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18905 REV.

LABORATORY / PILOT PLANT TESTS

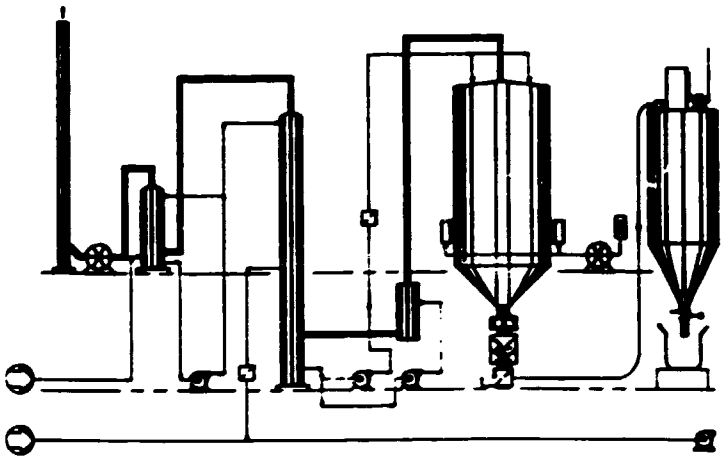
ON

BLUE DUST SAMPLES

NMDC

NATIONAL MINERAL DEVELOPMENT CORPORATION

FINAL REPORT (REVISED)



INTERNATIONAL STEEL SERVICES, INC.

PITTSBURGH, PENNSYLVANIA

CONTRACT NO. 6004

REVISION NO. 1

OCTOBER 31, 1991

TABLE OF CONTENTS

INTRODUCTION

The purpose of this project was to produce ferric chloride solution using the technology developed by International Steel Services for the processing of blue dust to high quality concentrates. The use of microwave heating has been investigated and found to be a more efficient and cost-effective energy source for the process than conventional heating methods. Pilot plant tests, utilizing microwave energy, have been conducted on iron oxide samples for digestion of iron oxide by hydrochloric acid to produce ferric chloride solution ($FeCl_3$). Through these tests, chemical parameters and their effect on the commercial plant design have been established. A portion of the leached liquor produced (210 liters) has been shipped to Dr. Meixner in Germany for further testing and evaluation.

The production of ferric chloride solution proceeds as the reaction below:

$$Fe_2O_3 + 6HCl \text{ ----> } 2FeCl_3 + 3H_2O \qquad (I)$$

The natural iron oxide found in blue dust is digested by hydrochloric acid to produce ferric chloride solution. This ferric chloride then, through a process known as spray roasting, will produce iron oxide suitable for many applications (e.g. soft ferrites particularly for power, telecommunication, and microwave applications).

EXPERIMENTAL

Equipment Design

The equipment used in the pilot plant testing was selected to meet the operating conditions (250° F,50 psi) necessary for reaction I to be completed. All of the pipes used were teflon lined for acid resistance purposes. For similar reasons, the valves used were made of kynar (PVDF). A sketch of the plant is shown in Figure 1. The top of the reaction vessel contained a 2" ball valve that served as a pressure relief point in the system. Directly below this relief valve was a 1' long glass pipe of 6" diameter. This piece had two outlets; one used as a port for a pressure gauge and the other as the inlet into the reaction vessel. This glass pipe was placed above a 1' long teflon-lined steel pipe of 6" diameter. Directly below this piece was another teflon-lined steel pipe which was 2' long and 6" in diameter. The reaction vessel thus was essentially composed of three main pieces of pipe (one glass pipe and two teflon-lined steel pipes). The bottom of the 2' long steel pipe was connected to two instrument tees placed at ninety degrees upon each other. The top instrument tee served as a port for a temperature gauge while the bottom tee was the outlet of the reaction vessel to the suction side of the pump. Below this tee was a magnetic stirrer which provided agitation within the reaction vessel. Connecting the outlet of the vessel to the inlet of the pump was a 1" ball valve followed by a 2' teflon-lined flexible steel hose of 1" diameter. The purpose of this valve was to eliminate the need to drain the reaction vessel should any leaks be found downstream.

