

OVERVIEW OF PROGRESS  
IN THE TMI-1 TUBE CLEANING EXPERIMENT

to

G.P.U. NUCLEAR

January 31, 1983

by

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INTRODUCTION

This is an interim report that presents preliminary results from studies performed at Battelle-Columbus Laboratories for G.P.U. Nuclear to evaluate and optimize a hydrogen peroxide cleaning process. This cleaning process is aimed at removing sulfur from corrosion pits in the Inconel-600 OTSG tubing that underwent intergranular stress corrosion cracking at Three Mile Island-Unit 1 (TMI-1) nuclear power plant.

The work described here is limited to experimental cleaning studies performed with Inconel-600 tubes which were removed from the TMI-1 steam generator. Supporting studies on the kinetics of sulfate production from the reaction between hydrogen peroxide and nickel-sulfide particles, and additional tube cleaning experiments will be presented in the final report.

The presentation of the results and the experimental procedure is given in a brief outline format because the main purpose of this report is to present an interim overview of the program. A comprehensive draft final report will be issued at the completion of the experimental work of the tube cleaning experiments or sometime in mid December, 1982.

## BACKGROUND

The most popularly held opinion concerning the mechanism of intergranular stress corrosion cracking of the TMI-1 once through steam generator (OTSG) tubes involves sulfur species attack on the Inconel-600 tubes. The sulfur, most likely in the form of polythionic acids and thiosulfate resulting from a series of oxidation/reduction steps during and after the incident, is known to cause intergranular stress corrosion cracking in Inconel-600. Support for this assumption came from surface analysis data of tubes showing sulfur levels in the range of  $\sim 30$   $\mu\text{g}/\text{sq.in.}$  area of the corroded tubes. In addition to that, experimental evidence demonstrating the ability of thiosulfates to induce stress corrosion cracking in the tube material prompted the investigation of a process to remove the sulfur species present in the affected areas of the tubes. The four major activities carried out during this investigation are summarized below.

- (1) Determining the levels and forms (if possible) of the sulfur species in the corrosion areas using both total sulfur, surface analysis, and ion chromatography (IC).
- (2) Defining the conditions for an effective cleaning process for sulfur removal using hydrogen peroxide by carrying out a series of "beaker tests".
- (3) Developing a global-rate expression that can be used as the basis for predicting the efficiency of the reaction during cleaning.
- (4) Applying the developed cleaning process to actual OTSG tubes provided by G.P.U. Nuclear and under the actual plant repair conditions of the tubes.

## SCOPE OF WORK

The scope of work aimed at ultimately defining the cleaning process under actual plant tube repair conditions was divided into two phases. The first phase involved carrying out oxidation, using hydrogen peroxide, of NiS which was assumed to be the predominant sulfur species present on the inside surface of the tubes. These reactions were carried out in "beaker tests". The second phase involved the adaptation of the "beaker test" NiS oxidation conditions to actual Inconel-600 tubes. Following is a summary of the main activities carried out during this program.

## LITERATURE SURVEY

The literature was surveyed for the known chemistry of nickel sulfide(s) oxidation reactions. The stoichiometry of the reaction, the effect of pH, and the nature of the pH adjusting reagents were emphasized. The article by S. Ahmed, et al., in "Corrosion" and the EPRI report by D. MacDonald and G. Gragnolino were used as starting points.

## DESIGN OF "BEAKER TESTS"

A "beaker test" was designed such that the amount of nickel sulfide, particle size, and total volume was appropriate for the periodic sampling for sulfate monitoring by ion chromatography (IC). NiS obtained in the smallest particle size available will represent the extreme case of reduced sulfur state. Each test involved the preparation of the solution and periodic sampling and analysis for sulfate by IC and the determination of the peroxide level at appropriate time intervals during the course of the reaction in order to establish the half-life of peroxide. This hopefully will define the optimum conditions for the oxidation reaction.

A series of four preliminary beaker tests were run to investigate (1) the difference between stabilized and unstabilized peroxide, (2) the effect of bright Inconel-600 surfaces on peroxide decomposition, (3) the

approximate reaction rate of thiosulfate ion with peroxide, and (4) the combined effect of stabilized peroxide, bright I-600, and 130°F temperature on peroxide decomposition rates. These tests are needed to minimize testing using actual TMI-1 tubing specimens.

#### CLEANING OF TUBES

A series of "beaker tests" were run to confirm the cleaning effectiveness of peroxide on TMI-1 specimens containing sulfur. Duplicate beakers were run at pH 8 and 2300 ppm B to simulate operations with the core in place and the other two were run at pH 10 and zero boron to simulate conditions with the core removed. A second series of tests were run under the above conditions except that sodium thiosulfate or sulfide were introduced at the same rate that sulfur was released.

#### CORROSION EXPERIMENTS

A series of "beaker tests" were run using U-bend specimens of 304SS (sens) and I-600 (sens) as well as C-rings made from TMI-I tubing with addition of sodium sulfide and hydrogen peroxide in order to test conditions inducing corrosion.

#### KINETICS STUDIES

The kinetics mechanism for the oxidation reaction was investigated. Experimental variables covered for the analysis included pH,  $H_2O_2$  concentration, boric acid concentration, temperature, stirring rate, and effect of air versus argon as a cover gas for the beaker tests.

The experimental data will be analyzed using a heterogeneous reaction model to define the reaction mechanism and establish a global-rate expression that can be used as the basis of an extended model for predicting the efficiency of  $H_2O_2$  oxidation for removal of NiS from steam generator tubes. The analysis of the experimental data will take into account dissolution of the NiS particles and mass transport effects.

The main analytical techniques employed during this program were ion chromatography (IC), total sulfur, infrared (IR), X-ray diffraction, scanning electron microscopy (SEM) coupled with energy dispersive X-ray (EDAX) analyses.

#### OVERVIEW OF PROGRAM

The program is progressing on schedule and is ~75% completed. All the experiments included in the original work plan with the exception of the tube cleaning and corrosion runs under oxygen as cover gas have been carried out. The deleted experiments were found to be unnecessary in view of the long reaction times experienced even in the presence of hydrogen peroxide. In addition to that, several "beaker tests" and new tube cleaning experiments were carried out. The additional tube cleaning runs involved Immuno1 treated and expanded tubes made available to us from B & W. Table 1 summarizes all the "beaker test" runs completed to date and the reaction conditions.

Work is currently on going to determine the total sulfur content of the tubes before and after cleaning as well as surface analysis of the tubes by SEM, EDAX, and IR techniques.

TABLE 1. "BEAKER TEST" RUNS COMPLETED

Description	pH	H <sub>2</sub> O <sub>2</sub> (ppm)	B (ppm)	S Form	Temperature
Beaker Run-1,2	8 (NH <sub>3</sub> )	200 (stabilized)	2300	NiS	Room Temperature
Beaker Run-3	8 (NH <sub>3</sub> )	100 (stabilized)	2300	NiS	Room Temperature
Beaker Run-4,5,6	8 (NH <sub>3</sub> )	200 (stabilized)	2300	NiS	Room Temperature
Beaker Run-7,8	8 (NH <sub>3</sub> )	200 (stabilized)	2300	NiS	32-35°C
Beaker Run-9,10	9 (NH <sub>3</sub> )	200 (stabilized)	2300	NiS	Room Temperature
Beaker Run-11,12	2.6 mg LiOH	200 (stabilized)	2300	NiS	Room Temperature
Beaker Run-13,14	8 (NH <sub>3</sub> )	200 (stabilized)	2300	NiS	Room Temperature*
Beaker Run-15,16	8 (NH <sub>3</sub> )	25 (maintained)	2300	NiS	Room Temperature
Beaker Run-17,18	7 (NH <sub>3</sub> )	25 (maintained)	2300	NiS	Room Temperature
Zero Run-1	8 (NH <sub>3</sub> )	200 (unstabilized)	2300	NiS (17 ppm)	Room Temperature
Zero Run-2	8 (NH <sub>3</sub> )	200 (unstabilized)	2300	NiS + I-600	Room Temperature
Zero Run-3	8 (NH <sub>3</sub> )	200 (unstabilized)	2300	Thiosulfate (20 ppm)	Room Temperature
Zero Run-4	8 (NH <sub>3</sub> )	200 (unstabilized)	2300	NiS + I-600	130°F
Tube Run-1	8 (NH <sub>3</sub> )	20 (maintained)**	2300	Tubes (3"-7")	130°F
Tube Run-2	8 (NH <sub>3</sub> )	20 (maintained)**	2300	Tubes (3"-7")	130°F
Tube Run-3	10 (LiOH)	20 (maintained)**	0	Tubes (3"-7")	130°F
Tube Run-4	10 (LiOH)	20 (maintained)**	0	Tubes (3"-7")	130°F
Corrosion Run-1	8 (NH <sub>3</sub> )	20 (maintained)**	2300	U-tubes, C-rings,	130°F (O <sub>2</sub> cover gas)
Corrosion Run-2	8 (NH <sub>3</sub> )	20 (maintained)**	2300	and sodium sulfide	130°F (O <sub>2</sub> cover gas)
Corrosion Run-3	10 (LiOH)	20 (maintained)**	0	(20 ppm)	130°F (O <sub>2</sub> cover gas)
Corrosion Run-4	10 (LiOH)	20 (maintained)**	0		130°F (O <sub>2</sub> cover gas)
Immunol Run-1	8 (NH <sub>3</sub> )	20 (maintained)**	2300	3-1, 3-2, 3-3	130°F
Immunol Run-2	8 (NH <sub>3</sub> )	20 (maintained)**	2300	3-4, 3-5, 3-6	130°F
Immunol Run-3	8 (NH <sub>3</sub> )	20 (maintained)**	2300	3-7, 3-8, 3-9	130°F
Immunol Run-4	8 (NH <sub>3</sub> )	20 (maintained)**	2300	4-1, 4-2, 4-3***	130°F
Imm. Exp. Run-1	8 (NH <sub>3</sub> )	20 (maintained)**	2300	All-13-2 #2***	130°F
Imm. Exp. Run-2	8 (NH <sub>3</sub> )	20 (maintained)**	2300	All-13-2 #10***	130°F
Imm. Exp. Run-3	8 (NH <sub>3</sub> )	20 (maintained)**	2300	All-13-5 #2	130°F
Imm. Exp. Run-4	8 (NH <sub>3</sub> )	20 (maintained)**	2300	All-13-5 #10	130°F
Imm. Exp. Run-1	8 (NH <sub>3</sub> )	20 (maintained)****	2300	All-13: B-1, B-2, B-3	130°F
				C-1, C-2, C-3	
Imm. Exp. Run-2	8 (NH <sub>3</sub> )	20 (maintained)****	2300	All-13: 1-1, 1-2, 1-3,	130°F
				4-1, 4-2, 4-3	
Imm. Exp. Run-3	8 (NH <sub>3</sub> )	20 (maintained)****	2300	All-13: 2-1, 2-2, 2-3,	130°F
				3-1, 3-2, 3-3	
Imm. Exp. Run-4	8 (NH <sub>3</sub> )	20 (maintained)****	2300	Bright Inconel-600	130°F
Imm. Exp. Run-5	8 (NH <sub>3</sub> )	20 (maintained)****	2300	All-13: 4-1 (from	130°F
				Immunol Run-4)	
Imm. Exp. Run-6	8 (NH <sub>3</sub> )	20 (maintained)****	2300	Reagent Blank	130°F

\* = Argon cover.

