization by WTS had an acid number of zero. This result implies that the Test No. 4 mixture was essentially neutral.

It should be noted that in Test No.3, the waste treatment sludge was not mixed with the acidic dump sludge and waste acid emulsion prior to incineration. Rather, the water acid emulsion was fed to the incinerator by a separate nozzle. The SO_2 emissions measured for this trial were the highest of all seven trials. These high emissions suggest that separate dosing of water acid emulsion (without prior mixing) to the incinerator may not be an effective method of sludge neutralization. Furthermore, this technique will result in higher SO_2 emissions than sludge mixtures of similar composition which have been pre-mixed.

Evidence of Waste Minimization for SO_2 Emissions

Table 2 provides the raw (uncorrected) and corrected SO_2 incinerator emissions versus time for each trial. Additionally, average, minimum, and maximum SO_2 values are calculated and provided in Table 2. The raw SO_2 emissions were corrected to 11% O_2 and to a dry basis. It should be noted, however, that these raw values were not corrected for pressure and to a standard temperature. Normally, these two additional corrections are minor and would not change the resultant "corrected" SO_2 value by more than 5 percent.

19

The average corrected incinerator SO_2 emissions concentration for the unneutralized trials (Test Nos. 1, 5, 6, and 7) was 1077 ppmv. The average corrected SO_2 emissions concentration for the neutralized trials (Tests 2 and 4), excluding Test No. 3, was also 1077 ppmv (2795 mg/m^3). If Test No. 3 is considered to be an "unneutralized" trial due to suspected poor mixing, then the average SO_2 emissions concentration for the unneutralized trials increases to 1562 ppmv (4077 mg/m^3). Considering Test No. 3 as an unneutralized trial, the average *unneutralized* SO_2 emissions were nearly 50% greater than the average *neutralized* SO_2 emissions (Test Nos. 2 and 4). Although the neutralized trials demonstrated lower average SO_2 emissions than the unneutralized trials, the reduction may not be statistically significant due to the high standard deviation of the SO_2 measurements. Additional future tests will be able to confirm the conclusion that neutralized batches yield significantly lower average SO_2 emissions.

Despite the variability of the test measurements, it should be noted that average neutralized SO_2 emissions of ~1075 ppmv (2795 mg/m^3) represent a reduction of 72% from previous SO_2 measurements of greater than 3836 ppmv (>10,000 mg/m^3) reported by Petrochema in 1993. Assuming one metric ton of Goudron sludge burned per hour in the plant's incinerator, 24 hours per day, 365 days per year, the mass reduction of SO_2 emissions from previously reported results is approximately 185 tons per year.

Table 3 provides a summary of the incineration test data including the results of the sulfur balance. Of special note is the column entitled, "% Feed S Emitted," which indicates the percentage of sulfur emitted as SO_2 relative to the sulfur fed in the burned waste (including the supplemental fuel sulfur). Again, there is evidence of some *actual* waste reductions for SO_2 when the sludge has been neutralized by the alkaline WTS. Specifically, only 89% of the sulfur fed in Test No. 2 and 43% of the sulfur fed in Test No. 4 were emitted from the incinerator stack as SO_2. The balance of the sulfur should be found as a sulfate salt in the incinerator ash.

SO_2 Emissions Compliance

Despite the variability in the test measurements, five of the seven trials achieved average SO_2 emissions which were less than Petrochema's permit limit of 1150 ppmv (3000 mg/m^3). Excluding Test No. 3, both neutralized trials (Test Nos. 2 and 4) demonstrated average SO_2 emissions which were below the permit limit. Therefore, Petrochema may operate its incinerators at the mixture proportions demonstrated in Test Nos. 2 and 4 with some confidence that they will not exceed their SO_2 permit limits on an average basis. Additional testing will be required by Petrochema to determine other sludge ratios which can also achieve compliance with their SO_2 permit limit.

5.4 Emissions Reductions and Potential Economic Savings

Based upon the initial test results for the neutralization of Goudron sludge, the following waste reduction and economic benefits can be realized:

20

- SO_2 emissions from the facility's incinerator when burning Goudron sludge can be reduced from 10,000 mg/m^3 (3836 ppmv) to at least the new air permit limit of 3000 mg/m^3 (1150 ppmv). Actual concentrations for neutralized sludge mixtures averaged 2795 mg/m^3 (1075 ppmv) or a net reduction of 72% over previously reported values. Assuming one metric ton of neutralized Goudron sludge per hour is burned in the incinerator on average and 24 hour/day operation, 365 days per year, a reduction of 185 metric tons/year of SO_2 emissions can be achieved.

- 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.

- 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. Landfill disposal costs are 1000 Slovak Korunas per metric ton plus 1500 Slovak Korunas in transportation costs for each 5 ton truckload. Assuming a 50% mixture of wastewater treatment sludge for each neutralized batch of Goudron sludge and one metric ton of neutralized Goudron sludge per hour is burned on average in the incinerator, estimated cost savings due to reduced landfill costs will be approximately 5,700,000 Slovak Korunas or US$185,000 annually. (Supporting calculations for landfill cost savings are provided as E-4 in Attachment E.)

5.5 Conclusions and Recommendations

Based upon the test results collected during the March 1994 testing of Goudron sludge neutralization and incineration, we conclude and recommend the following:

- Based upon the acid number measurements, mixing alkaline wastewater treatment sludge does appear to neutralize the acidic Goudron sludge components. However, Petrochema should continue to refine their mixing techniques to ensure more intimate contact of the alkaline and acidic materials. Better mixing should yield greater SO_2 emissions reductions.

- The results from Test No. 3 suggest that separate injection into the incinerator of WTS and Goudron sludge is not an effective mixing technique and yields relatively high SO_2 emissions.

- The Goudron sludge mixtures which were neutralized by WTS demonstrated average corrected incinerator SO_2 emissions of

approximately 2795 mg/m^3 (1075 ppmv). These values represent an 72% reduction from previously reported values of 10,000 mg/m^3 (3836 ppmv). This reduction is equivalent to a reduction of 185 metric tons of SO_2 annually.

- The sulfur material balances we performed indicate evidence of actual waste minimization of incinerator SO_2 emissions. More accurate total sulfur, combustion, and time-weighted SO_2 measurements in future tests are required to confirm these initial waste minimization reductions.

- All neutralized tests with pre-mixing of the feed components prior to incineration (Test Nos. 2 and 4) achieved compliance, on average, with Petrochema's new SO_2 permit limit of 3000 mg/m^3 (1150 ppmv). For the period 1993-1998, this compliance performance will save Petrochema approximately 775,000 Slovak Korunas, or about US$25,000. Petrochema should test additional sludge mixtures to determine other ratios which will achieve regulatory compliance.

- The usage of wastewater treatment sludge (WTS) as the neutralization agent will avoid disposing of WTS in Slovak landfills. It is estimated that the minimization of this waste material will save Petrochema 5,700,000 Slovak Korunas (US$185,000) annually in disposal and transportation costs.

- In the initial seven trials, we tested only mixtures containing "old" Goudron sludge. In the future, Petrochema should test neutralized mixtures of "fresh" Goudron sludge for SO_2 emissions. Fresh Goudron sludge, which is more acidic than old Goudron sludge, will require a greater degree of neutralization prior to incineration. Based upon future test results for fresh Goudron sludge and wastewater treatment sludge, Petrochema may need to reconsider testing lime [$Ca(OH)_2$] as the neutralizing agent. The use of lime presents many special challenges.