EXPERIMENTAL

Equipment Design (cont'd)

A Jupiter pump (#MCP25-1225) was used to provide circulation through the system. The outlet of the pump was connected to a 3/4 " tee valve by a 1' long teflon pipe of 1" diameter. This valve was used to take samples of the reaction mixture at various times during the course of the reaction. It was also used to drain the system at the end of each run. Immediately following the drain valve was a 1" valve used to contain the reaction mixture in the system. The 1" valve was then connected to the inlet of the waveguide by a 3' long teflon-lined flexible steel hose of 1" diameter. This pipe was flanged to an 8' long teflon pipe of 1" diameter through the waveguide. A solid teflon pipe was used through the waveguide because of the microwave heating at this point in the system. The other end of this teflon pipe (at the outlet of the waveguide) was connected back to the inlet of the reaction vessel by a 10' long teflon-lined flexible steel hose of 1" diameter. Photographs of the major parts of the system can be found with brief descriptions in Figure 2.

Operating Conditions

The capacity of the reaction vessel was approximately 25 liters. During each run, 20 liters of 18%(w/w) hydrochloric acid was reacted with 6-8 pounds of iron oxide. Initially, the power output of the microwave was 15 kilowatts. This output was decreased to 10 kilowatts when the system reached 35 psi and 200° F. At the operating conditions of 50 psi and 250° F, the power output was varied between 2-5 kilowatts in order to maintain these conditions. A typical batch run required at least 2 hours for appreciable completion of the reaction to occur. At the end of this time, 20 liters of approximately 20% ferric chloride solution was produced.

Sample Analysis

ICP analysis was performed on several samples of ferric chloride solution. The samples were taken every twenty minutes over a two hour period. The ICP scan of these samples provided information on both the initial concentrations and the change in concentrations of certain elements present in the leached liquor. Results of the analysis performed on the 30 gallon drum and the 55 gallon drum, shipped to India and Germany respectively, can be found in Figure 2 (see page 5). These results show a substantial amount of iron present in the solutions. Acid-base titration analysis of the two drums confirms that the majority of this iron is present as $FeCl_3$ due to the fact that no hydrochloric acid was found to be present in the product solutions. Thus the reaction proceeded to completion as shown below:

$$Fe_2O_3 + HCl \text{ ----------> } FeCl_3 + H_2O$$

Figure 2

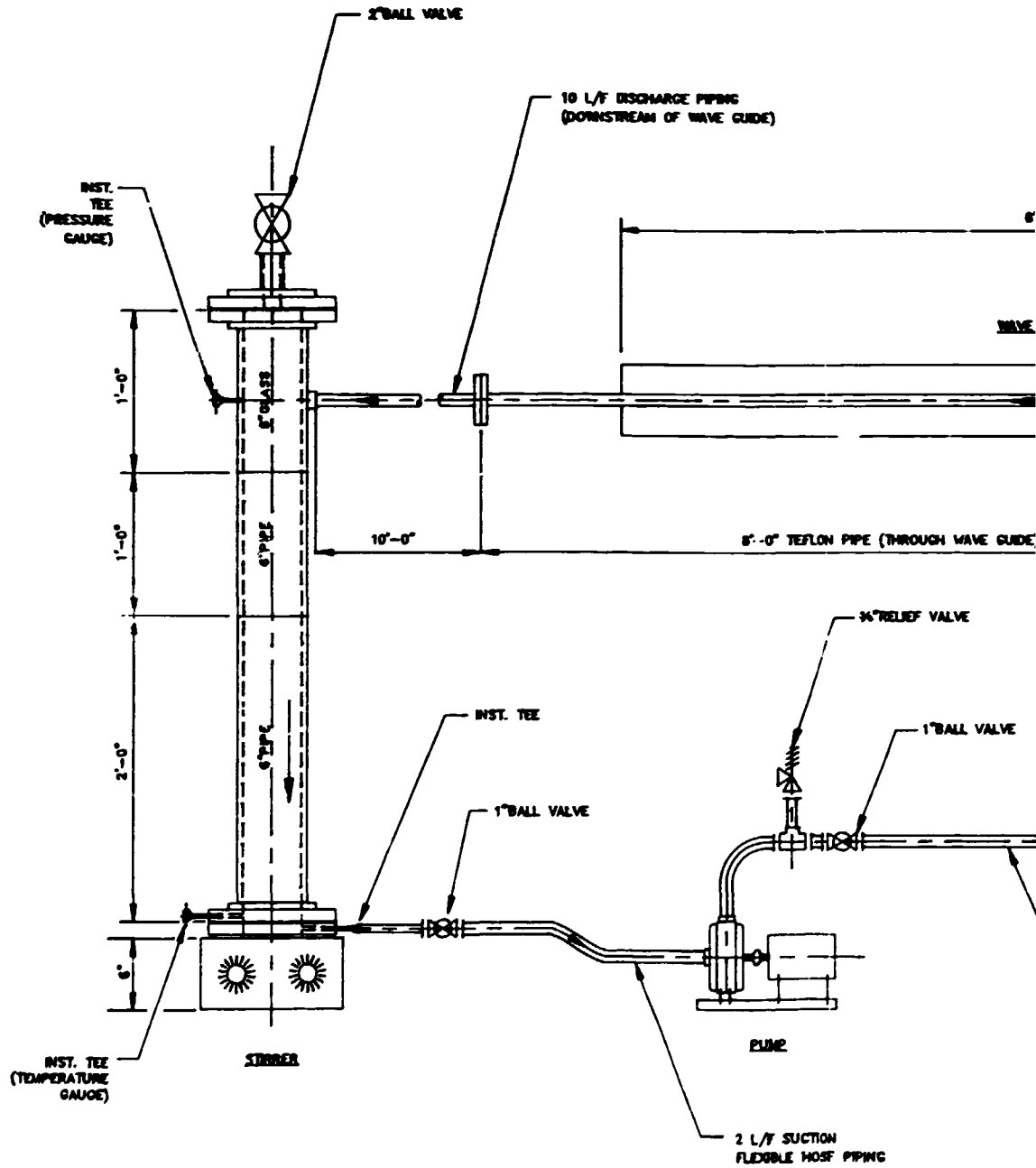
Milligrams per liter

Element	30 Gallon Drum	55 Gallon Drum
Zn	16.60	15.40
Pb	5.59	7.32
Ca	195	212
Ni	11.70	12.70
Cr	40.60	45.70
Si	2.63	3.44
Al	67.40	77.10
Cu	20.40	23.80
K	5.70	5.47
Mg	39.1	43.40
Mn	373	423
Na	52.2	52.2
S	63.1	59.4
Fe	6.1×10^4	7.1×10^4