\*\* = Unstabilized H<sub>2</sub>O<sub>2</sub>.

\*\*\* = These pieces were not immunol treated.

\*\*\*\* = DuPont Perone H<sub>2</sub>O<sub>2</sub>.

## EXPERIMENTAL SECTION

A brief description of the experimental procedures followed during this program are given below:

### BEAKER TEST

A "beaker test" typically contains the following reagents in a one liter glass beaker equipped with a magnetic stirrer:

- 500 ml distilled (DI) water
- 6.57 g  $H_3BO_3$  (2300 ppm B)
- Enough 5:100 and  $NH_4OH:H_2O$  to bring pH to desired level
- 8.5 mg NiS
- 319  $\mu$ l 31.3 percent  $H_2O_2$  in one liter water for 100 ppm  $H_2O_2$

Where actual tubes were used, a 3-inch long tube was used instead of the NiS. The tube was either sliced longitudinally or cut into 3-inch segments in order to maximize surface contact with the solution. In addition, only enough solution was used to cover the tubes most typically 150 ml with all constituents scaled down appropriately.

### SURFACE ANALYSIS

To characterize the sulfur attack on the inside surfaces of the Inconel-600 steam generator tubes, and aid in assessing the cleaning efficiency of hydrogen peroxide, a series of tube surface examinations were conducted using scanning electron microscopy with energy dispersive x-ray analysis (SEM/EDAX), ESCA, and infrared spectroscopy.

The SEM/EDAX studies were performed with an ISI-100 SEM equipped with a Tracor Northern Model TN-2000 energy dispersive system. Tube samples were sectioned and examined both on the ID surface and in cross-section before and after cleaning. The examinations included scanning electron microscopy at different magnifications, energy dispersive x-ray measurements for semiquantitative elemental analysis, and x-ray mapping to show the spacial distribution of elements in the tube samples. Depth of the EDAX elemental analysis runs between 75 and 150  $\mu$ m. The sensitivity for sulfur

detection is about 0.5 weight- percent (w/o) on the ID tube surface and 0.1 w/o for the tube cross section.

ESCA measurements were performed using a Leybold-Heraeus Model LHS-10 Auger/ESCA surface analysis system. The ESCA analyses which were performed on the ID surfaces of the tube samples, cover an effective area of about 1.3 cm x 1 cm. Combined with argon-ion sputtering at 4 KeV, profiles of the different elements, along with their oxidation states, can be determined as a function of surface film thickness or depth below the surface of the solid base. Analysis depth from the surface is approximately 20 Å. The detection limit for sulfur is in the range of 0.1 to 0.2 atomic percent.

Infrared analyses were performed using both diffuse reflectance and microabsorption techniques. A Digilab Model 10 FTTR (Fourier transform infrared spectrometer) with a Harrick DRA-P5D diffuse reflectance accessory was used for the surface reflectance measurements and a Digilab Model 14 with appropriate condensing optics was used for the microabsorption measurements.

#### ION CHROMATOGRAPHIC CONDITIONS

Both the Model 16 and Model 10 Dionex ICS were used under the following conditions for sulfate analysis:

Eluent: 0.003 M  $\text{NaHCO}_3$  and 0.0024 M  $\text{Na}_2\text{CO}_3$

30 percent flow rate

Standard preclean and anion analytical column

Sensitivity: x1 or x3.

#### TOTAL SULFUR ANALYSIS

The standard  $\text{Br}_2/\text{H}_2\text{O}/\text{HNO}_3$  reagent was used to oxidize all sulfur forms to  $\text{SO}_4^{=}$  and the sulfate was then analyzed using IC.

### HYDROGEN PEROXIDE ANALYSIS

The hydrogen peroxide levels were monitored using Chemetrics kit which employs the reagent ammonium thiocyanate plus ferrous iron in acid solution to give a red-orange color with hydrogen peroxide. The test is based on the oxidation of iron by peroxide and the formation of the intensely colored ferric thiocyanate complex. The intensity of the color increased with the amount of hydrogen peroxide present in the solution. It was found that the presence of nitrite ions will also give a positive response with this reagent. Since nitrite ions were found to form during the cleaning process, most likely as a result of  $\text{NH}_4\text{OH}$  oxidation by hydrogen peroxide, a small amount of sulfamic acid was added prior to analysis in order to remove this interference.

In addition to monitoring the peroxide levels using the Chemetrics kit, the "Spectrophotometric Determination of Hydrogen Peroxide with 8-Quinolinol," Analytical Chemistry, Vol. 39, No. 1 (1967) was used for preparing secondary standards.

### CORROSION TEST

The corrosion test was conducted by immersing 3 C-rings made directly from IN600 TMI tubes and 3 U-bend made from sensitized IN600 and Type 304 stainless steel in the form of 0.062 inch commercial sheet stock in the test solution. This solution contained 2300 ppm B as  $\text{H}_3\text{BO}_3$  adjusted to pH 8 using ammonium hydroxide or pH 10 using lithium hydroxide and no boron. In all test solutions, the level of hydrogen peroxide was maintained at 20 ppm and a sodium sulfide solution having a concentration of 7.95  $\mu\text{g/ml}$  was continuously pumped at a rate of 2 ml/hr for a period of seven days of the 14-day test.

## RESULTS

Details on the TMI-1 Inconel-600 tube samples used in the beaker cleaning experiments are presented in Table 2. The OD of the tubes is 5/8-inch, with a wall thickness of  $0.036 \pm 0.001$  inch. Typical data for the Inconel-600 alloy are summarized in Table 3. Results available at this time from the total sulfur analyses on various tube samples are given in Table 4. The results of the total sulfur analyses and other work still in progress, along with the corrosion experiments that have already been completed, will be covered in the final report. Details on each of the beaker cleaning series experiments are described below.

CLEANING SERIES 1

This series of cleaning experiments were performed on samples from four different TMI-1 tubes as identified in Table 2. Prior to being received by Battelle, the tubes had been cleaned prior to shipment by B & W using techniques such as running a felt plug through them, and then eddy current tested for cracks, but had not been treated with Immulon. The beaker cleaning tests were conducted at 130°F with duplicate samples at pH 8 and pH 10, with a total solution volume of 150 ml in each beaker. Each beaker contained a 2-1/2-inch length of tube that had been cut in half along its longitudinal axis. Samples of solution were removed periodically from each beaker for sulfate analysis by ion chromatography and hydrogen peroxide analysis by the colorimetric method. Hydrogen peroxide was added as required to maintain its concentration at 20 ppm, and make-up water with appropriate pH was added as needed to keep the solution volume at 150 ml.

The results of the sulfate and peroxide measurements are shown as a function of reaction or cleaning time in Figures 1 through 4. In general, the total sulfate removed from the tubes at the end of the runs

TABLE 2. DETAILS ON TMI-1 TUBE SAMPLES USED FOR BEAKER CLEANING EXPERIMENTS

Beaker Cleaning Series	Beaker Test No.	Tube Sample Identification		Sample Treatment	Form of Tube Sample	Tube Sample Length, in.	Tube Sample Weight, g	
		Tube No.	Sample No.				Before Cleaning	After Cleaning
1	Tube Run-1	A 71-126	--	None	2 split halves	2-1/2, 2-1/2	--	--
	Tube Run-2	A 78-32-2	--	None	2 split halves	2-1/2, 2-17/32	--	--
	Tube Run-3	A 88-11	--	None	2 split halves	2-23/32, 2-25/32	--	--
	Tube Run-4	B 8-25	--	None	2 split halves	2-17/32, 2-9/16	--	--
2	Immunol Run-1	A 111-13	3-1,3-2,3-3	(a)	3 whole tubes	1-1/4	--	--
	Immunol Run-2	A 111-13	3-4,3-5,3-6	(a)	3 whole tubes	1-1/4	--	--
	Immunol Run-3	A 111-13	3-7,3-8,3-9	(a)	3 whole tubes	1-1/4	--	--
	Immunol Run-4	A 111-13	4-1,4-2,4-3	(b)	3 whole tubes	1-1/4	--	--
3	Imm. Exp. Run-1	A 111-13	2-2	(c)	2 split halves	3	13.897	13.897
						3	13.479	13.479
	Imm. Exp. Run-2	A 111-13	2-10	(d)	2 split halves	3-1/32	14.779	14.779
						3-1/32	12.685	12.685
	Imm. Exp. Run-3	A 111-13	5-2	(e)	2 split halves	3-1/32	13.458	13.456
						3-1/32	13.967	13.965
	Imm. Exp. Run-4	A 111-13	5-10	(f)	2 split halves	3-1/32	12.949	12.948
						3-1/32	14.349	14.348

(a) Immunol treated tube section exposed to explosion debris from explosive expansion tests.

(b) No Immunol treatment. Untreated tube section exposed to explosion debris from explosive expansion tests.

(c) Untreated tube sample exposed to explosion debris from explosive expansion of tube.

(d) Untreated tube sample in explosively expanded transition region.

(e) Immunol treated tube sample exposed to explosion debris from explosive expansion of tube.

(f) Immunol treated tube sample in explosively expanded transition region.

TABLE 3. PROPERTIES OF INCONEL-600\*

Density	8.43 g/cm <sup>3</sup>
Melting Range	2470 - 2575°F
Specific Heat	0.106 BTU/lb -°F (32-212 °F)
Thermal Expansion Coefficient	7.4 x 10 <sup>-6</sup> in./in./F
Thermal Conductivity	8.6 Btu/ft.-hr.-°F (32-212 °F)
Tensile Modulus of Elasticity	31 x 10 <sup>6</sup> psi
Torsional Modulus of Elasticity	11 x 10 <sup>6</sup> psi
Poisson's Ratio	0.29

Nominal Composition, Percent

Nickel	76.0
Chromium	15.5
Iron	8.00
Manganese	0.5
Silicon	0.25
Carbon	0.08
Copper	0.25
Sulfur	0.008 (Max. 0.015)

\*From Huntington Alloys Handbook, Fourth Edition, The International Nickel Company (1968).