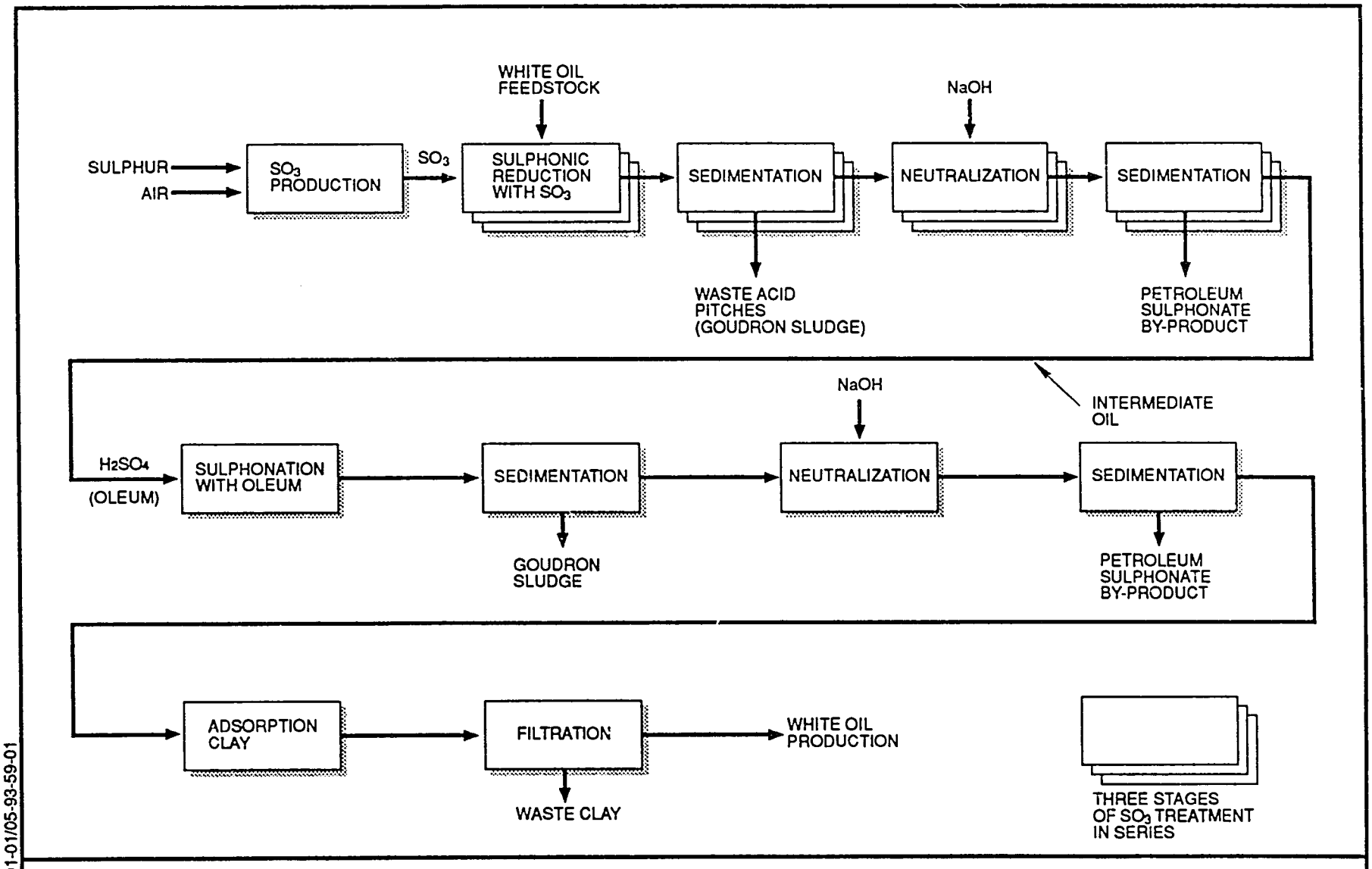

Figure 1. Process Flow Digram - White Oil Production

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

RADIAN CORPORATION

23

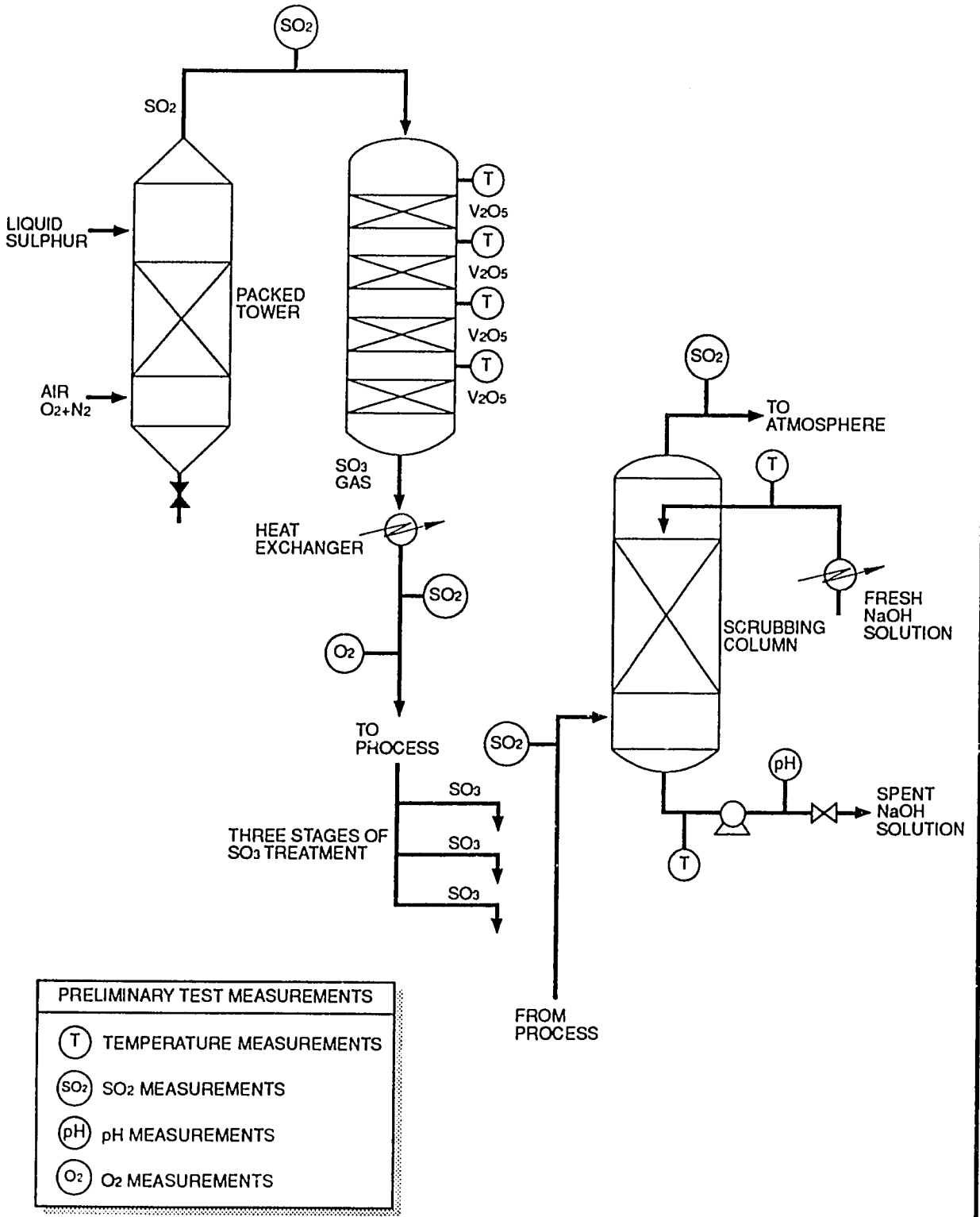

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Figure 2. Process Flow Diagram - SO_3 Production in the White Oil Plant

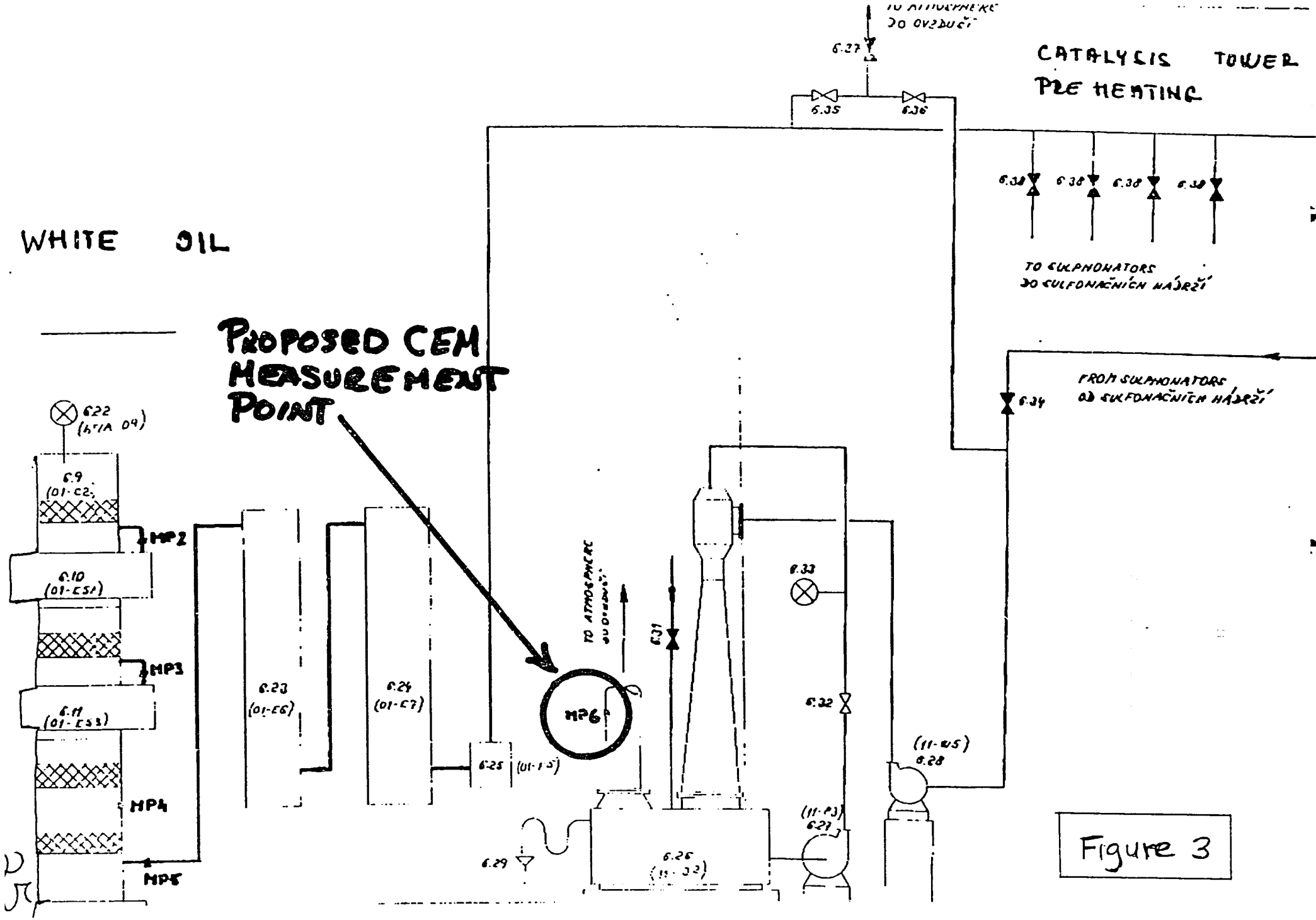

CATALYSIS TOWER
PRE HEATING
WHITE OIL
PROPOSED CEM MEASUREMENT POINT
TO ATMOSPHERE
DO OVZDUŠÍ
6.27
6.35
6.36
6.38
6.38
6.38
6.38
TO SULPHONATORS
DO SULFONAČNÍCH NÁDRŽÍ
FROM SULPHONATORS
OD SULFONAČNÍCH NÁDRŽÍ
6.34
6.22
(MIA 04)
6.9
(01-C2)
MP2
6.10
(01-ESA)
MP3
6.11
(01-ESB)
MP4
MP5
6.23
(01-E6)
6.24
(01-E7)
6.25
(01-FS)
MP6
TO ATMOSPHERE
DO OVZDUŠÍ
6.31
6.33
6.32
(11-WS)
6.28
(11-PS)
6.27
6.29
6.26
(11-SS)