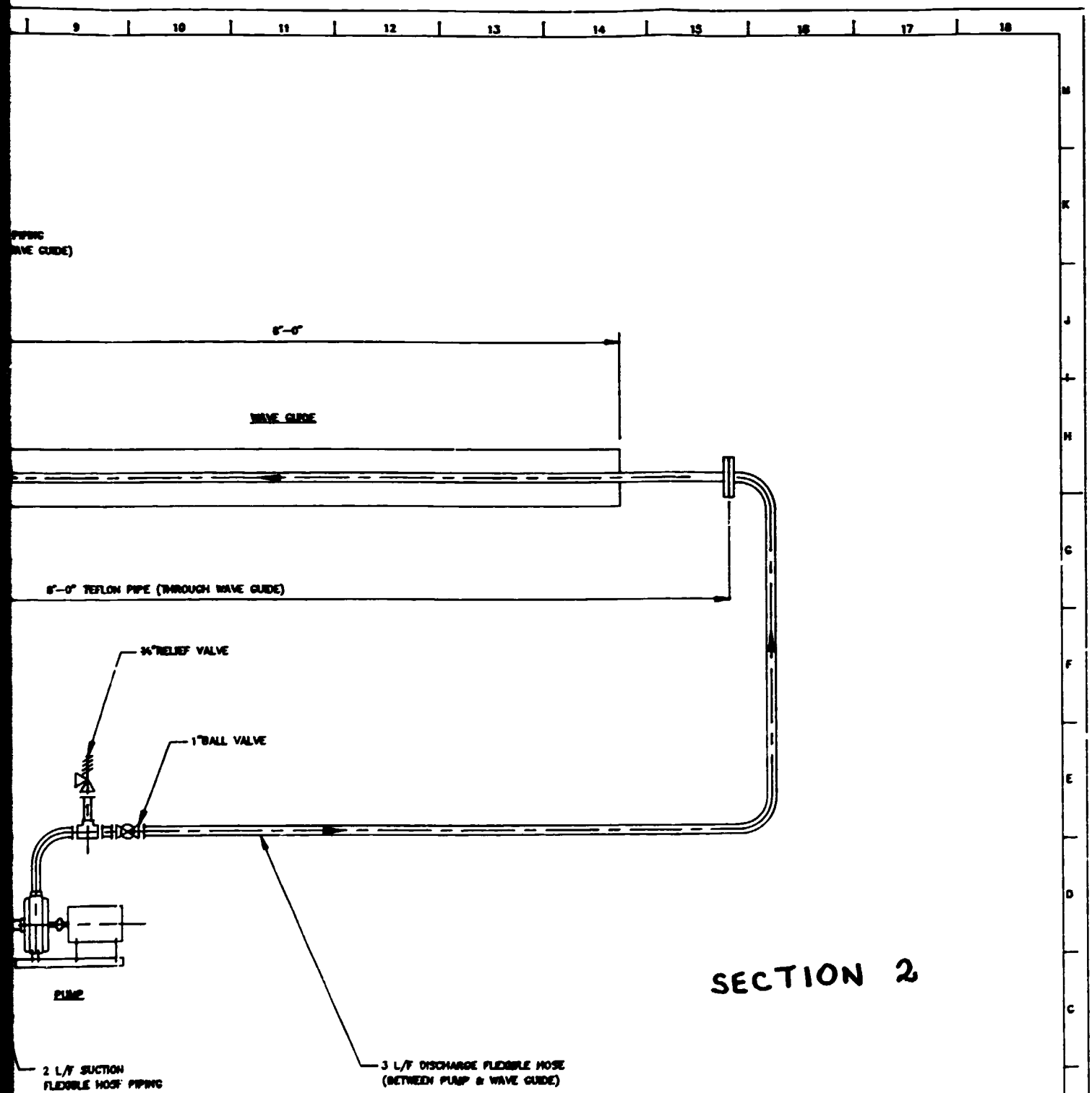
RESULTS AND DISCUSSION

The goals of the pilot plant project were successfully achieved. The utilization of microwave heating instead of conventional heating methods proved to be efficient and effective in this process. More than 300 liters of ferric chloride solution was produced and shipped to Germany and India for further testing and evaluation. Because of the limitations of the equipment design, the system was operated at 50 psi and 265^{o} F. An average reaction time was determined to be approximately two (2) hours to achieve appreciable conversion of Fe_2O_3 to $FeCl_3$ under the operating conditions mentioned above. ICP analysis on various samples confirmed substantial completion of the reaction. It seems that the reaction time can be reduced if the