TABLE 4. SUMMARY OF TOTAL SULFUR ANALYSES ON TUBE SAMPLES

Sample Identification	Tube Treatment	Sample Condition	Sample Form	Tube Length Analyzed, in.	Tube Sample Weight, g	Weight Loss after Br <sub>2</sub> /HNO <sub>3</sub> Oxidation, %	Total Sulfur Analysis $\mu\text{g SO}_4$ (b)	ID Surface Area, in. <sup>2</sup>	Density of Sulfur per unit ID Area, $\mu\text{g/in.}^2$
Tube No. A 71-126 Top 1 in.	None	As received	Whole tube	1-3/64	-	-	33.0	1.822	18.11
Tube No. A 71-126 Bottom 1 in.	None	As received	Whole tube	1-7/64	-	-	75.5	1.933	39.12
Tube No. A 78-32-2	None	As received	Whole tube	1-5/16	-	-	42.0, 62.0	2.284	18.39, 27.15
Tube No. A 88-11	None	As received	Whole tube	1-1/32	-	-	69.0	1.794	38.46
Tube No. B 8-25 Top	None	As received	Split tube halves	1-1/16, 1-3/32	-	-	100.0	1.775	56.34
Tube No. B 8-25 Bottom	None	As received	Split tube halves	29/32, 1-3/32	-	-	84.0	1.646	51.03
Tube No. B-111-62-TA Top	None	As received	Whole tube	1-3/64	-	-	52.0	1.822	28.54
Tube No. 146-6	None	As received	Split tube halves	1-32, 15/16	-	-	76.0	1.621	46.89
Tube No. A 71-126	None	After cleaning	Whole tube		11.5930	0.76	18.0	2.190	8.22
Tube No. A 78-32-2	None	After cleaning	Whole tube		11.4876	0.86	15.0	2.170	6.91
Tube No. A 88-11	None	After cleaning	Whole tube		13.5018	0.76	26.0	2.551	10.19
Tube No. B 8-25	None	After cleaning	Whole tube		11.1300	0.76	12.0	2.114	5.68
Tube No. A 111-13, Sample No. 3-2	Immunol/Expanded	After cleaning	3 tube pieces	(a)	7.3728	1.82	77.5	1.393	55.64
Tube No. A 111-13, Sample No. 3-4	Immunol/Expanded	After cleaning	Whole tube	1-1/16	9.323	1.51	47.0	1.856	25.32
Tube No. A 111-13, Sample No. 3-9	Immunol/Expanded	After cleaning	Whole tube	1-3/32	10.2216	1.31	27.0	1.931	13.98
Tube No. A 111-13, Sample No. 4-3	Expanded	After cleaning	Whole tube	1-1/16	10.0831	1.19	14.5	1.905	7.61
Tube No. A 111-13, Sample No. 3	Immunol/Expanded	As received	Whole tube	1	9.4987	2.12	37.0	1.795	20.61
Tube No. A 111-13, Sample No. 4	Expanded	As received	Whole tube	1	9.4566	1.47	37.0	1.787	20.71
Tube No. A 111-13, Sample No. 3-8	Immunol/Expanded	Cleaned/Polished	Whole tube	1-1/4	10.7237	0.91	26.0, 39.0 <sup>(c)</sup>	2.026	12.83, 19.25
Tube No. A 111-13, Sample No. 3-9	Immunol/Expanded	Cleaned/Polished	Whole tube	1-1/4	9.9434	0.88	23.0 <sup>(c)</sup>	1.879	12.24
Tube No. A 111-13, Sample No. 2-1	Expanded	As received	Whole tube	1	9.5116	0.91	8.0	1.797	4.25
Tube No. A 111-13, Sample No. 2-11	Expanded	As received	Whole tube	1	9.4533	0.82	14.0	1.786	7.04
Tube No. A 111-13, Sample No. 5-3	Immunol/Expanded	As received	Whole tube	1	9.5154	1.11	14.0, 11.0	1.798	7.79, 6.12
Tube No. A 111-13, Sample No. 5-9	Immunol/Expanded	As received	Whole tube	1	9.5391	1.07	12.0, 24.0	1.802	6.66, 13.32
Tube No. A 111-13, Sample No. 2-2	Expanded	After cleaning	Split tube halves	1, 1	9.0048	0.97	18.0, 240	1.701	10.58, 14.11
Tube No. A 111-13, Sample No. 2-10	Expanded*	After cleaning	Split tube halves	1, 1	8.7783	0.90	16.0	1.657	9.66
Tube No. A 111-13, Sample No. 5-2	Immunol/Expanded	After cleaning	Split tube halves	1, 1	9.5753	1.10	22.0	1.771	12.42
Tube No. A 111-13, Sample No. 5-10	Immunol/Expanded*	After cleaning	Split tube halves	1, 1	10.1655	0.92	24.0	1.921	12.49

\* Expansion transition zone.

(a) 29/32, 15/16, 25/32 in.

(b) Average of blanks subtracted

(c) Blanks not subtracted

corresponded closely to total sulfur measurements made on a representative sample from the same tube. In the case of the pH 10 experiments, more peroxide addition was required to maintain the 20 ppm target level.

#### SEM/EDAX Studies

SEM/EDAX examinations were performed on both as-received and hydrogen-peroxide cleaned samples. A photomicrograph and x-ray maps for sulfur, iron, chromium and nickel are shown in Figures 5 through 7 for a representative area attacked by sulfur in the cross section of Tube Number 146-6. These results show sulfur penetration into the Inconel surface along the grain boundaries. The x-ray maps indicate that the regions exhibiting significant sulfur levels were also depleted in both nickel and iron. Figures 8 and 9 show EDAX spectra for Inconel-600 base metal and a sulfur contaminated region in an uncleaned sample from Tube 146-6. The sulfur level in the contaminated region was measured as 5.2 weight percent. Direct EDAX measurements on the ID tube surface gave an average sulfur concentration of about 0.7 weight percent.

SEM/EDAX examination of samples from Tube Run-1 and -3 showed no sulfur above the detection limit of 0.1 - 0.2 weight percent. Typical areas of sulfur attack in the sample from Tube No. 88-11 (Tube Run-3) after cleaning at pH 10 are shown in Figures 10 and 11. An EDAX spectrum obtained at Point 2 in Figure 11 is presented in Figure 12. Even at the extreme depths of attack, no residual sulfur was observed.

#### Infrared Studies

An infrared reflectance spectrum obtained for a sample from Tube Number 146-6 is given in Figure 13. This sample is considered to be representative of the uncleaned and untreated tube samples as removed from the TMI-1 steam generator. The spectrum shows weak infrared bands in the  $2600 - 3000 \text{ cm}^{-1}$  region which indicate a thin hydrocarbon film.

CLEANING SERIES 2

The samples used in this series of beaker cleaning experiments were taken from pieces 3 and 4 from TMI-1 steam generator Tube Number A 111-13. Piece 3 was treated with Immunol and then exposed to debris from an explosive tube expansion while piece 4 was exposed to explosion debris without Immunol treatment. The beaker cleaning experiments were all carried out at pH 8 with three samples from tube piece 3 and one sample from tube piece 4. Each of the four beakers contained a single whole tube sample 1-1/4-inch in length. The volume of the peroxide cleaning solution used in each beaker was 200 ml. The beaker cleaning experiments were conducted at a temperature of 130° F using the same procedures as described for the first series of cleaning experiments.

The results of the peroxide and sulfate measurements associated with the Series 2 cleaning experiments with Immunol treated tube samples are summarized in Figures 14 - 17. Immunol Run-1, -2, and -3 which involved Immunol treated tube samples show greater hydrogen peroxide stability than Immunol Run-4, which involved an untreated tube sample. Sulfate production was about the same in the four runs. The maximum anticipated sulfate production based on total sulfur analyses on uncleaned representative samples is considerably lower than the final concentrations measured in the beaker cleaning. This discrepancy is currently being investigated.

Total sulfur measurements on the cleaned samples showed presence of residual sulfur. In the case of sample number 4-3 from Immunol Run-4, the residual sulfur amounted to about 14.5 µg as sulfate. The  $\text{Br}_2\text{HNO}_3$  oxidation procedure for the sulfur analysis dissolved about 120 mg of the sample. If the Inconel-600 contained the maximum level of sulfur of 0.015 percent, as listed in Table 3, this could account for as much as 55 µg of sulfate. Total sulfur measurements made on the Inconel-600 base metal gave sulfur contents in the range of 0.03-0.04 w/o.

### SEM/EDAX Studies

Both uncleaned and peroxide cleaned samples were examined by SEM/EDAX. Within the limits of sensitivity, no appreciable residual sulfur was detected on the cleaned samples. Details on these measurements will be presented in the final report.

### Infrared Studies

To provide background for examining Immunol coated samples, spectra were run on two different lots of Immunol (Lot Numbers B-2-62 and B-46-99) supplied by Babcock and Wilcox. Lot Number B-2-62 was used for the treatment of the samples involved in this program. The spectra in Figures 18 and 20 were obtained in transmission on thin films of the two different Immunol solutions, and are characterized predominantly by strong water absorption. Water constitutes about 95 percent of these solutions. Transmission spectra for Immunol residues prepared by evaporating the two solutions on ZnSe substrates are shown in Figures 19 and 21. A diffuse reflectance spectrum for Lot Number B-46-99 Immunol smeared on an Inconel-600 plate and then dried under an infrared lamp for one hour is shown in Figure 23. The infrared spectra show no significant differences between the two different lot numbers of Immunol.

Infrared diffuse reflectance spectra on an uncleaned section from piece 3 from Tube A 111-13 and sample Numbers 3-1, 3-3, and 3-6, which were peroxide cleaned, were all similar and showed no evidence of Immunol. A typical spectrum for these samples is shown in Figure 23. The spectra were characterized by  $\text{CH}_2$  and  $\text{CH}_3$  bands with intensity ratios in the range from 2:1 to 3:1. The intensities of these bands are quite low, indicating the presence of a very small amount of material.

The only evidence for the presence of anything besides a hydrocarbon was observed on sample Number 3-3. In this case, the spectrometer beam was focused on a dark spot on the ID surface of the tube sample.

The spectrum is given in Figure 24. The strong broad band centered at  $1250\text{ cm}^{-1}$  is characteristic of inorganic material. The band frequency is indicative of either a nitrite or possibly a bisulfate.

The infrared diffuse reflectance spectra for an uncleaned sample of tube piece 4 and the peroxide cleaned samples were essentially identical. A typical spectrum is given in Figure 25(a). The weak doublet near  $1000\text{ cm}^{-1}$  is characteristic of isotactic polypropylene (Figure 25(b)). Relative intensities of the bands around  $2900\text{ cm}^{-1}$  differ somewhat from those usually found in normal isotactic polypropylene films.