Figure 3

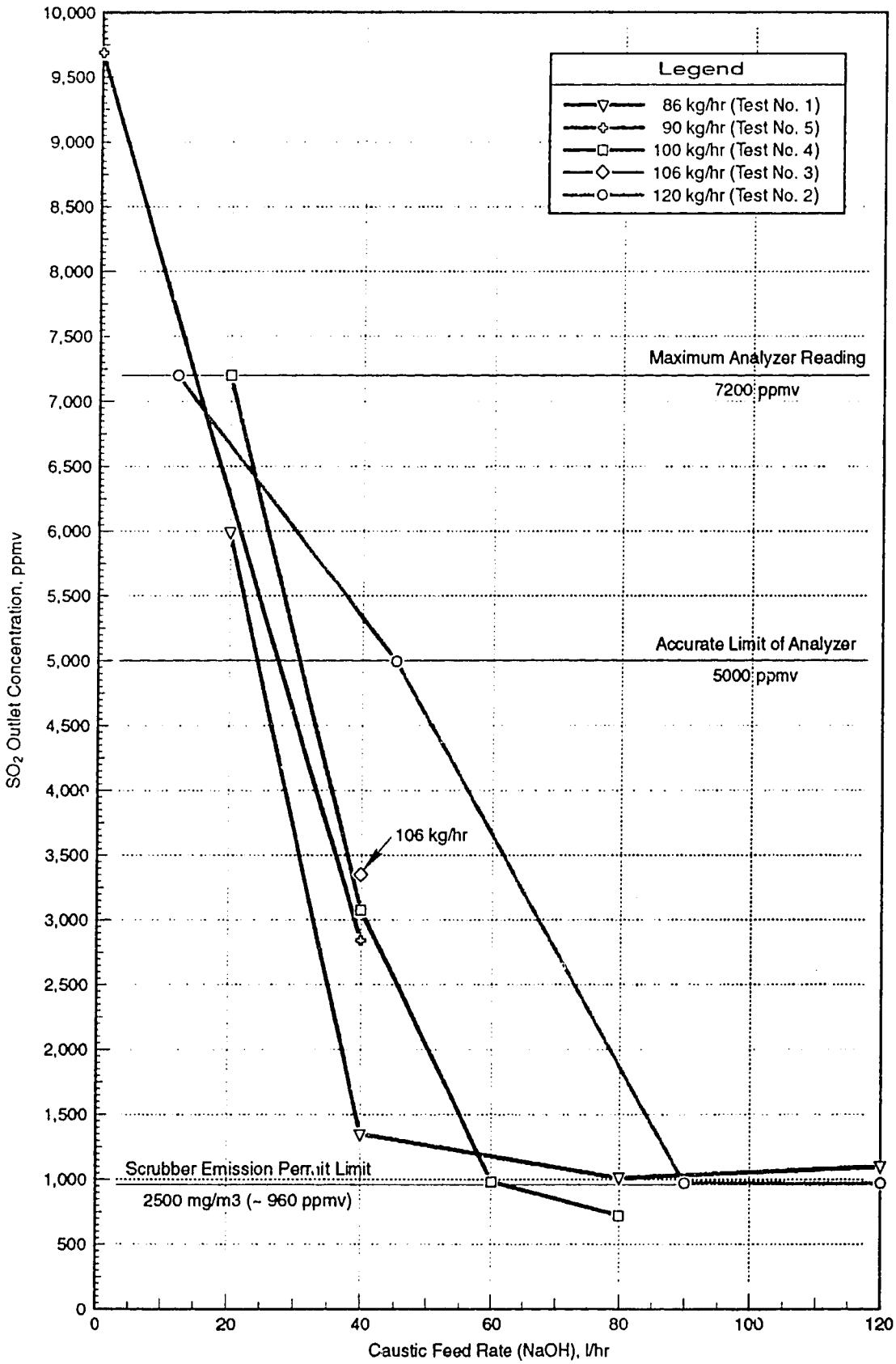


Figure 4. Scrubber Outlet SO_2 Concentration vs. Caustic Feed Rate

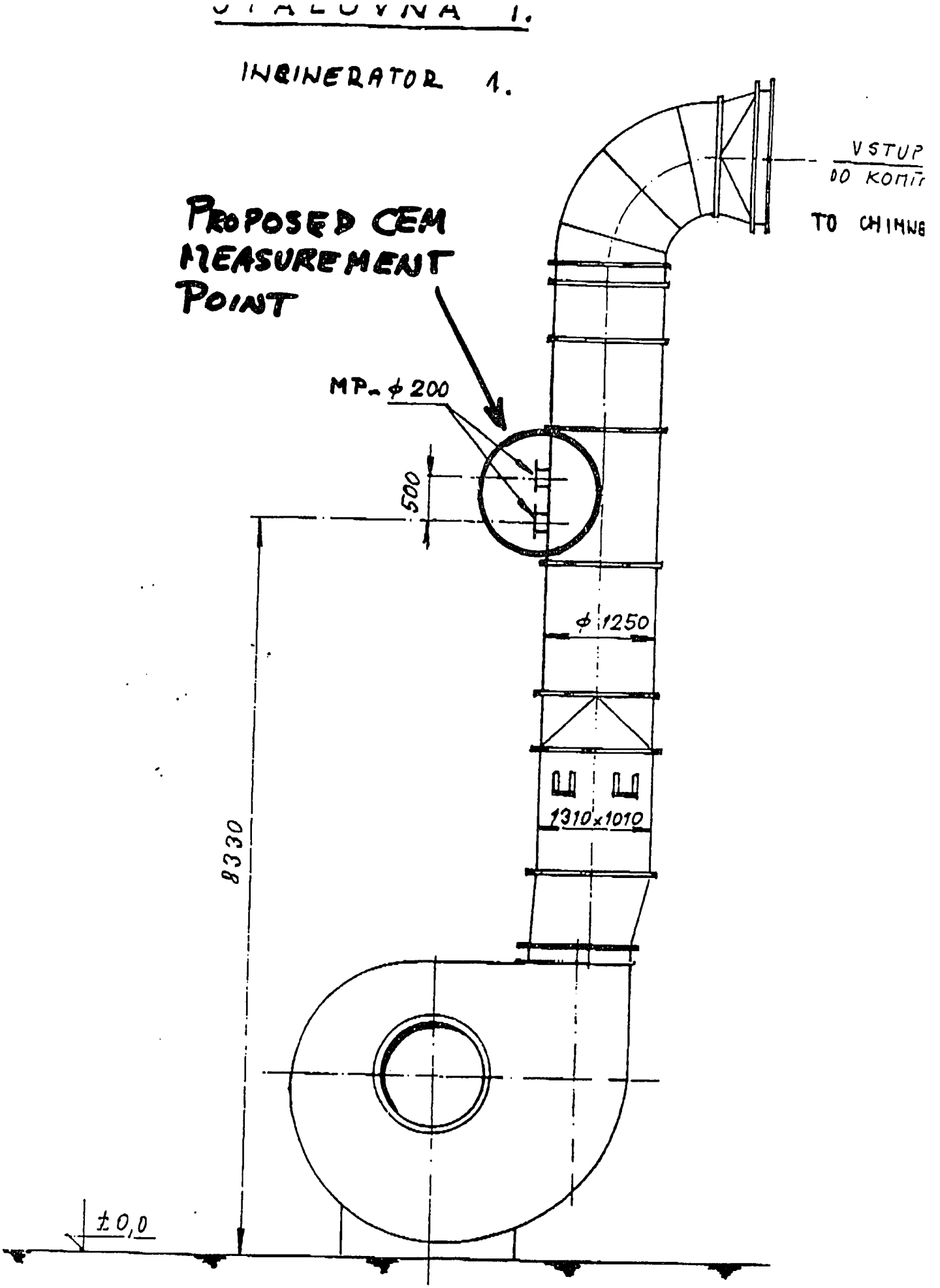


Figure 5

MP - MEASURING PLACES OF SO_2

INCINERATOR 2.

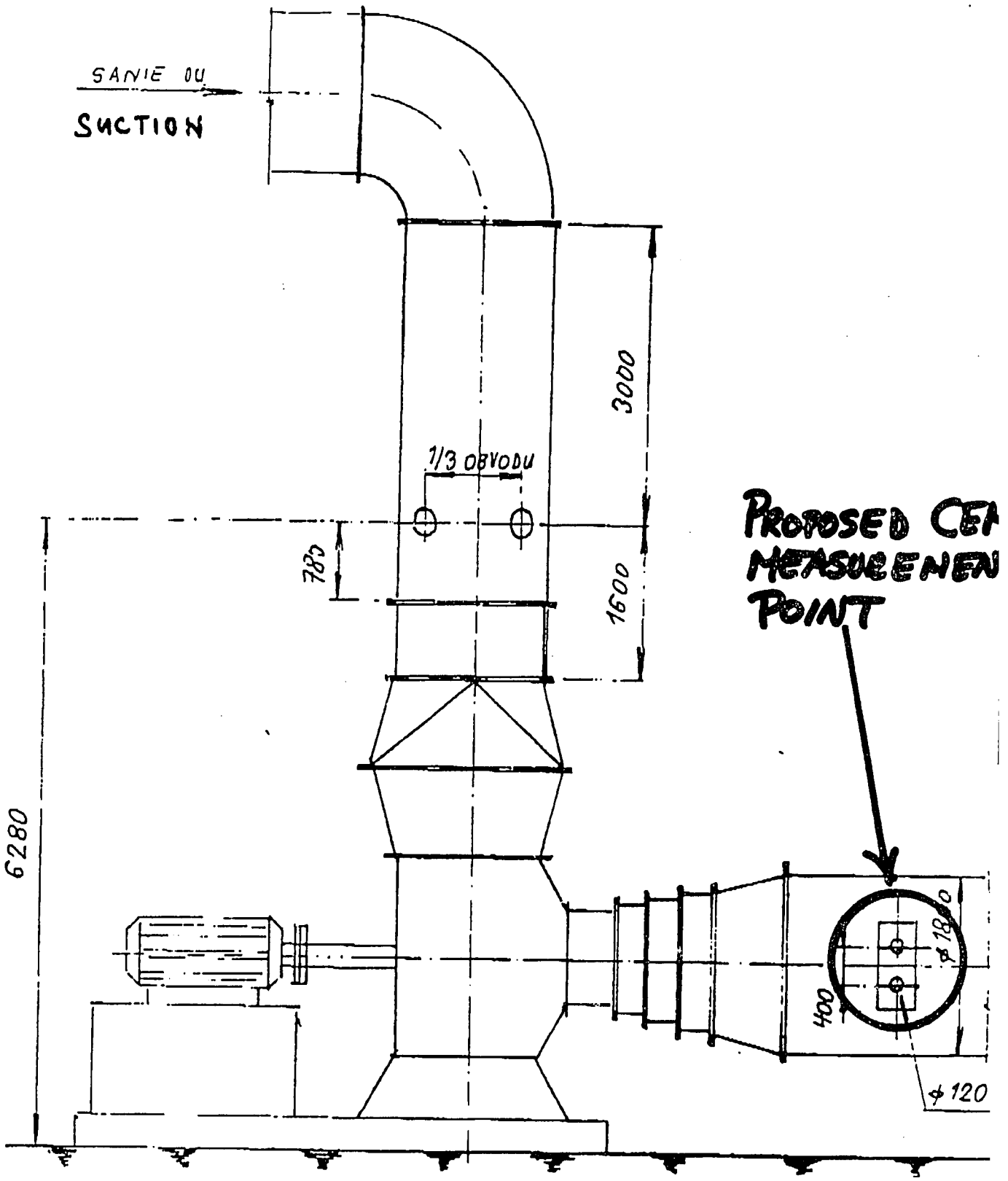


Figure 6 MP- MEASURING PLACES OF SO_2

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 smoły
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

Test No.	Total Feed, Kg	Feed Composition	% By Wt in Waste	Waste Characteristics					Waste Sulfur Content, Kg		Total S in Waste, Kg
				Water, %	Acid No.	H2SO4, %	Oil. %	Total S, %	By Acid No.(a)	By % Sulfur	
1	4000	WAE	100.0	68	132.5			1.94	212.0	77.6	77.6
2	4000	SD	50.0	52	53.4	2.04		2.26	85.4	45.2	
		WTS	50.0	64	3.75			0.58	6.0	11.6	56.8
3	3600	SD	37.5	52	53.4	2.04		2.26	28.8	30.5	
		WTS	37.5	64	3.75			0.58	2.0	7.8	
		WAE (b)	25.0	68	132.5			1.94	47.7	17.5	55.8
4	3600	SD	33.3	52	53.4	2.04		2.26	25.6	27.1	
		WTS	33.3	64	3.75			0.58	1.8	7.0	
		CS	33.3	15			3.8	0.67		8.0	42.1
5	1500	SEW	100.0	61	2.2			0.42	94.4	6.3	6.3
6	3350	SEW	22.0	61	2.2			0.42	46.4	3.1	
		CS	78.0	15			3.8	0.67		17.5	20.6
7	1200	SD	100.0	52	53.4	2.04		2.26	18.3	27.1	27.1

a) Assuming all sulfur in waste is sulfuric acid
b) WAE not mixed with DS/WTS; fed separately into incinerator.

WAE - Water acid emulsion from dump
SD - Sludge from dump
WTS - Wastewater Treatment Sludge
S - Sludge with no additional description
CS - Oil contaminated soil
SEW - Sewage with no additional description

Table 2. SO2 EMISSION DATA SUMMARY (a)

Test No. 1			Test No. 2			Test No. 3			Test No.4		
	SO2 Conc., ppm			SO2 Conc., ppm			SO2 Conc., ppm			SO2 Conc., ppm	
Time	Measured	Corrected	Time	Measured	Corrected	Time	Measured	Corrected	Time	Measured	Corrected
0930	305	888	0900	574	1160	1200	3020	6795	1030	209	609
0935	240	699	0905	505	1020	1205	1694	3812	1035	420	1223
0940	191	556	0910	626	1265	1210	2043	4597	1040	258	751
0945	31	90	0915	558	1127	1215	1384	3114	1045	475	1383
0950	28	82	0920	470	950	1220	2249	5060	1050	190	553
0955	25	73	0925	632	1277	1225	1648	3708	1055	470	1369
1000	800	2329	0930	774	1564	1230	1138	2561	1100	174	507
1005	610	1776	0935	610	1232	1235	3020	6795	1105	353	1028
1010	520	1514	0940	685	1384	1240	1784	4014	1110	370	1077
1015	275	801	0945	471	952	1245	1381	3107	1115	201	585
1020	194	565	0950	678	1370	1250	1241	2792	1120	390	1136
1025	229	667	0955	449	907	1255	1429	3215	1125	390	1136
1030	628	1829	1000	723	1461	1300	685	1541	1130	479	1395
1035	527	1535	1005	405	818	1305	1214	2732	1135	304	885
1040	355	1034	1010	456	921	1310	842	1895	1140	378	1101
1045	346	1007	1015	471	952	1315	1443	3247	1145	516	1502
1050	421	1226	1020	445	899	1320	1003	2257	1150	459	1337
1055	377	1098	1025	618	1249	1325	1357	3053	1155	381	1109
1100	52	151	1030	608	1228	1330	988	2223	1200	454	1322
1105	673	1960	1035	689	1392						
1110	45	131	1040	436	881						
1115	727	2117	1045	520	1051						
1120	719	2094	1050	382	772						
1125	649	1890	1055	377	762						
1130	415	1208	1100	463	935						
Avg	375	1093		545	1101		1556	3501		362	1053
Max	800	2329		774	1564		3020	6795		516	1502
Min	25	73		377	762		685	1541		174	507

a) Corrected SO2 concentrations calculated at 11 percent O2 in the emission gases. SO2 concentrations are not corrected to standard temperature and pressure.