operating parameters (temperature and pressure) are enhanced. However, it appears that due to the use of teflon pipe in the microwave heating, this may not be possible. For future commercial applications, a multi-stage batch system is being investigated as a more effective means of utilizing microwave energy. This system would alleviate many of the problems (i.e. operating conditions, equipment failure) encountered in the pilot plant tests under the continuous plug-flow system. Details of this multistage batch reactor set-up are currently being finalized.

Figure 1



SECTION 1



SECTION 2

MICROWAVE PROCESS

DRAWN
CHECKED
SCALE 1 1/2"=1'-0"

No. 61-0001

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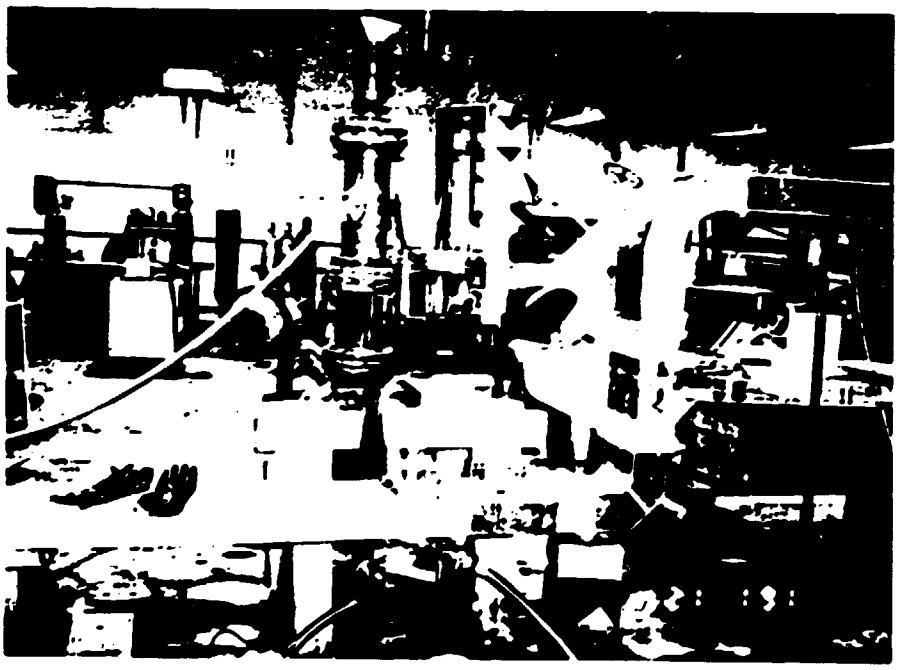
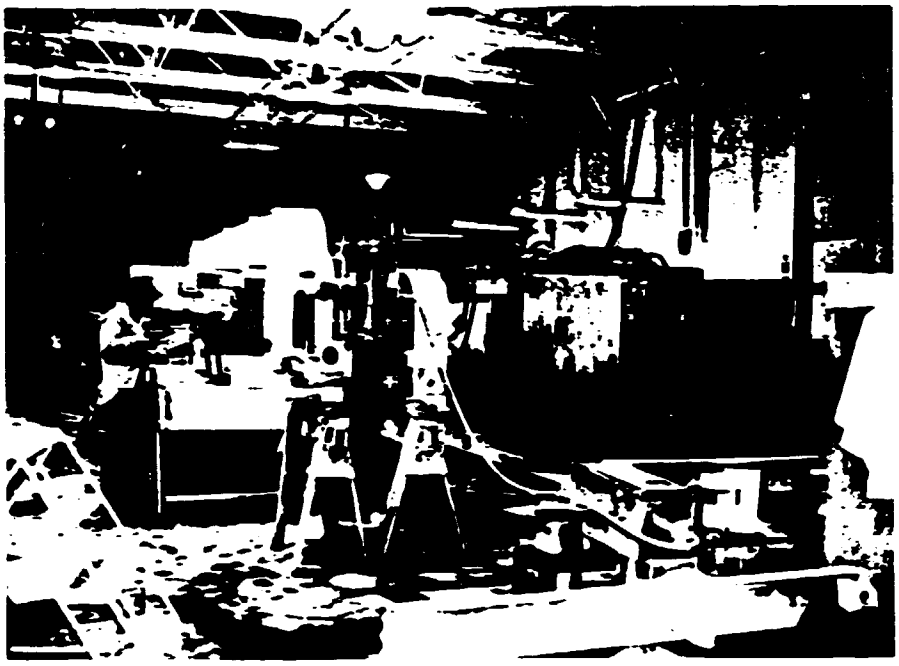
DEPT. APPROVALS