The transmission spectrum of a small dark-colored particle removed from the ID surface of uncleaned tube piece 4 is presented in Figure 27. This spectrum, which was obtained using a microtransmission technique, is identical to that for isotactic polypropylene. The relative intensity difference in the spectrum in Figure 25 may be associated with crystallinity differences in the material coated on the tube surface. Another possible explanation is spectral distortions that are sometimes observed with the diffuse reflectance technique due to optical interference effects.

### CLEANING SERIES 3

The Series 3 cleaning experiments were performed with pieces 2 and 5 from the same tube (A 111-13) as the samples used for the Series 2 experiments. Piece 5 was treated with Immunol and explosively expanded while piece 5 was expanded without Immunol treatment. Sample Numbers 2-10 and 5-10 used in Immunol Expansion Run-2 and -4 were from the expansion transition zone, and Sample Numbers 2-2 and 5-2 used in Immunol Expansion Run-1 and -3 were from a distance of about 14 inches from the explosively expanded transition zone.

For the beaker cleaning tests, the tube samples, which were about 3-inches long, were split in half axially. In each beaker, the cleaning solution volume was 150 ml.

Debris from the explosive expansion was collected from the ID surfaces of the samples before cleaning and examined using both SEM/EDAX and micro-FTIR.

The Series 3 beaker tests were conducted in the same manner as the previous beaker cleaning experiments. In the Series 3 experiments, total sulfate production was nearly the same and followed similar sulfate concentration/time curves for all four beakers. The sulfate and hydrogen peroxide concentration data are given in Figures 27-30. The curves tended to level off asymptotically after about 50 hours, then after about 100 hours increased again, leveling off after a total reaction time of nearly 250 hours.

In general, sulfate production persisted longer than was observed with either the Series 1 or 2 beaker cleaning tests. At about 215 - 220 hours into the runs, the apparent hydrogen peroxide concentrations in the beaker cleaning solutions increased to nearly 200 ppm in the case of the Immunol treated tube samples, and to about 80 ppm with the untreated samples, and then decayed over a period of about 170 hours to values approaching the peroxide target level of 20 ppm. This anomalous transient in the peroxide concentration is tentatively attributed to build up of nitrite in the cleaning solution due to a catalytic surface reaction on Inconel between nitrogen and atomic oxygen from the peroxide to form nitrate with nitrite as an intermediate. The nitrite produces a false indication of peroxide with the color test used to determine the hydrogen peroxide concentration. Formation of nitrate is observed in the cleaning solutions by ion chromatographic measurements for sulfate. The nitrate formation data are currently being collected and analyzed.

#### SEM/EDAX Studies

Uncleaned and cleaned samples were studied by SEM/EDAX. Results will be presented in the final report.

### ESCA Studies

ESCA studies were conducted on tube sample numbers 2-5 and 5-5 to investigate the nature of the residual film on the surface of the untreated and Immunol treated tubes after exposure to explosive debris from the expansion process. Results from these studies are being correlated with the infrared data and will be reported in the final report.

### Infrared Studies

The uncleaned sample Number 2-7 and the peroxide cleaned sample Number 2-10 both showed the same polypropylene material as observed with untreated samples from piece 4 of tube number A 111-13. A typical spectrum for sample number 2-10 after cleaning is presented in Figure 31. Presence of the Immunol prevents adherence of the polypropylene material. Once formed, the polypropylene is unaffected by the peroxide cleaning process. However, presence of the polypropylene does not appear to appreciably influence the rate of removal of sulfur by the hydrogen peroxide cleaning process. The absorption spectrum for sample Number 2-7, which was an uncleaned sample from about 5 inches from sample Number 2-10, was diminished in intensity indicating a lower density of polypropylene. These spectra differed significantly from those obtained for sample Number 2-2. The spectrum for sample Number 2-2 is given in Figure 32. The intensity of the absorption is considerably less than that observed with sample Numbers 2-7 and 2-10 with negligible absorption at  $2960\text{ cm}^{-1}$ . The spectrum for sample number 2-2 indicates that less material is present on the sample surface and that fewer methyl groups are present. The spectrum appears to show a contribution from polyethylene.

The spectrum for sample Number 5-7 is also quite similar to that observed with samples from piece 4. A diffuse reflectance spectrum for the uncleaned sample is shown in Figure 33. This spectrum also shows the presence of polypropylene. Particles removed from the ID surface of this sample were also identified as isotactic polypropylene.

Spectra for the two peroxide cleaned sample Numbers 5-10 and 5-2 and the uncleaned sample Number 5-5 showed both similarities and differences among themselves and with sample Number 2-7. The spectrum of sample number 5-2, which is also fairly representative of 5-5 and 5-10, is given in Figure 34. This spectrum shows a decreased intensity at  $2960\text{ cm}^{-1}$  due to less methyl absorption. Debris particles removed from the ID surface of sample Number 5-10 before cleaning were composed of either polyethylene or polypropylene. A transmission spectrum of a polyethylene particle is shown in Figure 35.

The infrared spectra showed no evidence of Immulon on the tube sample surfaces.

#### CORROSION RESULTS

As a result of the tests described in the Experimental Section, no corrosion due to the cleaning process was observed. Highlights of the data are summarized in Tables 3-12 in Appendix B.

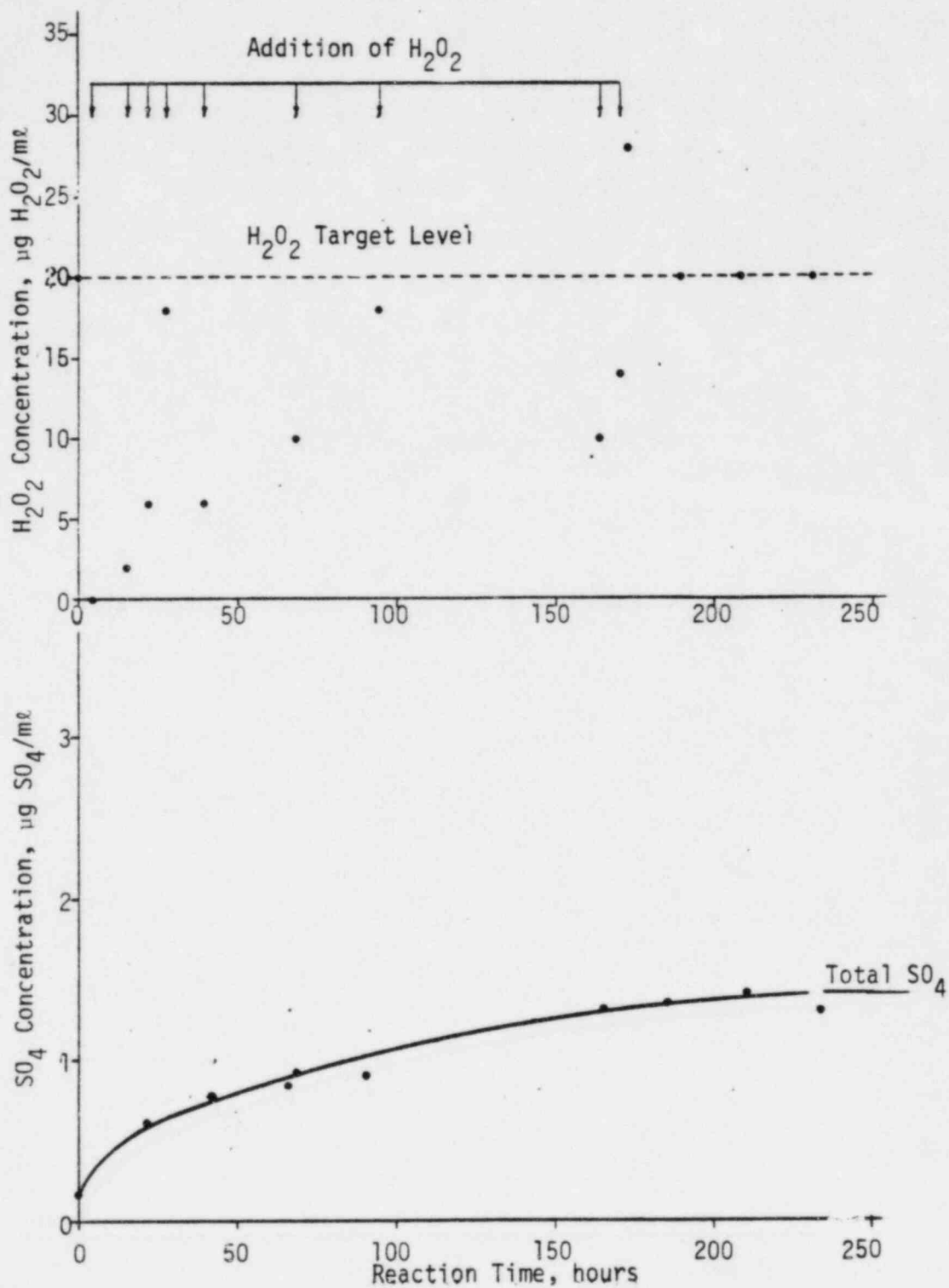


Figure 1. Hydrogen Peroxide and Sulfate Concentrations as a Function of Reaction Time for Tube Run-1 at pH 8 and 130°F.