Test No.5			Test No.6			Test No.7		
	SO2 Conc., ppm			SO2 Conc., ppm			SO2 Conc., ppm	
Time	Measured	Corrected	Time	Measured	Corrected	Time	Measured	Corrected
0900	97	200	1100	72	149	1240	761	1421
0905	63	130	1105	100	206	1245	765	1429
0910	5	10	1110	108	223	1250	1186	2215
0915	70	144	1115	195	402	1255	1506	2813
0920	235	485	1120	352	726	1300	1578	2948
0925	278	573	1125	437	901	1305	1704	3183
0930	139	287	1130	203	419	1310	1095	2045
0935	126	260	1135	213	439	1315	809	1511
0940	121	250	1140	279	575	1320	1614	3015
0945	179	369	1145	178	367	1325	735	1373
0950	137	283	1150	439	905	1330	2311	4317
0955	135	278	1155	529	1091	1335	1495	2793
1000	133	274	1200	410	846	1340	806	1506
			1205	240	495			
			1210	286	590			
			1215	240	495			
			1220	380	784			
			1225	307	633			
			1230	470	969			
Avg	132	273		286	590		1259	2351
Max	278	573		529	1091		2311	4317
Min	5	10		72	149		735	1373

a) Corrected SO2 concentrations calculated at 11 percent O2 in the emission gases. SO2 concentrations are not corrected to standard temperature and pressure.

Table 3. PETROCHEMA INCINERATION TEST DATA SUMMARY

Test Data					Waste Feed Data (a)			Incinerator Conditions			Sulfur Emissions (b)		% Feed S
No.	Date	Start Hr	End Hr	Run Hrs	Type	Wt, Kg	S, Kg(c)	Temp, C	Excess O2, %	Flow, m3/hr	SO2, ppm	Kg (d)	Emitted
1	3/3/94	930	1130	2	WAE	4000	77.6	600-700	17.5	99136	375	26	34
2	3/9/94	900	100	2	SD/WTS	4000	56.8	700-900	16	99136	545	51	89
3	3/17/94	1200	1330	1.5	SD/WTS/WAE	3600	55.8	700-900	16.5	99136	1556	148	266
4	3/25/94	1030	1200	1.5	SD/WTS/CS	3600	42.1	650-850	17.5	99136	362	18	43
5	3/30/94	900	1000	1	SEW	1500	6.3	650-850	16.1	99136	132	0	0
6	4/15/94	1100	1230	1.5	SEW/CS	3350	20.6	650-850	16.1	85472	286	9	42
7	4/22/94	1240	1340	1	SD	1200	27.1	700-850	15.6	85472	1259	67	246

a) WAE - Water Acid Emulsion
SD - Sludge from Dump
WTS - Wastewater Treatment Sludge
CS - Oil Contaminated Soil
SEW - Sewage; no additional description

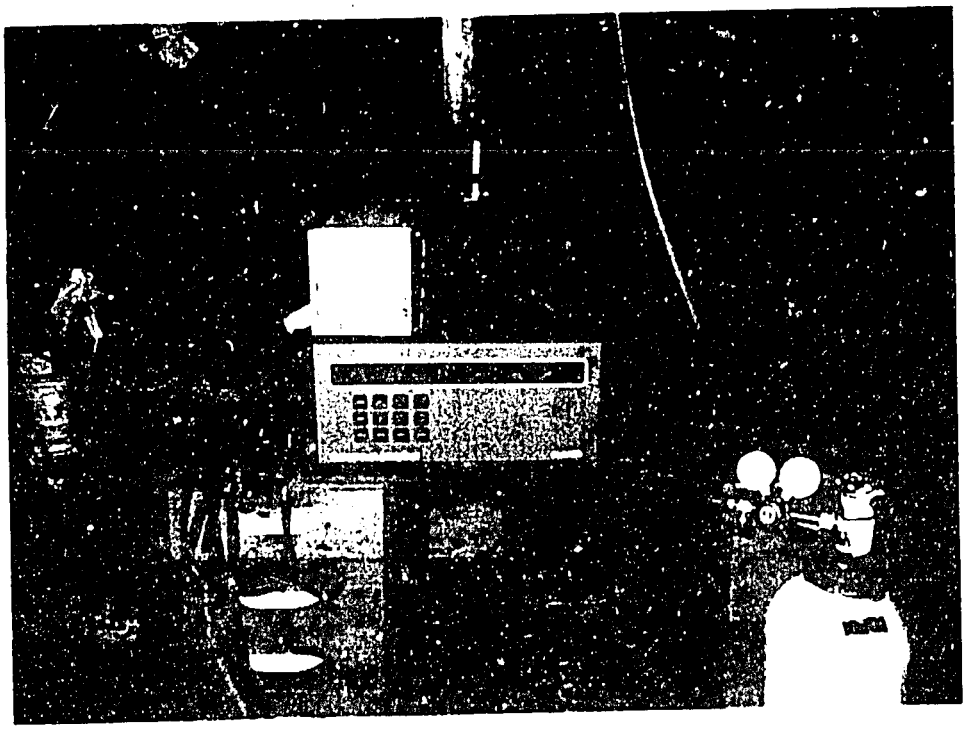
b) Determined from SO2 CEM measurements.

c) Based on total sulfur analysis of waste feed.

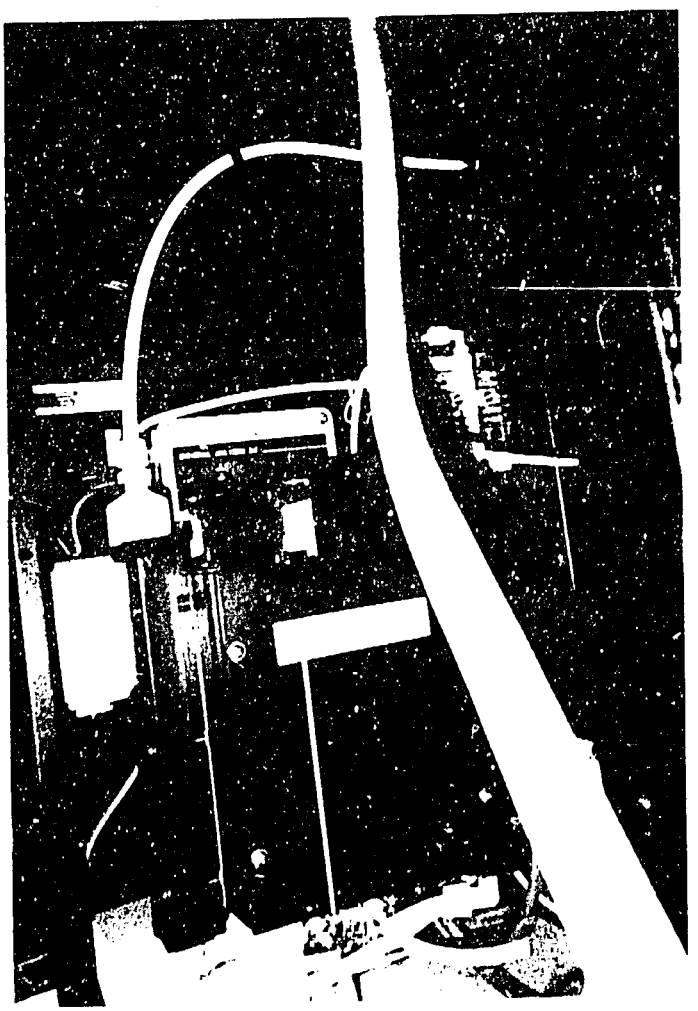
d) Corrected for sulfur contribution from incinerator fuel; fuel sulfur 2% by weight.

ATTACHMENT A

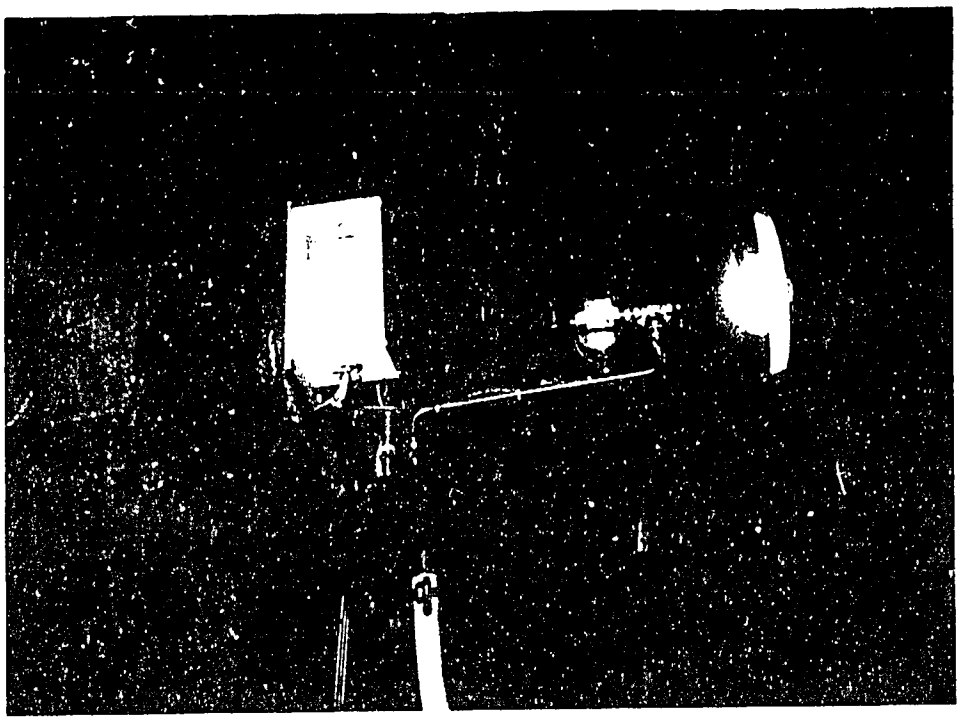
DECEMBER 1993 VISIT PHOTOGRAPHS



ROSEMOUNT ANALYTICAL MODEL 890 SO_2 ANALYZER



UNIVERSAL ANALYZERS SAMPLE CONDITIONING SYSTEM



UNIVERSAL ANALYZERS SO_2 SAMPLE COLLECTION PROBE

PROJECT TEAM MEMBERS

RADIAN
CORPORATION

ATTACHMENT B

WHITE OIL PLANT OPTIMIZATION
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) ACTUAL 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	1800 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	0
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

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 TRAILING TO INCREASE SLIGHTLY AFTER IT WAS RECORDED TO BE 4762 ppmv – ESTIMATED TO BE ~5000 ppmv

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:
Poznámka
WAIT BETWEEN 1/2 HOUR TO 1 HOUR BETWEEN 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 MEASUR