CONTRACT No.

OVERVIEW OF PROCESS SHOWING REACTION VESSEL, WAVEGUIDE, AND PUMP

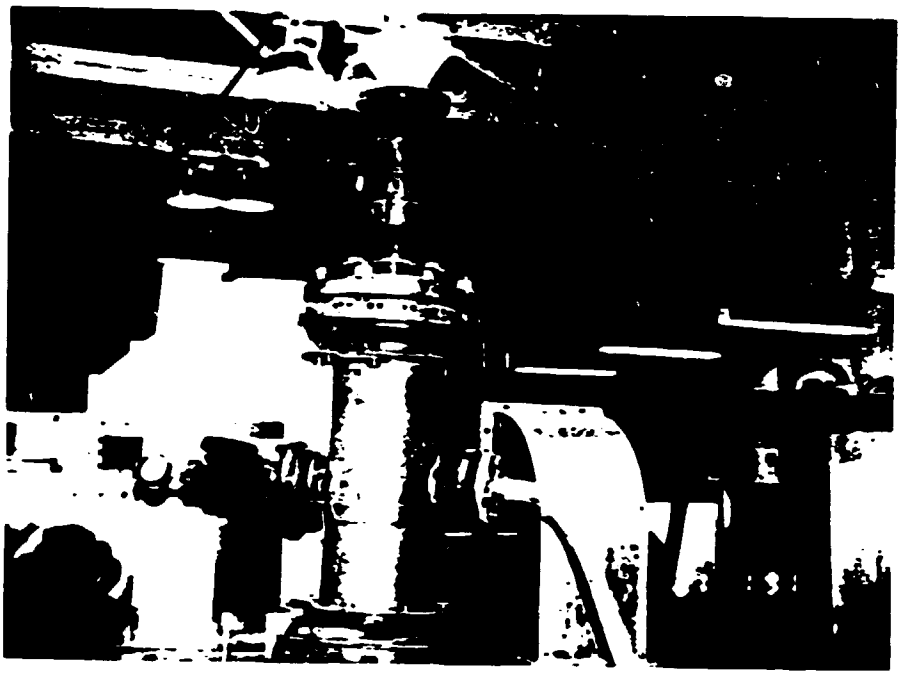


FRONT VIEW OF PROCESS SHOWING REACTION VESSEL AND WAVEGUIDE

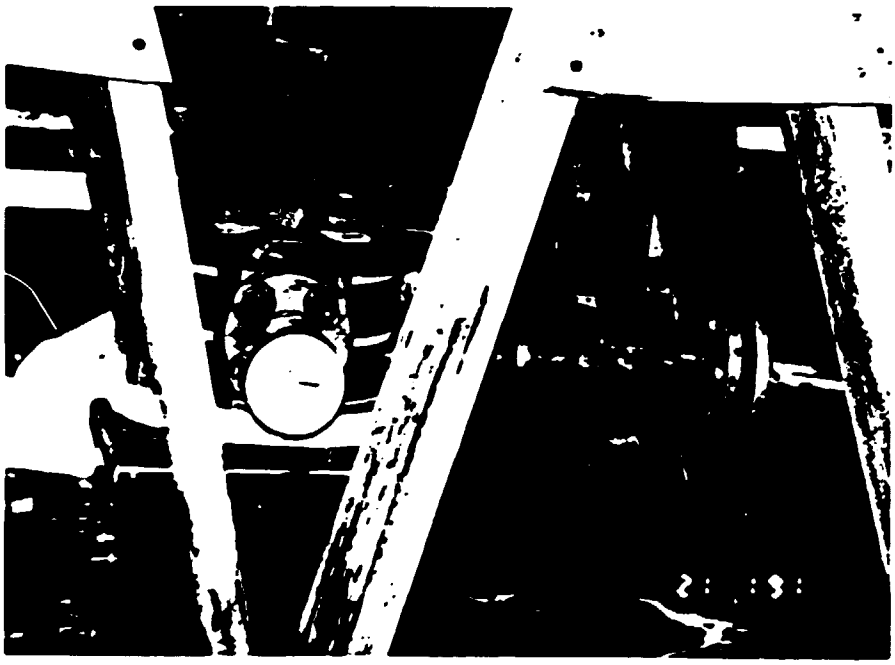


SIDE VIEW OF OVERALL PROCESS

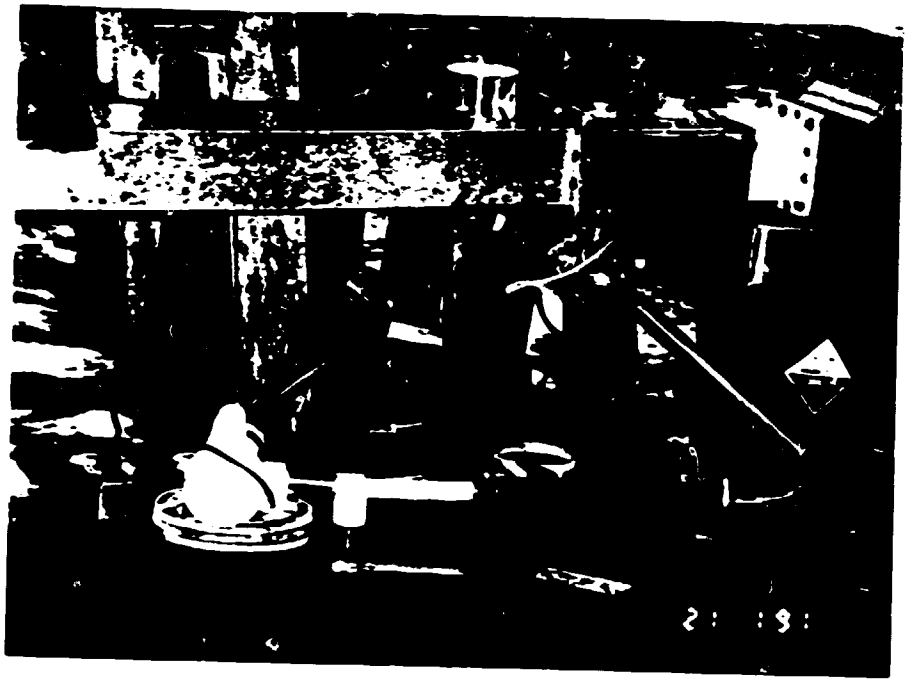
RELIEF VALVE AND [illegible] BLAZE PIPE AT TOP OF [illegible]