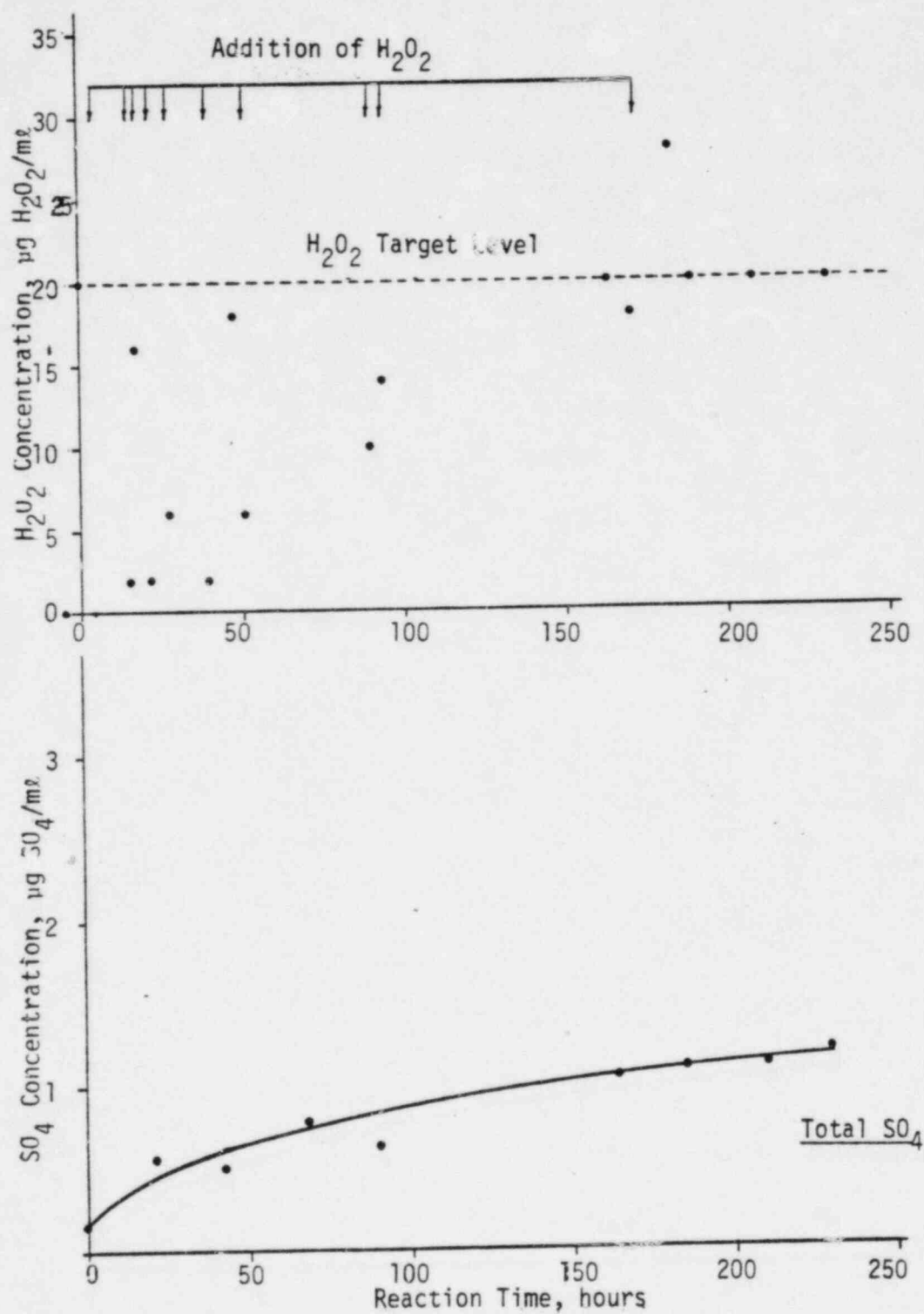


Figure 2. Hydrogen Peroxide and Sulfate Concentrations as a Function of Reaction Time for Tube Run-2 at pH 8 and 130°F.

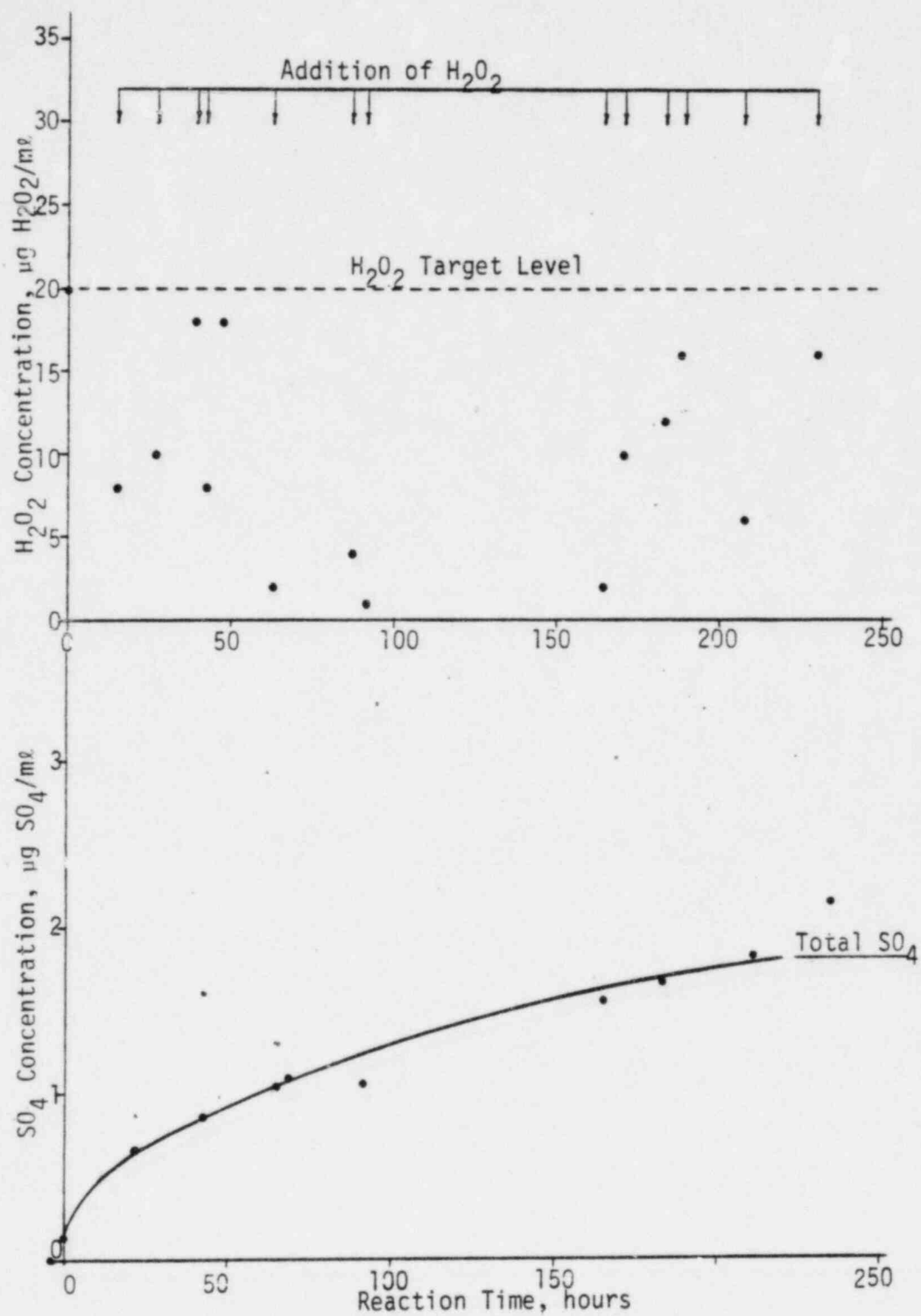


Figure 3. Hydrogen Peroxide and Sulfate Concentration as a Function of Reaction Time for Tube Run-3 at pH 10 and 130°F.

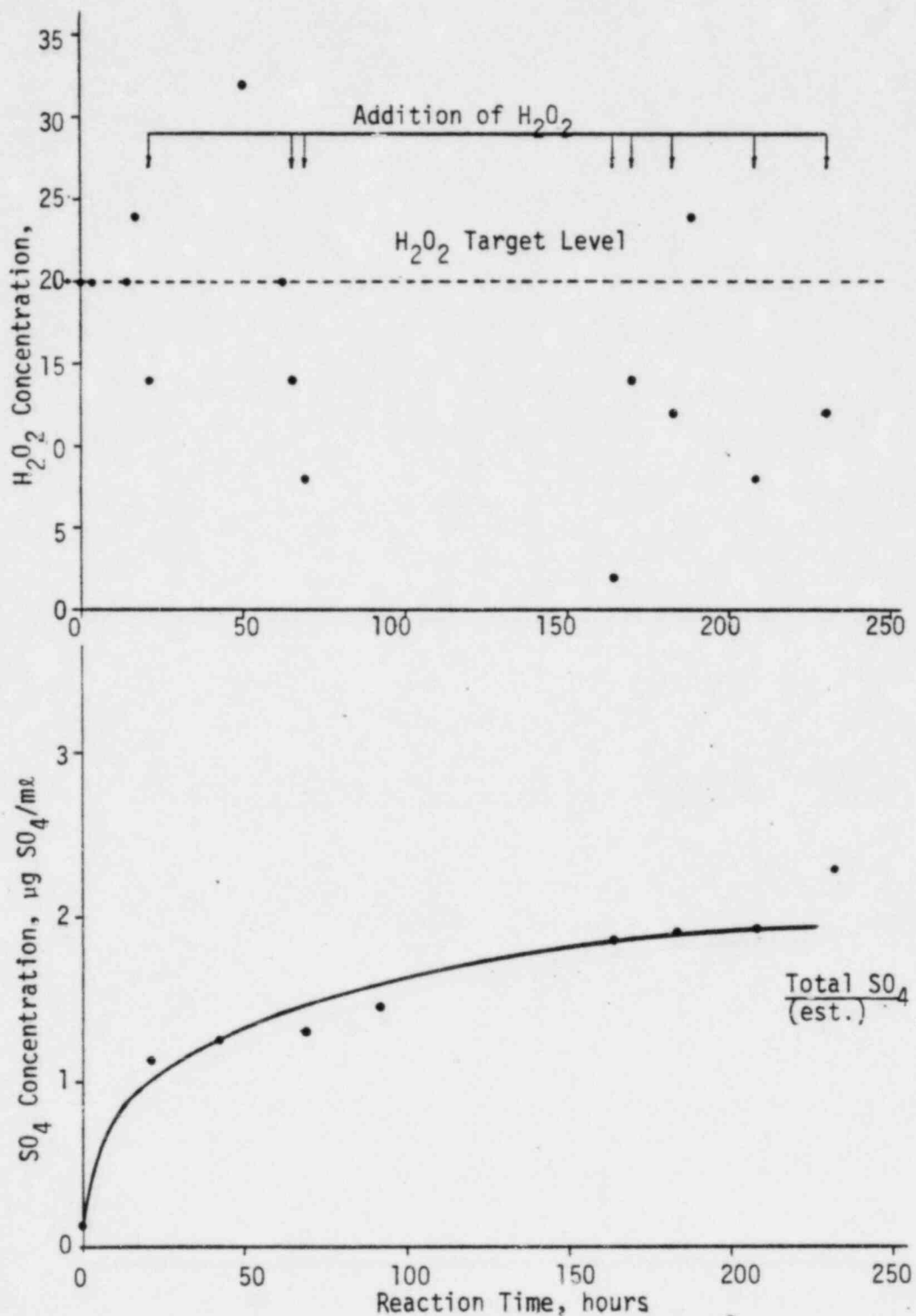
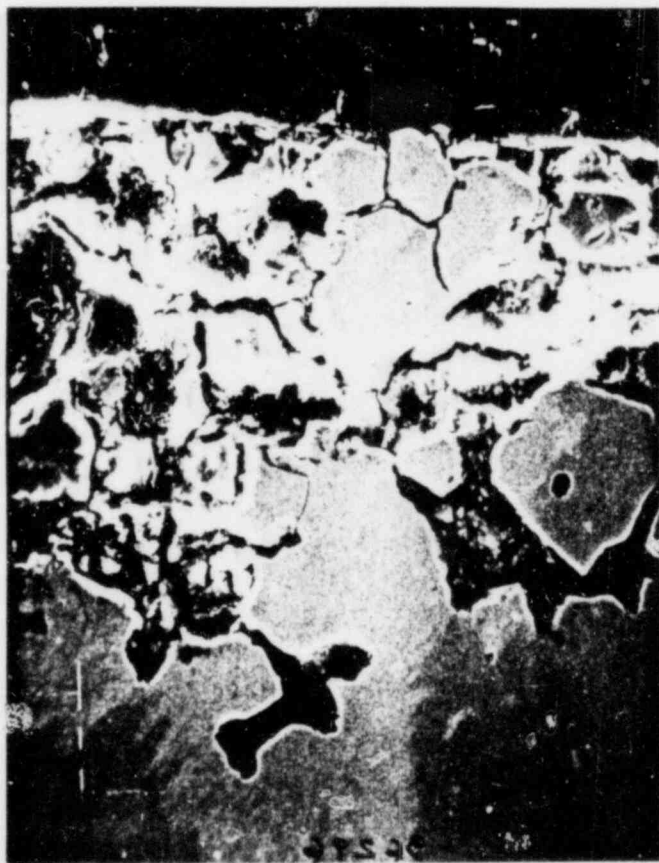