(4) FIRST COMPLIANCE MEASUREMENT — COMP 720 ppmV WITH EMISSION LIMIT OF 960 ppmV (2 mg/

PETROCHEMA - WHITE OIL PLANT
Petrochema - Biele oieje

CAUSTIC SCRUBBER OPTIMIZATION
Optimalizácia lúhovej pračky plynov

DATA SHEET
List pre zber dát

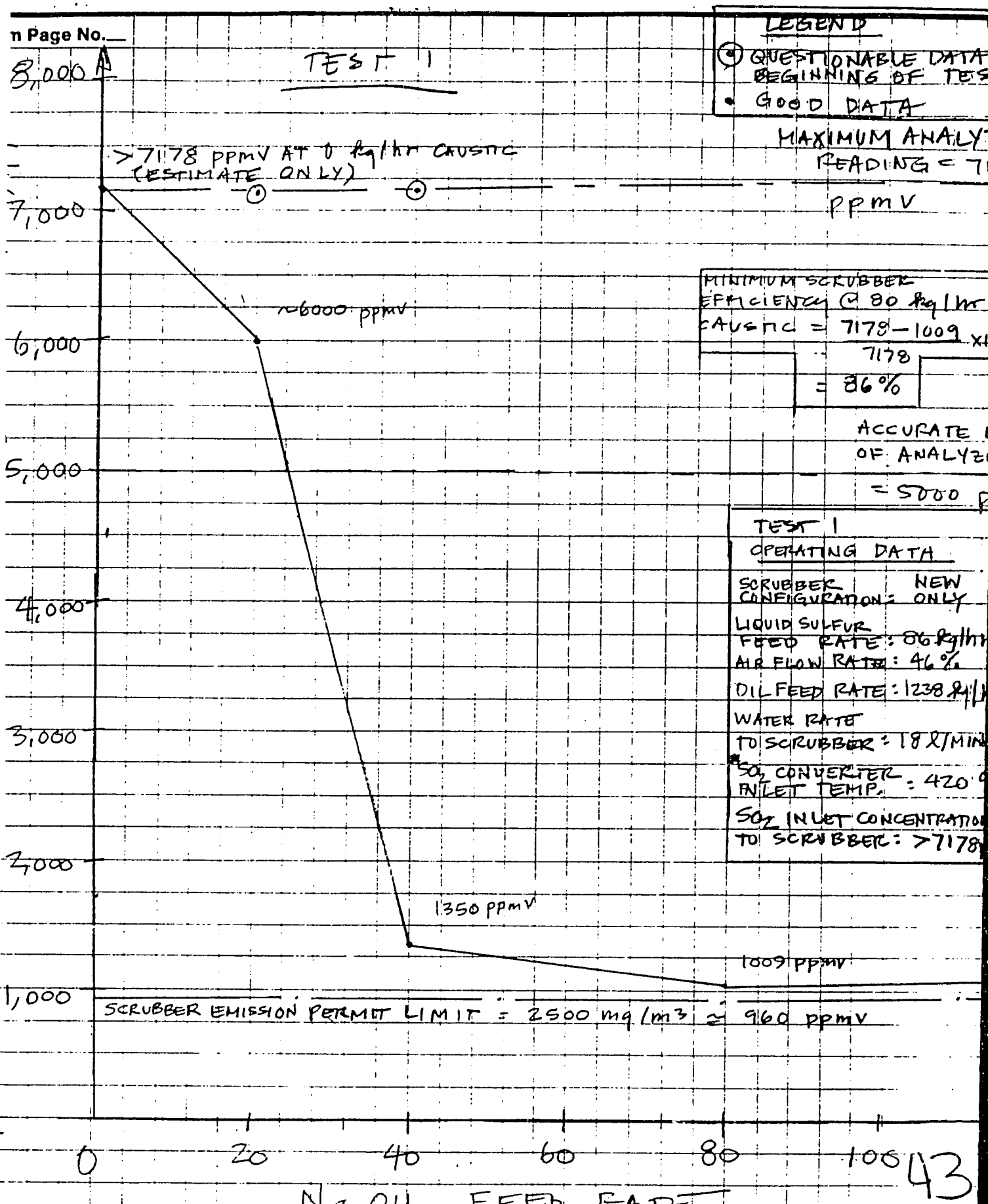
GENERAL INFORMATION Všeobecné informácie	
TEST DATE Dátum skúšky	12/5/93
SCRUBBER CONFIGURATION Konfigurácia práčky	NEW SCRUBBER ONLY
LIQUID SULFUR FEED RATE Nástrek kvapalnej síry	90 kg/hr
OIL FEED RATE Nástrek oleja	1900 l/hr OR 1634 kg/hr
WATER FLOW RATE TO SCRUBBER Nástrek vody do pračky	16 l/MIN
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

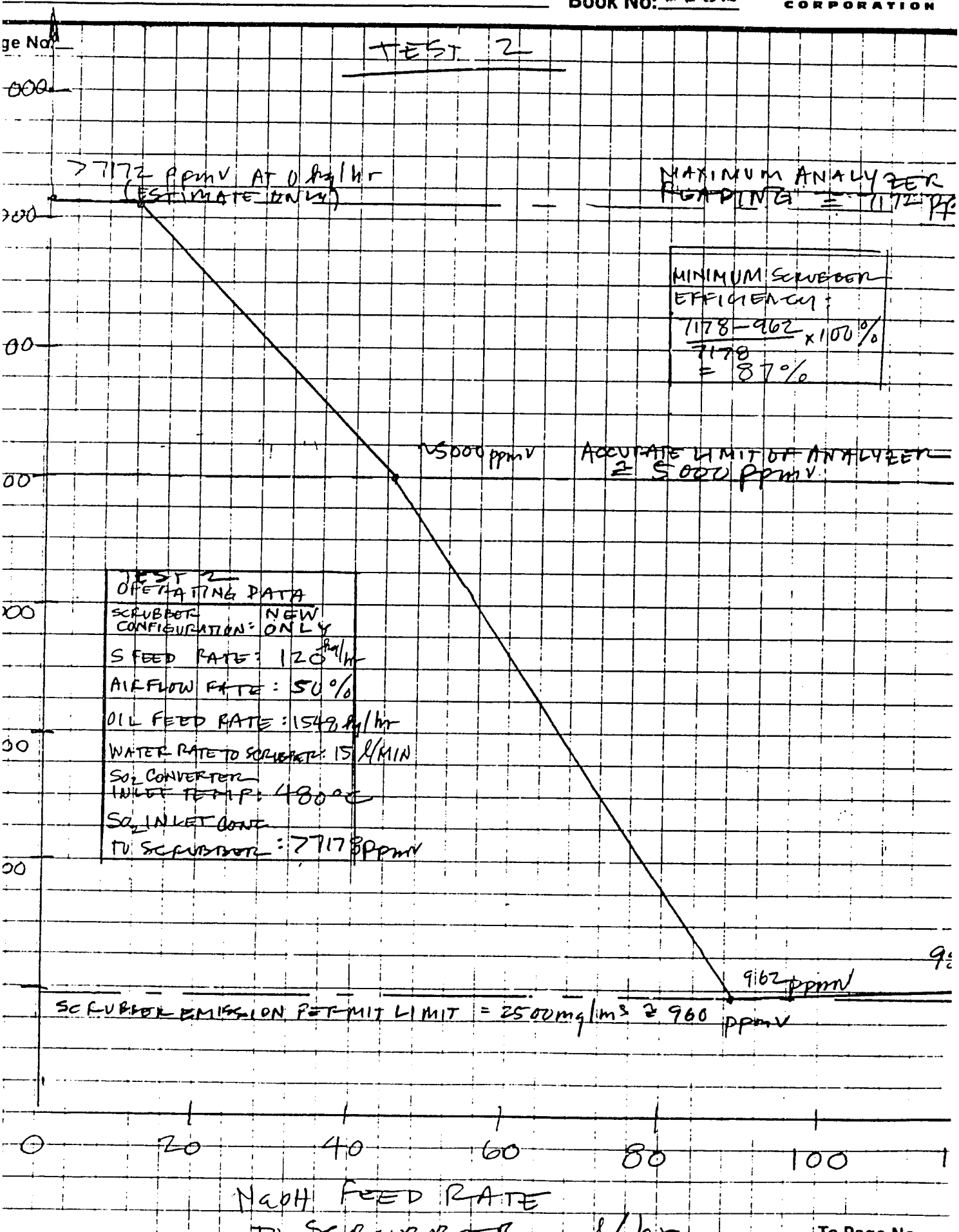
(1) SEE TEST COMMENTS (2) & (3) FROM TRIAL NO. 1
(2) INLET SO_2 CONCENTRATION WAS MEASURED ON-SCALE USING ABOUT ~3.7 DILUTION FACTOR OF AIR TO SAMPLE.



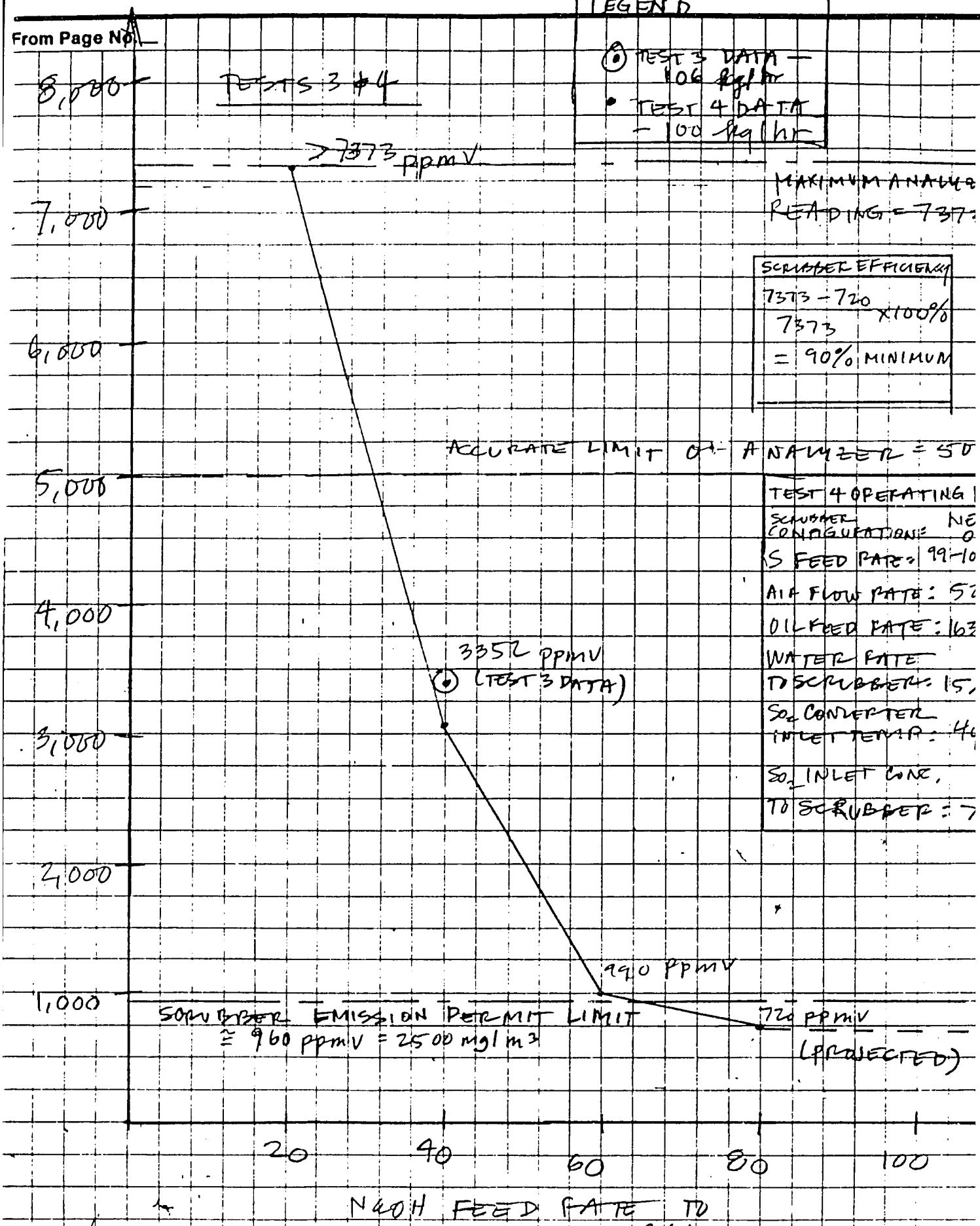
Witnessed & Understood by me, | Date | Invented by | Date

* SEE ATTACHED DATA SHEET FOR CONVERTER BED TEMPERATURES DURING TEST

Recorded by


TEST 2
>7172 ppmv AT 0 kg/hr
(ESTIMATE ONLY)
MAXIMUM ANALYZER READING = 7172 PP
MINIMUM SCRUBBER EFFICIENCY:
(7178 − 962) / 7178 × 100%
= 87%
~5000 ppmv
ACCURATE LIMIT OF ANALYZER ≈ 5000 ppmv
TEST 2
OPERATING DATA
SCRUBBER CONFIGURATION: NEW ONLY
S FEED RATE: 120 kg/hr
AIRFLOW RATE: 50%
OIL FEED RATE: 1549 kg/hr
WATER RATE TO SCRUBBER: 15 l/MIN
SO2 CONVERTER INLET TEMP: 480°C
SO2 INLET CONC TO SCRUBBER: 7178 ppmv
962 ppmv
SCRUBBER EMISSION PERMIT LIMIT = 2500 mg/m³ ≈ 960 ppmv
0
20
40
60
80
100
NaOH FEED RATE TO SCRUBBER, l/hr

Project No. 28332
Book No.
TITLE
From Page No.