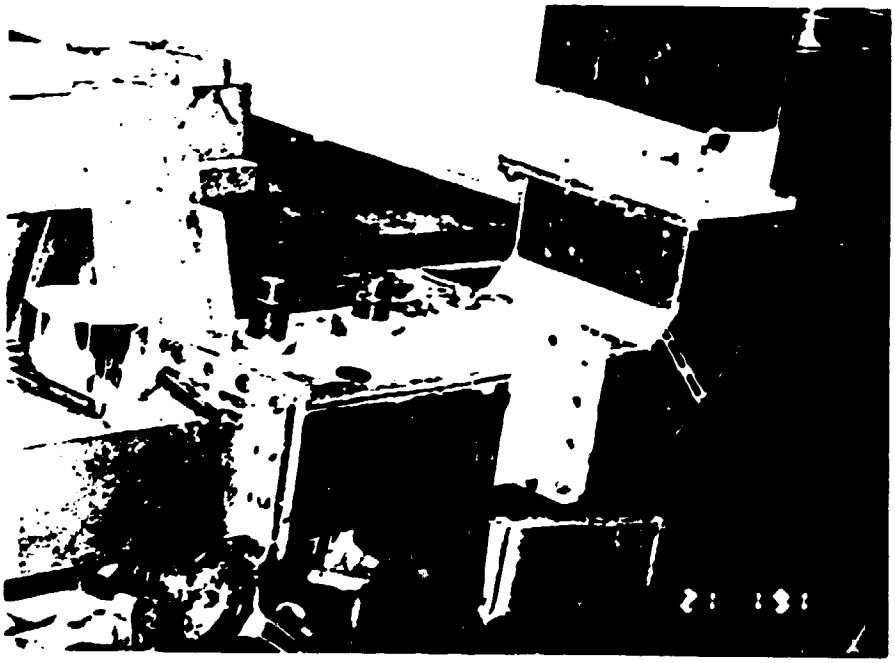
TOP OF REACTION VESSEL SHOWING INLET TO VESSEL, PRESSURE GAUGE, AND RELIEF VALVE



BOTTOM OF REACTION VESSEL SHOWING TEMPERATURE GAUGE, OUTLET OF VESSEL, AND THE MAGNETIC STIRRER (BLUE BOX)