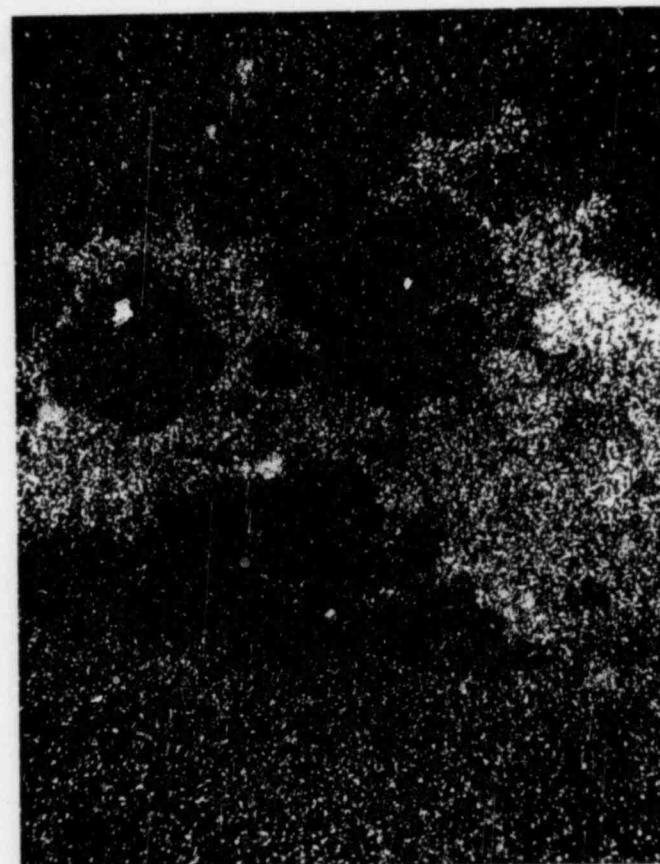
Figure 4. Hydrogen Peroxide and Sulfate Concentrations as a Function of Reaction Time for Tube Run-4 at pH 10 and 130°F.



36296

Photomicrograph

500X

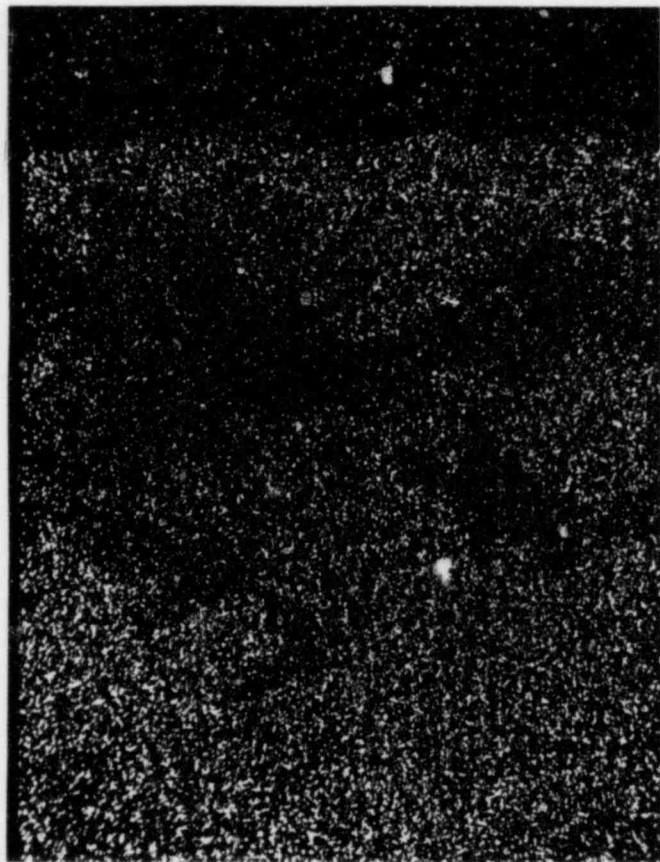


36212

Sulfur X-Ray

500X

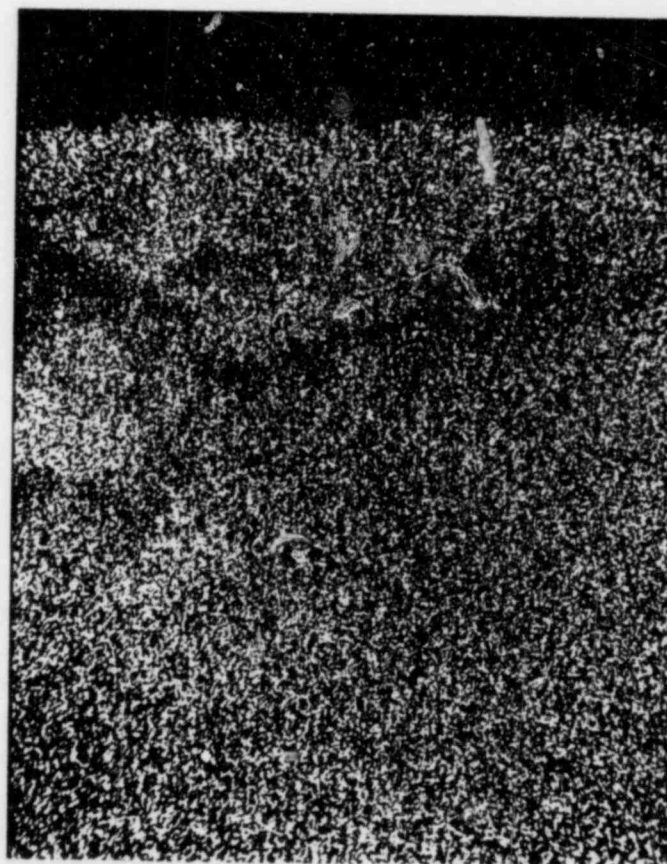
Figure 5. SEM Photomicrograph and X-Ray Map for Sulfur Contaminated Area in Cross Section of As-Received Inconel-600 Tube Sample.



36219

Iron X-Ray Map

500X

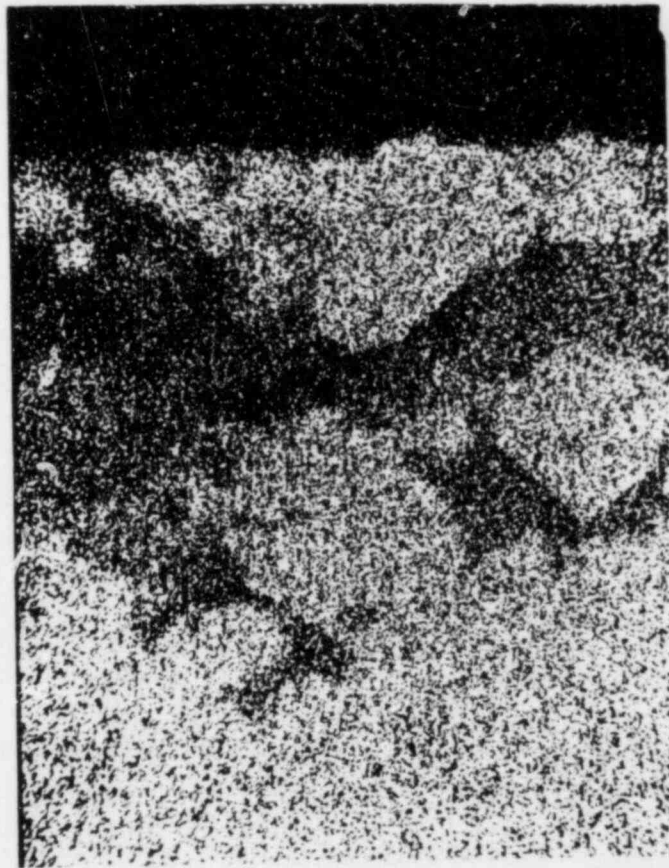


36218

Chromium X-Ray Map

500X

Figure 6. X-Ray Maps for Sulfur Contaminated Area in Cross Section of As-Received Inconel 600 Tube Sample.



36217

500

Figure 7. Nickel X-Ray Map for Sulfur Contaminated Area in Cross Section of As-Received Inconel-600 Tube Sample.