To Pag

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Recorded by

45

Project No. 28332
Book No.

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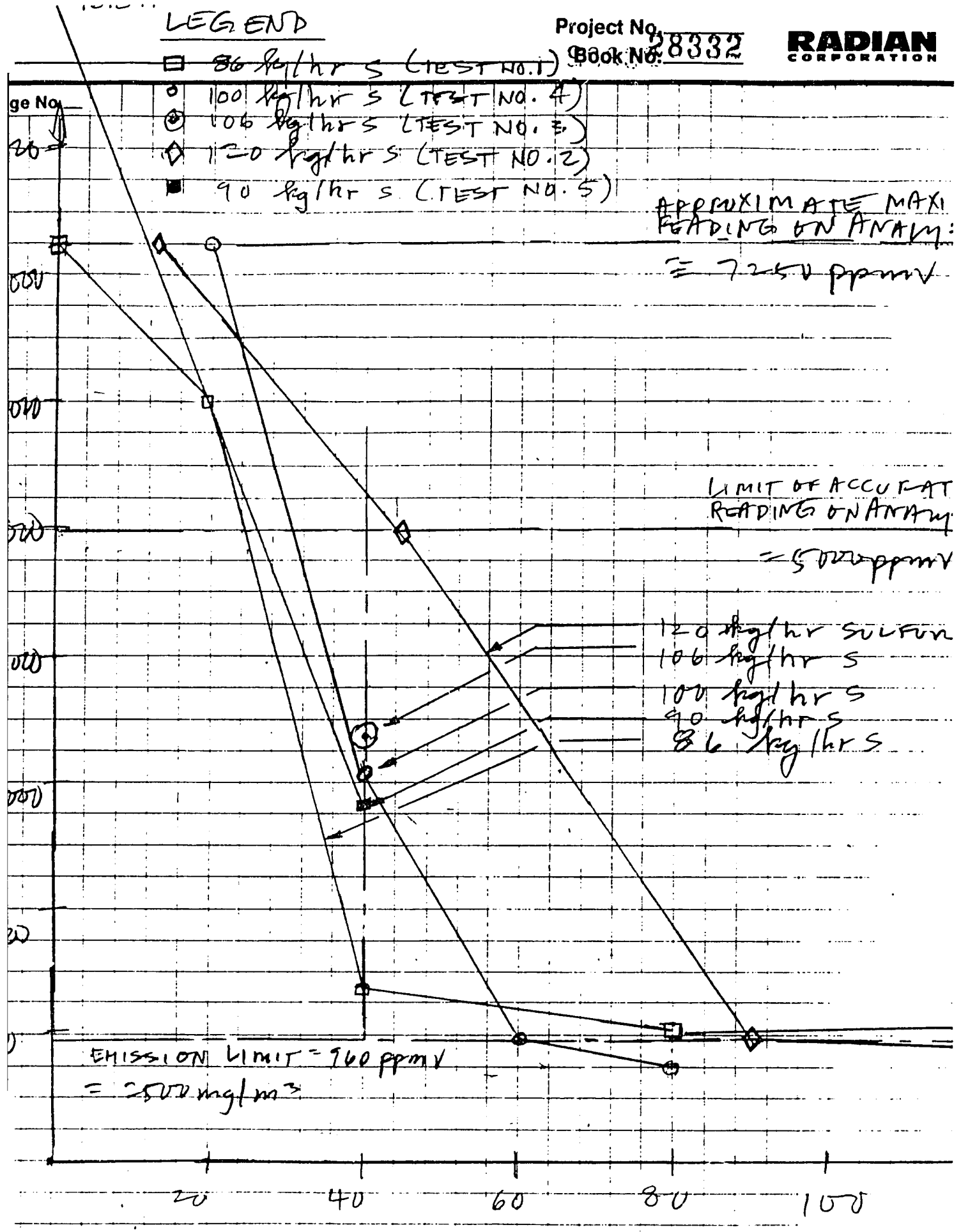

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d & Understood by me, | Date | Invented by | Date 46
Recorded by

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CALCULATION SHEET

CALC. NO. —

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

PROJECT SO_3 OPTIMIZATION - WHITE OIL PLANT JOB NO. PETROCHEMA WA MINIMIZATION DET

SUBJECT TEST DATA — TEMPERATURE PROFILES SHEET 1 OF 1 SHEE

	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					
2/3	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

5.12.1943

Teplota v °C						Konverzná veža						prosadenie					Tlak			
Síra		Pec	Sili.	sušič		hla	I.	II.	III.	IV.										
01 V1	T 228	01 H1	01 E4	01 vrch	Sp.	Výstup	Hesd				Výstup SO_2	01 Síra	01 K1	NaOH 11 E4		11 J-2 PH	01 H1	hod.	para	Činnosť 01 -V2
143		580					440	470	405		355		17	44						
143		590					440	470	405		360		17	46						
142		595					440	470	405		360		17	46						
143		580					445	475	405		360		17	46						
143		585					440	470	405		360		17	46						
143		590					440	470	405		360		17	46						
143		585					440	470	405		355		17	46						
143		585					440	470	405		355		17	46						

48

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ATTACHMENT C

WHITE OIL PLANT OPTIMIZATION
SAMPLE CALCULATIONS

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CALCULATION SHEET

CALC. NO. C-1

ATURE [signature] DATE 12/27/93 CHECKED _____ DATE _____

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

ECT CONVERTER EFFICIENCY SHEET 1 OF 3 SHEETS

ALCULATION / SO_2 MATERIAL BALANCE

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

= 180 kg SO_2 IN

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

= 56.1 kg SO_2 OUT

50

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CALCULATION SHEET

CALC. NO. C-1

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

PROJECT SO_2 OPTIMIZATION – WH-OIL PLT JOB NO. PETROCHEMA WASTE MINIMIZATION DEMON

SUBJECT CONVERTER EFFICIENCY / SO_2 MATERIAL BALANCE SHEET 2 OF 3 SHEETS

CONVERTER EFFICIENCY (MAXIMUM – SEE ASSUMPTION NO. 3)

$$= \frac{(180 - 56.1)\ \text{kg } SO_2 \text{ REAC}}{180\ \text{kg } SO_2 \text{ IN}} \times 1$$

$$= \boxed{68.8\%}$$

MAXIMUM CATALYTIC CONVERTER EFFICIENCY

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

CONCLUSION: CATALYST IS OPERATING WELL BELOW ITS DESIGN EFFICIENCY

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

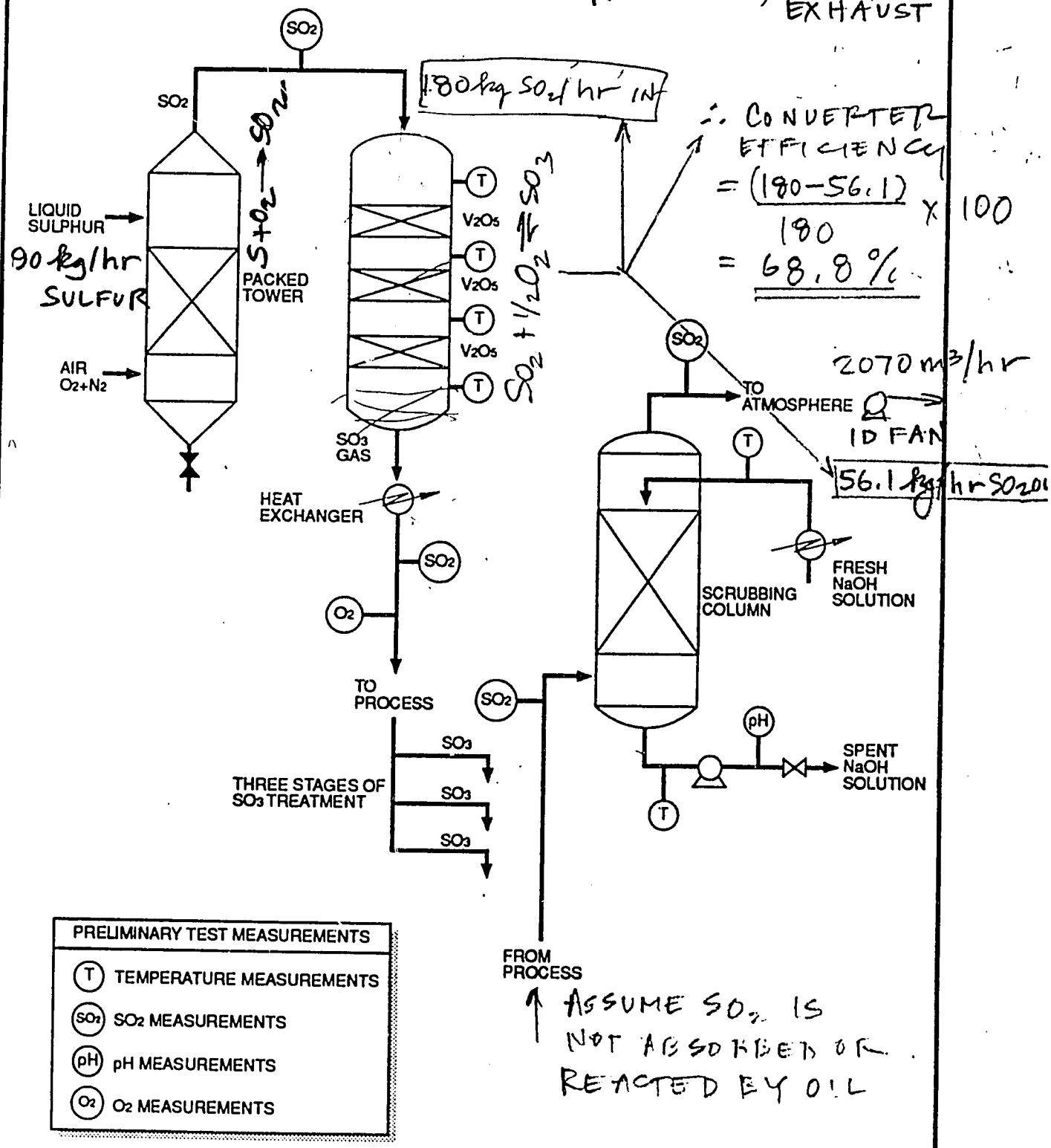

Figure C-1. Process Flow Diagram - SO_3 Production in the White Oil Plant

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

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CALCULATION SHEET

CALC. NO. C-2

SIGNATURE [illegible] DATE 12/28/93 CHECKED _____ DATE _____

PROJECT SO_3 OPTIMIZATION - WHITE ILL PLT JOB NO. for TRO CHEMA WASTE MINIMIZ

SUBJECT CAUSTIC SCRUBBER EFFICIENCY CALCULATIONS SHEET 1 OF 1 SHEETS

CAUSTIC SCRUBBER EFFICIENCIES

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

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

$$= 72.7\%$$

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

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

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

$$= 93\%$$

53

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

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

ASSUMED VALUE DUE TO OFF-SCALE READING

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CALCULATION SHEET

CALC. NO. C-3

ATURE [signature] DATE 1/29/94 CHECKED _____ DATE _____

ECT SO_2 OPTIMIZATION - WHITE OIL PLANT JOB NO. PETROCHEMA WASTE MINIMIZATI DEMONSTRATION

ECT 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

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

96 % CONVERTER EFFICIENC

% SCRUBBER EFFICIENCY

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

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

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

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

POTENTIAL SO_2 OUTLET EMISSIONS FROM SCRUBBER WITH ADDITION OF NEW CATALYST

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CALCULATION SHEET

CALC. NO. C-4

SIGNATURE M Pardenchak DATE 1/29/94 CHECKED _____ DATE _____

PROJECT SO_3 OPTIMIZATION - WHITE OIL PLANT JOB NO. PETROCHEMA WASTE MINIMIZ 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 60 - 70 ℓ/hr TO 10 - 20 ℓ/hr