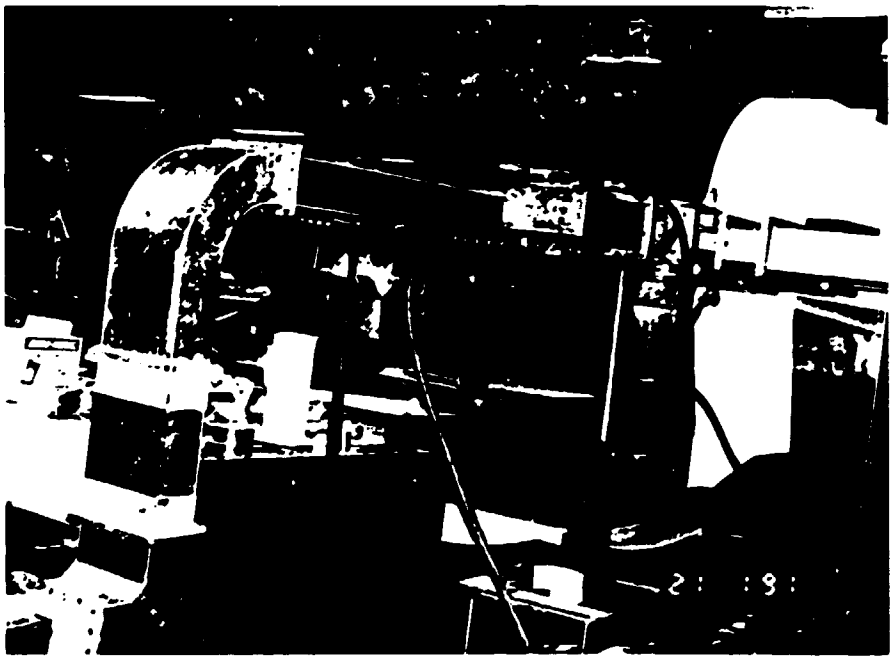


PUMP INLET FROM BOTTOM OF REACTION VESSEL AND PUMP OUTLET TO THE WAVEGUIDE

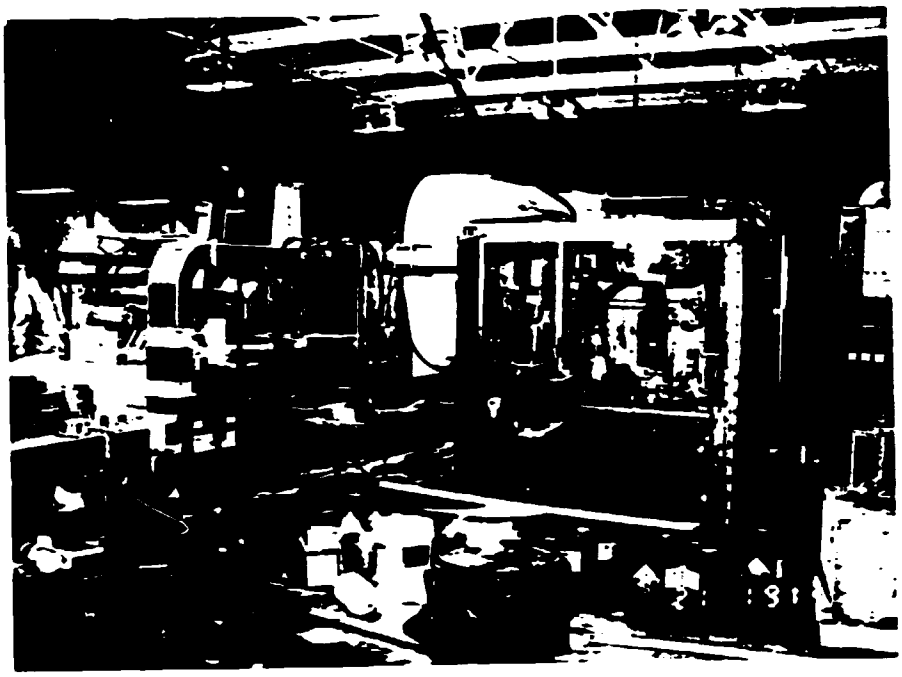


WAVEGUIDE FROM MICROWAVE SHOWING INLET TO THE WAVEGUIDE FROM OUTLET OF PUMP

MAGNETIC STIRRER AT BOTTOM OF REACTION VESSEL



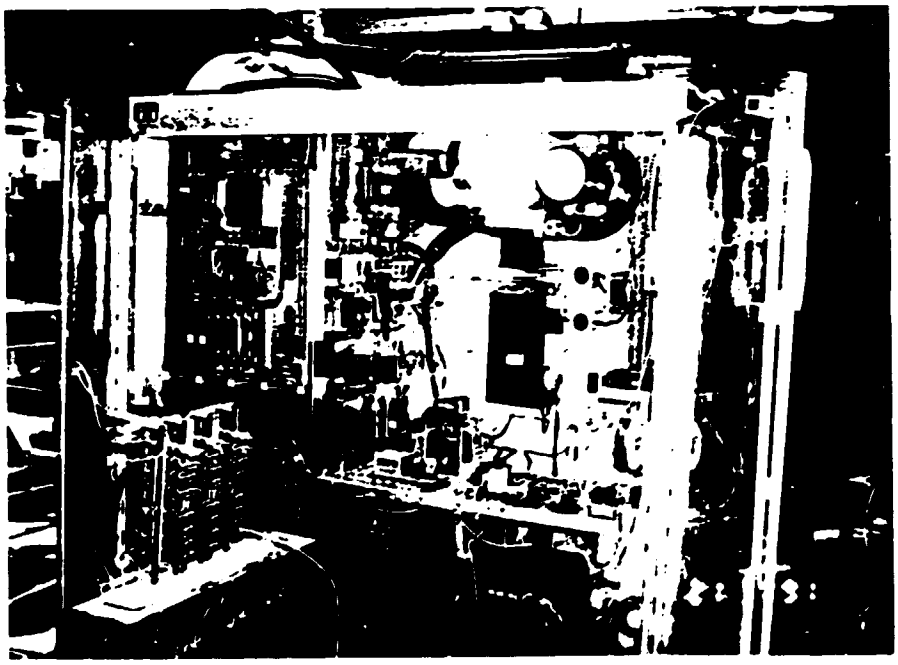
BEGINNING OF WAVEGUIDE FROM MICROWAVE



MICROWAVE, MURIATIC ACID CONTAINERS, IRON OXIDE BIN, AND WAVEGUIDE TO REACTION VESSEL

MURIATIC ACID CONTAINERS AND IRON OXIDE BIN

MICROWAVE CONTROL PANEL



ELECTRICAL WIRING OF MICROWAVE

FINAL COMMENTS

The following comments are incorporated as an addition to the subject report:

1. During the test period, samples to monitor the reaction rate were taken by analyzing the solultion for Fe only

Sample Time	Fe in Solution % W/W
0 Min	0.0
30 Min	4.3
60 Min	6.1
80 Min	7.9
100 Min	9.1

2. Based on our earlier work, it is known that conventional heating would require 6 - 8 hours for complete digestion compared to less than two hours for complete digestion by using Microwave techniques.

This reduction in digestion time would not only reduce total energy requirements, but also equipment sizes.