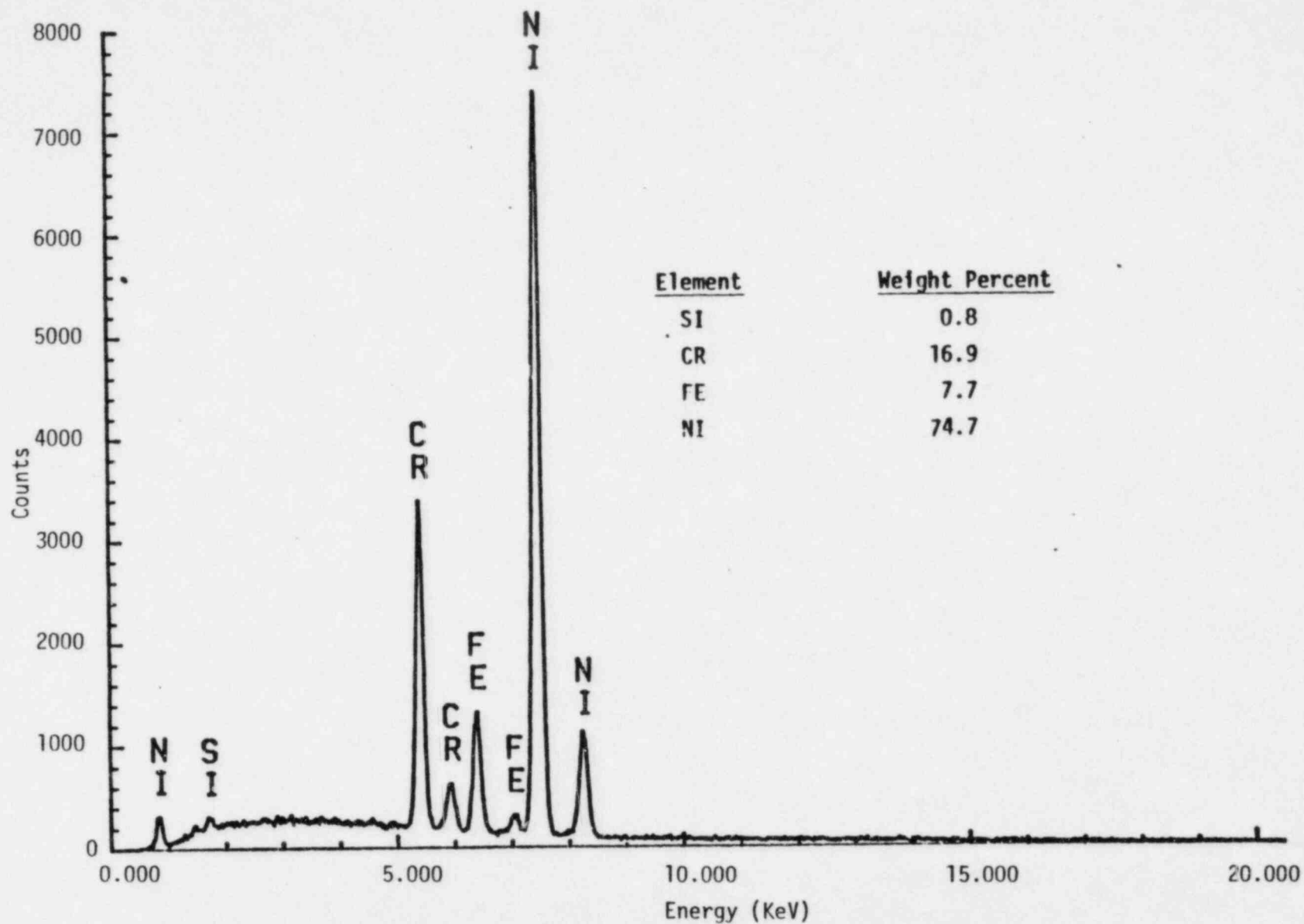


Figure 8. Energy Dispersive X-Ray Spectrum for Base Metal in As-Received Inconel-600 Tube.

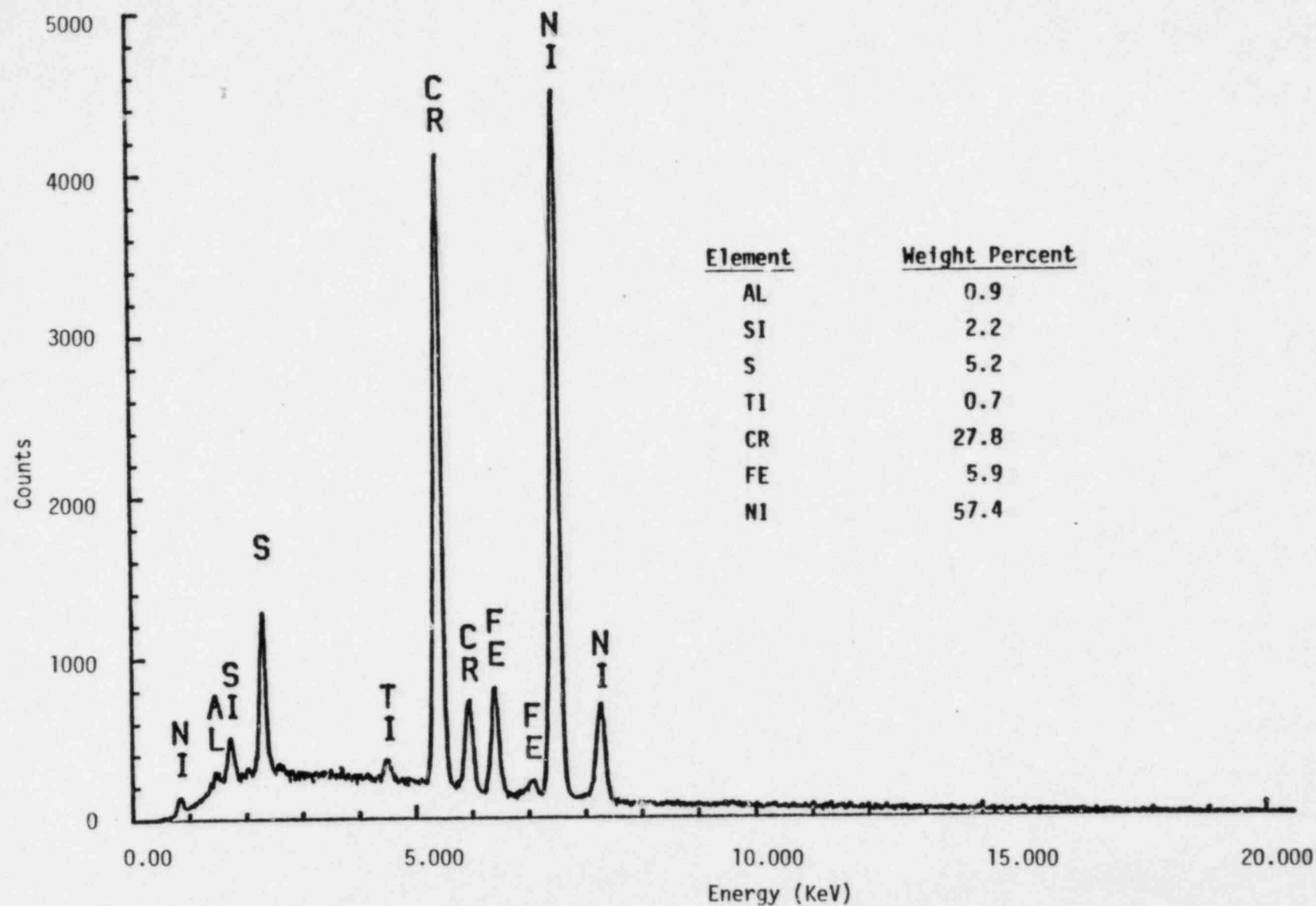


Figure 9. Energy Dispersive X-ray Spectrum for Sulfur Contaminant Area C) in Cross Section of As-Received Inconel-600 Tube.



36441

2000X

Figure 10. SEM Photomicrograph of Sulfur Contaminated Area in Cross Section of Inconel-600 Tube Sample after Cleaning with  $\text{H}_2\text{O}_2$  at pH 10.



36432

7500X

Photomicrograph

Figure 11. SEM Photomicrograph of Sulfur Contaminated Area in Cross Section of Inconel-600 Tube Sample after Cleaning with  $\text{H}_2\text{O}_2$  at pH 10.

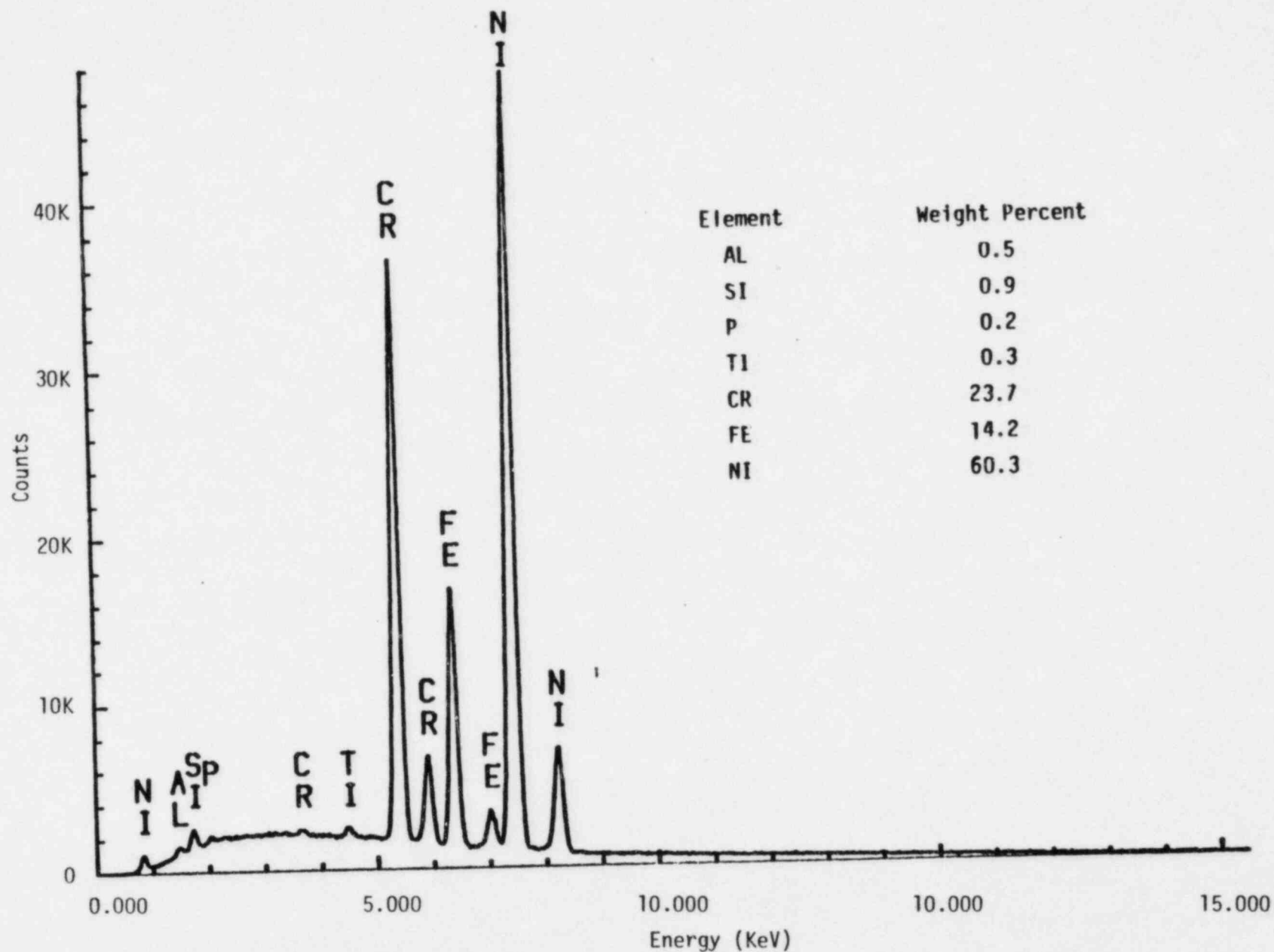


Figure 12. Energy Dispersive X-Ray Spectrum for Sulfur Contaminated Area (Area 2) in Cross Section of Inconel-600 Tube Sample After Cleaning with  $H_2O_2$  at pH<sub>8</sub>.