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

96% CONVERSION ASSUMED

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

$= 0.125$ 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

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

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

SPECIFIC GRAVITY OF 45 WT% NaOH SOLUTION

55

∴ 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

ATURE [signature] DATE 1/29/94 CHECKED _____ DATE _____

ECT SO_3 OPTIMIZATION – WHITE OIL PLANT JOB NO. PETROCHEMA WASTE MINIMIZATI ~~DEMONSTRATION~~

ECT CAUSTIC & LIQUID SULFUR SAVINGS SHEET 2 OF 3 SHEETS
TH ADDITION OF NEW CATALYST

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

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

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

100 WT%

SPECIFIC GRAVITY – 45 WT% SOLUTION

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

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

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

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)
~ 96% (DESIGN CONVERSION WITH NEW CATALYST)

BASIS: 100 kg/hr USING OLD CATALYST

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

$0.26 \times \frac{100 \text{ kg S}}{\text{hr}}$ = 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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ATTACHMENT D

GOUDRON SLUDGE NEUTRALIZATION AND INCINERATION TEST DATA MARCH 1994

ŠTÁTNY PODNIK, DUBOVÁ, 976 97 NEMECKÁ

ENSKÁ REPUBLIKA Tel.:0867/926182 0867/926142 Fax.:0867/92286, 0867/92208

EMA

TELEFAX

KOMU/TO Edward Andrachak
El Segundo, Ca 90215

DÁTUM/DATE 4. 5. 1994
POČET STRÁN/NO OF PAGES 7
FAX: 001 310 640 8940

OD KOHO/FROM Ing. Jozef Šuráb
Technical and Production Director

VEC/OBJECT

Dear Sir,

I send you results of measurements SO_2 - emissions from the incinerator.

I send you choice of seven the most objective measurements because of technical reasons - like there was downtime of incinerators, sludge from dump could not be exploited during winter month, mixing and combustion compound of wastes was demanding on time.

Text data:

Trial No	1
Date	3rd of March 1994
Test start time	9,30
Test end time	11.30
Test duration	2 hours
Incinerator type	incinerator of dangerous wastes II
Incinerator temperature	600 - 700 ^{o}C
Incinerator excess O_2	17,5 %
Flue gas flow rate	99 136 m^3/hour

Burnt waste		water acid emulsion from dumps
Quality burnt waste	water	68 %
	acid number	132,5 mg NaOH/g
	sulphur	1,94 %
Total burnt mass		4 000 kg

So_2 stack emissions

time:	9,30	9,35	9,40	9,45	9,50	9,55
ppm:	305	240	191	31	28	25
time:	10,00	10,05	10,10	10,15	10,20	10,25
ppm:	800	610	620	275	194	229
time:	10,30	10,35	10,40	10,45	10,50	10,55
ppm:	628	527	355	346	421	377
time:	11,00	11,05	11,10	11,15	11,20	11,25
ppm:	52	673	45	727	719	649
time:	11,30					
ppm:	415					

Trial No	**2**
Date	9th of March 1994
Test start time	9,00
Test end time	11,00
Test duration	2 hours
Incinerator type	incinerator of dangerous wastes II
Incinerator temperature	700 - 900 ^{o}C
Incinerator excess O_2	16 %
Flue gas flow rate	99 136 m^3/hour
Burnt waste	sludge from dump: waste from wastewater treatment plant = 1 : 1

Quality burnt waste:	water 50 %
	sulphur 0,8 %
	acid number 1,6 mgNaOH/g
	sulphuric acid 0,19 %
Total burnt mass	4 000 kg

SO_2 stack emissions

time:	9,00	9,05	9,10	9,15	9,20
ppm:	574	505	626	558	470
time:	9,25	9,30	9,35	9,40	9,45
ppm:	632	774	610	685	471
time:	9,50	9,55	10,00	10,05	10,10
ppm:	678	449	723	405	456
time:	10,15	10,20	10,25	10,30	10,35
ppm:	471	445	618	608	689
time:	10,40	10,45	10,50	10,55	11,00
ppm:	436	520	382	377	463

Trial No	3
Date	17th of March 1994
Test start time	12,00
Test end time	13,30
Test duration	1,5 hours
Incinerator type	incinerator of dangerous vastes II.
Incinerator temperature	700 - 900 ^0C
Incinerator excess O_2	16,5 %
Flue gas flow rate	99 136 m^3/hour
Burnt waste	water acid emulsion from dump and sludge from dump and WWT sludge = 0,6 : 0,9 : 0,9

Quality burnt waste sludge and WWT sludge:	water	50 %
	sulphur	0,8 %
	acid number	1,6 mgNaOH/g
	sulphuric Acid	0,19 %
water acid emulsion:	water	68 %
	sulphur	1,94 %
	acid number	132,5 mgNaOH/g
Total burnt mass	3 600 kg	

SO_2 stack emissions

time:	12,00	12,05	12,10	12,15	12,20
ppm:	3020	1694	2043	1384	2249
time:	12,25	12,30	12,35	12,40	12,45
ppm:	1648	1138	3020	1784	1381
time:	12,50	12,55	13,00	13,05	13,10
ppm:	1241	1429	685	1214	842
time:	13,15	13,20	13,25	13,30	
ppm:	1443	1003	1357	988	

Trial No	4
Date	25th of March 1994
Test start time	10,30
Test end time	12,00
Test duration	1,50 hours
Incinerator type	Incinerator of dangerous wastes II
Incinerator temperature	650 - 850 ^{o}C
Incin. excess O_2	17,5 %
Flue gas flow rate	99 136 m^3/hour
Burnt waste	sludge and WWT sludge and contaminated earth by oil = 1 : 1 : 1

62

Quality burnt waste	water	39 %
	acid number	0 ~~mgKOH/g~~
	ash	31,82 %
Total burnt mass	3 600 kg	

SO_2 stack emissions

time:	10,30	10,35	10,40	10,45	10,50
ppm:	209	420	258	475	190
time:	10,55	11,00	11,05	11,10	11,15
ppm:	470	174	353	370	201
time:	11,20	11,25	11,30	11,35	11,40
ppm:	390	390	479	304	378
time:	11,45	11,50	11,55	12,00	
ppm:	516	459	381	454	

Trial No	5	
Date	30th of March 1994	
Test start time	9,00	
Test end time	10,00	
Test duration	1 hour	
Incinerator type	incinerator of dangerous wastes II	
Incinerator temperature	650 - 850 ^{o}C	
Incin. excess O_2	16,1 %	
Flue gas flow rate	99 156 m^3/hour	
Burnt waste	sewage	
Quality burnt waste	water	61 %
	sulphur	0,42 %
	acid number	2,2 mgKOH/g
Total burnt mass	1 500 kg	

SO_2 stack emissions

time:	9,00	9,05	9,10	9,15	9,20
ppm:	97	63	5	70	235
time:	10,25	10,30	10,35	10,40	10,45
ppm:	278	139	126	121	179
time:	10,50	10,55	11,00		
ppm:	137	135	133		

Trial No	6
Date	15th of April 1994
Test start time	11,00
Test end time	12,30
Test duration	1,5 hours
Incinerator type	incinerator of dangerous wastes I
Incinerator temperature	650 - 850 ^{o}C
Incin. excess O_2	16,1 %
Flue gas flow rate	85 472 m^3/hour
Burnt waste	sewage and contaminated earth by oil = 0,5 : 1,75
Quality burnt waste	sewage - water 61 % sulphur 0,42 % acid number 2,2 mg/KOH/g earth - water 15 % sulphur 0,67 % oil 3,8 %
Total burnt mass	3 350 kg

SO_2 stack emissions

time:	11,00	11,05	11,10	11,15	11,20
ppm:	72	100	108	195	352
time:	11,25	11,30	11,35	11,40	11,45
ppm:	437	203	213	279	178

time:	11,50	11,55	12,00	12,05	12,10
ppm:	439	529	410	240	286

time:	12,15	12,20	12,25	12,30
ppm:	240	380	307	470

Trial No	7
Date	22nd of April 1994
Test start time	12,40
Test end time	13,40
Test duration	1 hour
Incinerator type	incinerator of dangerous wastes I
Incinerator temperature	700 - 850 °C
Incin. excess O_2	15,6 %
Flue gas flow rate	85 472 m^3/hour
Burnt waste	sludge from dump
Quality burnt waste	water 52 %
	sulphur 2,26 %
	sulphuric acid 2,04 %
	acid number 53,4 mg/KOH/g
Total burnt mass	1 200 kg

SO_2 stack emissions

time:	12,40	12,45	12,50	12,55	13,00
ppm:	761	765	1186	1506	1578

time:	13,05	13,10	13,15	13,20	13,25
ppm:	1704	1095	809	1614	735

time:	13,30	13,35	13,40
ppm:	2311	1495	806

If you have same questions, I'll like to answer on it.

Best regards

65

Radislav

MEMORANDUM

TO: Mr. Jozef Surab
Technical and Production Director

FROM: Mr. Edward Andrechak EMA

COPY: Bhushan Lodh, Mrs. Olga Hauskrechtova

DATE: May 9, 1994

SUBJECT: Questions Regarding Incinerator Test Data

Thank you for sending the incinerator test data last week. We have reviewed the test results and have the following questions about the incinerator test data.

General

1. What is the difference in Incinerator Type? Are Incinerator of dangerous wastes II and Incinerator of dangerous wastes I different incinerators?

2. Is it correct that the Acid Number was determined with NaOH in some tests and KOH in other tests?

3. What was the fuel for the incinerator or incinerators? What was the fuel feed rate and the sulfur content of the fuel used in the incinerator or incinerators?

4. For each test, identify whether test was run with neutralized waste or unneutralized waste?

5. What are the gas temperatures and humidity conditions for the flue gas flow rates given for each test.

6. Are the test durations given in the test data equal to the time required for the total mass of waste to be burned in the incinerator?

Test No. 2

1. Is the first set of waste analysis data for Test No. 2 for the combined sludge from dump and waste from the wastewater treatment plant? A separate waste analysis is given for the water acid emulsion from the dump.

2. If the first set of waste analysis data is not for the combined wastes, please provide the analysis for each type waste, if available.

3. Is the waste from wastewater treatment plant used in Test No. 2 the same material as the wastewater treatment sludge used in Tests Nos.3 and 4?

4. Is there any explanation for the large variation in SO_2 stack emissions during this test? The values range from 25 to 800 ppm SO_2.

Test No. 3

1. Is the first set of waste analysis data for Test No. 3 for the combined sludge from dump and the wastewater treatment sludge?

2. If the analysis is not for the combined waste, please provide the analysis for each type waste, if available.

Test No. 4

1. Is the waste analysis data for the combined sludge, wastewater treatment plant sludge, and the contaminated earth?

2. If the analysis is not for the combined waste, please provide the analysis for each type waste, if available.

3. What is the percent (%) sulfur in the wastes burned in this test?

4. Is the sludge used in this Test the same material as the sludge from the dump used in Tests Nos. 2, 3, and 7?

Test No. 5

1. The Test Start Time is shown as 0900 hr, the Test End Time is shown as 1000 hrs and the Test Duration is shown at 1 hour. However, SO_2 data is given for the time period 0900 to 1100 hours. Is there an explanation for the difference in these time periods?

2. Is there any explanation for the low SO_2 stack emission during the first 20 minutes of this test?

PETROCHEMA

ŠTÁTNY PODNIK, DUBOVÁ, 976 97 NEMECKÁ

ENSKÁ REPUBLIKA Tel.:0867/926182 0867/926142 Fax.:0867/92286, 0867/92208

TELEFAX

KOMU/TO: Edward Andrechak
El Segundo

DÁTUM/DATE: 19. 5. 1994

POČET STRÁN/NO OF PAGES:

FAX: 001 310 640 8940

OD KOHO/FROM: Ing. Mária Babiaková

VEC/OBJECT

Dear Sir,

I answer on your questions from your fax 9th of May 1994-

General

1. The difference in Incinerators is only in capacity of burnt wastes:
   capacity of Incinerator I. - 2 200 kg/hour
   capacity of Incinerator II. - 3 700 kg/hour

2. Acid number my be determined by NaOH and KOH according to Czechoslovak norm. It is dependent on laboratory, wich method is use.

3. The bunker oil was used as fuel.

4. Sludge was neutralized by only WWT and mixed wastes was burnt in test No. 2, 3, 4.

5. Temperatures and humidity conditions for the gas wasn't measured we haven't instrument for their measuring.

6. Ushered total mass of burnt wastes are always amounts of burnt wastes for ustered time

test No. 1	-	4 000 kg/ 2 hours
test No. 2	-	4 000 kg/ 2 hours
test No. 3	-	3 600 kg/ 1,5 hours
test No. 4	-	3 600 kg/ 1,5 hours
test No. 5	-	1 500 kg/ 1 hour
test No. 6	-	3 350 kg/ 1,5 hours
test No. 7	-	1 200 kg/ 1 hours

Test No. 2

1. Ustered analysis data is date for mixed wastes (sludge from dump and WWT).

2. Analysis date for sludge:
   water - 52 %
   sulphur - 2,26 %
   sulphuric acid - 2,04 %
   acid number - 53,4 mgKOH/g
   analysis data for WWT: water 64 %
   sulphur 0,58 %
   acid number 3,75 mgKOH/g

3. Yes, it is.

4. We suppose, that many various date in SO_2 stack emissions is due to diskontinual dosage wastes (test No. 1)

Test No. 3

1. Ustered analysis data is date for mixed wastes (sludge from dump and WWT). Water acid emulsion is dosed to incinerator by separate burner.

2. Analysis date for water acid emuslion:
   water - 68 %
   sulphur - 1,94 %
   acid number - 132.5 mgNaOH/g

Nr. 4

contaminated earth by oil)

2. Analysis date for contaminated earth:
   water - 15 %
   sulphur - 0,67 %
   oil - 3,8 %

3. Percent (%) sulphur in the burnt wastes is total sulphur determinated by Xrays with Dohrmann system 702.

4. Yes, it is.

Test No. 5

1. There is mistahe. Time of test is 9,00, 9,05 ..... 9,20, 9,25, 9,30 ..... 10,00.

2. We suppose that varioue date for CO_2 stack emission is dependent on immediate quality [illegible]

2. Analysis date for water acid emuslion:

water	-	68 %
sulphur	-	1,94 %
acid number	-	132,5 mgNaOH/g

Test No. 4

1. Ushered analysis date is date for mixed wastes (sludge, WWT, contaminated earth by oil)

2. Analysis date for contaminated earth:

water	-	15 %
sulphur	-	0,67 %
oil	-	3,8 %

3. Percent (%) sulphur in the burnt wastes is total sulphur determinated by Xrays with Dohrmann system 702.

4. Yes, it is.

Test No. 5

1. There is mistake. Time of test is [illegible] 9,30 ..... 10,00.

2. We suppose that various date for SO_2 stack emission is dependent on immediate quality emulsion from dump.

Best regards

RADIAN
CORPORATION

ATTACHMENT E

GOUDRON SLUDGE NEUTRALIZATION AND INCINERATION SAMPLE CALCULATIONS

ADIAN PORATION

CALCULATION SHEET

CALC. NO. E-1

TURE J. E. HOWES DATE 7/18/94 CHECKED GWM DATE 7/25/94

CT GOUDRON SLUDGE NEUTRALIZATION JOB NO. PETROCHEMA WASTE MINIMIZATION DEMONSTRATION

CT ESTIMATION OF FUEL SULFUR SHEET 1 OF 1 SHEETS

ESTIMATION OF FUEL SULFUR USING F-FACTOR

ASSUMPTIONS: F-FACTOR = 9190 DSCF/MMBtu (EPA METHOD 19)
HEATING VALUE = 18,540 Btu/lb
FUEL SULFUR = 2.0 % BY WEIGHT
STACK GAS O_2 = 18 % BY VOLUME

INCINERATOR II

TOTAL STACK GAS FLOW (FUEL + DILUENT GASES) = 1.94×10^6 DSCF/HR

STACK GAS FLOW FROM FUEL COMBUSTION

GAS FLOW FROM FUEL = $(1.94 \times 10^6)\left(\frac{20.9-18}{20.9}\right) = 2.69 \times 10^5$ DSCF/HR

HEAT INPUT (MMBtu/HR) = $\frac{2.69 \times 10^5 \text{ DSCF/HR}}{9190 \text{ DSCF/MMBtu}} = 29$ MMBtu/HR

FUEL CONSUMPTION = $\frac{29 \times 10^6 \text{ Btu/HR}}{1.854 \times 10^4 \text{ Btu/lb}} = 1564$ lbs/HR

STACK GAS SULFUR FROM FUEL = (1564 lbs/HR)(0.02) = 31.28 lbs/HR
= 14.19 KG/HR

INCINERATOR I

(TOTAL STACK GAS FLOW = 1.67×10^6 DSCF/HR)

GAS FLOW FROM FUEL = $(1.67 \times 10^6)\left(\frac{20.9-18}{20.9}\right) = 2.32 \times 10^5$ DSCF/HR

HEAT INPUT (MMBtu/HR) = $\frac{(2.32 \times 10^5 \text{ DSCF/HR})}{9190 \text{ DSCF/MMBtu}} = 25$ MMBtu/HR

FUEL CONSUMPTION = $\frac{25 \times 10^6 \text{ Btu/HR}}{1.854 \times 10^4 \text{ Btu/lb}} = 1348$ lb/HR

STACK GAS SULFUR FROM FUEL = (1348 lb/HR)(0.02) = 26.96 lb/HR
= 12.2 KG/HR

RADIAN CORPORATION

CALCULATION SHEET

CALC. NO. E-2

SIGNATURE JE HOWES DATE 6/12/94 CHECKED GMA DATE 6/21/94

PROJECT GOULDSON SLUDGE NEUTRALIZATION JOB NO. PETROCHEMA WASTE MINIMIZATION DEMONS

SUBJECT STACK GAS FLOW CORRECTION SHEET 1 OF 1 SHEET

STACK GAS FLOW CORRECTION TO DRY, STD CONDITIONS

ASSUMPTIONS: GAS MOISTURE = 15% by volume
GAS TEMP = 350°F

INCINERATOR II - STACK GAS FLOW = 99,136 m^3/HR

CORRECTED FLOW DRY, 68°F = $(99{,}136)(1-0.15)\left(\frac{528}{810}\right)$ = 54,928 DSC

= 1,939,507 DSCF

INCINERATOR I - STACK GAS FLOW = 85,472 m^3/HR

SAME ASSUMPTIONS

CORRECTED FLOW DRY, 68°F = $(85{,}472)(0.85)\left(\frac{528}{810}\right)$ = 47,358 DSCM

= 1,672,205 DSCF/

FLOW CORRECTION FACTORS

INCINERATOR II = 0.55

INCINERATOR I = 0.55

(REPORTED FLOW)(FACTOR) = FLOW AT STD CONDITIONS (SAME CONDITIONS AT WHI PPM SO_2 WAS MEASURED

74

10-88-3070

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RPORATION

CALCULATION SHEET

CALC. NO. E-3

ATURE JE HOLMES DATE 6/12/94 CHECKED GMA DATE 6/21/94

JECT GOLDMON SLUDGE NEUTRALIZATION JOB NO. PETROCHEMA WASTE MINIMIZATION DEMONSTRATION

ECT ppm SO_2 TO kg SULFUR CONVERSIONS SHEET 1 OF 1 SHEETS

CONVERSION - ppm SO_2 TO Kg SULFUR EMISSION

$$1 \text{ ppm } SO_2 = 2.662 \text{ mg/m}^3$$
$$= 2.662 \times 10^{-6} \text{ Kg } SO_2/\text{m}^3$$

MW - SO_2 = 64
MW - S = 32

$$1 \text{ ppm } SO_2 = (2.662 \times 10^{-6} \text{ Kg } SO_2/\text{m}^3)\left(\frac{32}{64}\right)$$
$$= 1.331 \times 10^{-6} \text{ Kg S/m}^3$$

75

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CALCULATION SHEET

CALC NO E-4

SIGNATURE EM ANDRECHAK DATE 7/24/94 CHECKED — DATE —

PROJECT GOUDRON SLUDGE NEUTRALIZATION JOB NO PETROCHEMA WASTE MINIMIZATION DEMONST

SUBJECT LANDFILL DISPOSAL COST SAVINGS SHEET 1 OF ~~2~~ 1 SHEETS

ESTIMATION OF LANDFILL DISPOSAL & TRANSPORTATION COSTS

BASIS: ASSUME 1 METRIC TON PER HOUR OF NEUTRALIZED GOUDRON SLUDGE IS BURNED, 24 HOURS/DAY, 365 DAYS PER YEAR (ONE INCINERATOR ONLY).

OTHER ASSUMPTIONS

- THE 2nd INCINERATOR IS USED FOR BURNING OTHER PETROCHEMA WASTES;
- THE NEUTRALIZED GOUDRON SLUDGE MIXTURE IS 50% WASTEWATER TREATMENT SLUDGE (WTS) BY PROPORTION (WEIGHT BASIS);
- LANDFILL DISPOSAL COSTS ARE 1,000 SLOVAK KORUNAS PER METRIC TON (PROVIDED BY MR. SLIZE OF PETROCHEMA); AND
- TRANSPORTATION COSTS ARE 1,500 SLOVAK KORUNAS PER 5 TON TRUCKLOAD = 300 (ALSO PER MR. SLIZE OF PETROCHEMA).

REDUCTION IN WTS TO BE LANDFILLED = 1 METRIC TON SLUDGE MIXTURE / HOUR 76

50% PROPORTION

× 0.5 TONS WTS / TON NEUTRALIZED MIXTURE | 24 HRS / DAY | 365 DAYS / YR | (1,000 + 300) S.Kr / METRIC TON

ANNUAL DISPOSAL/TRANSPORTATION COST SAVINGS = 5,694,000 S.Kr/YE (≈ US$185,000)

10-88-30702

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