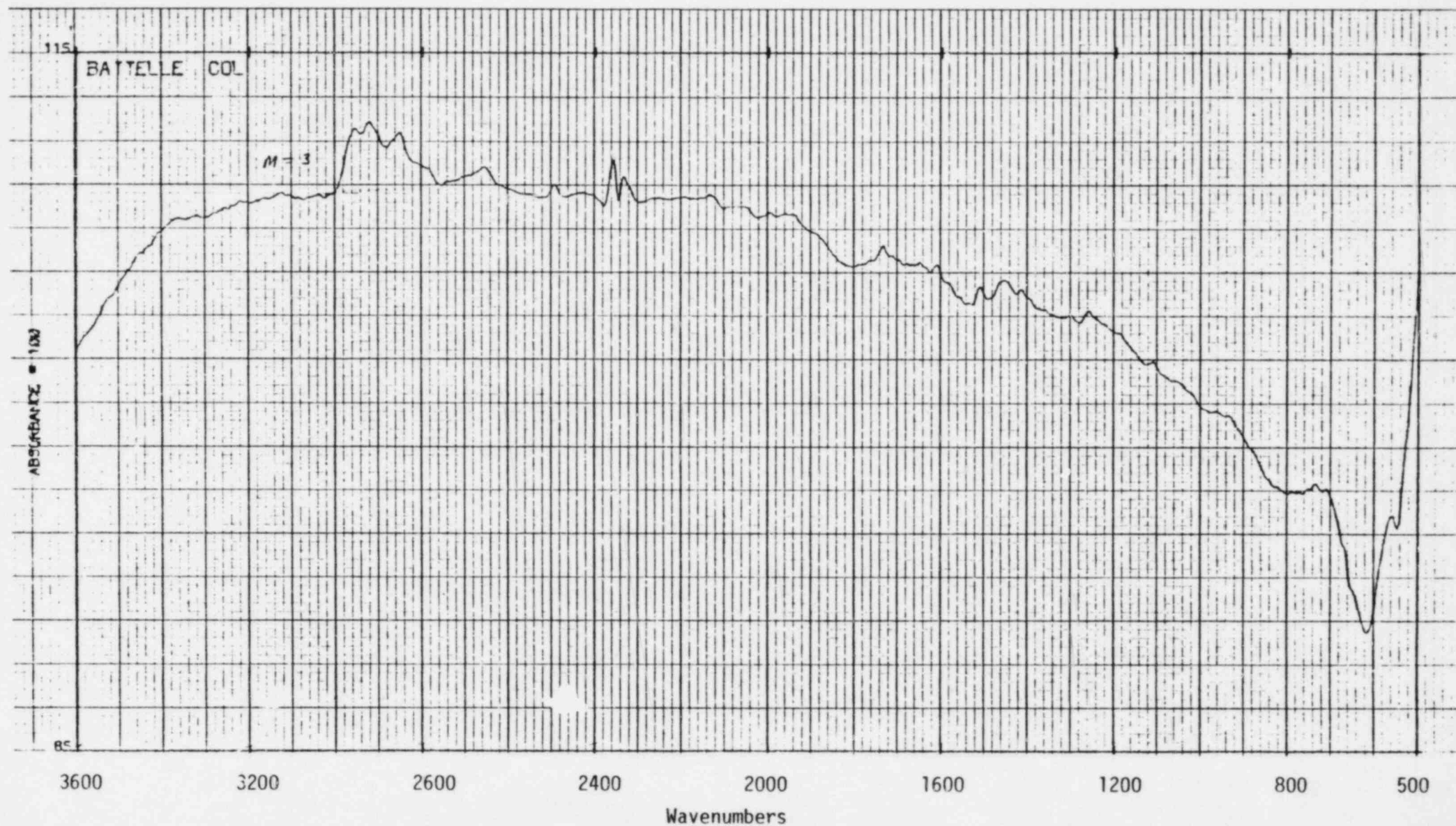


Figure 13. Infrared Diffuse Reflectance Spectrum for Dark Region on ID of Sample from Tube 146-6 (J Run 146A).

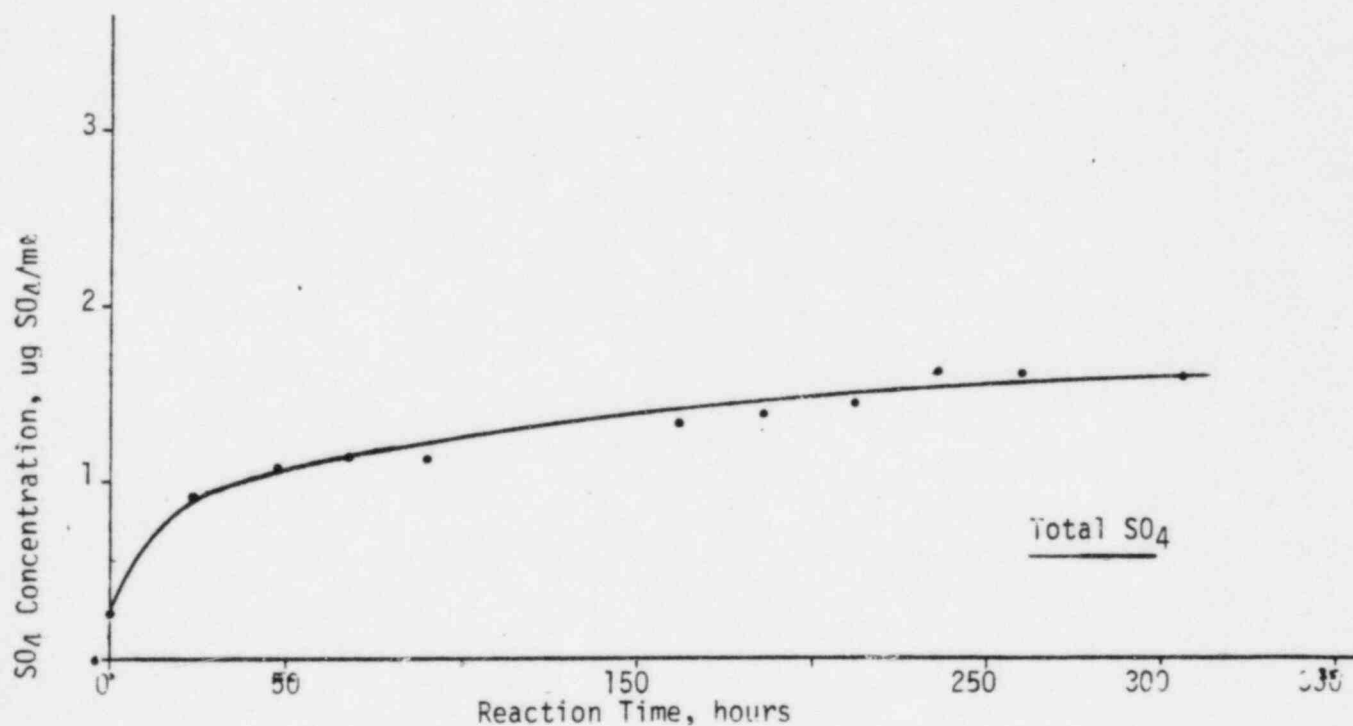
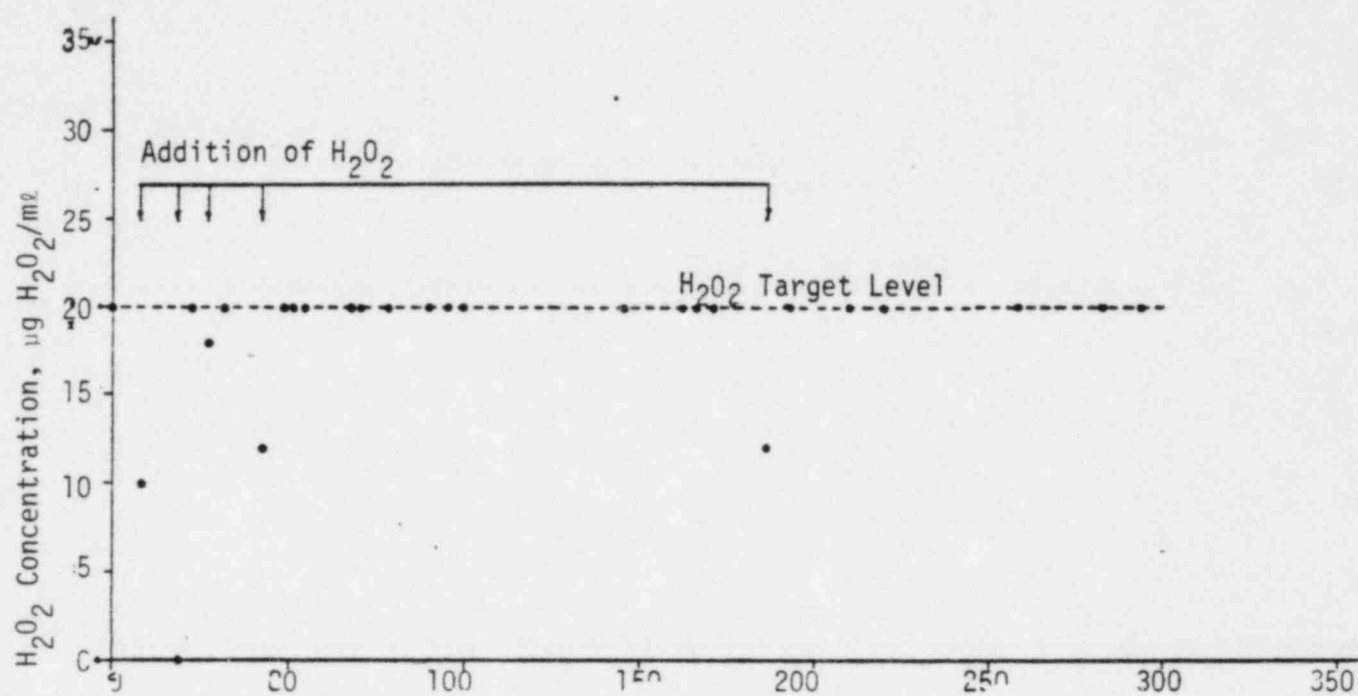


Figure 14. Hydrogen Peroxide and Sulfate Concentrations as a Function of Reaction Time for Immunol Run-1 at pH8 and 130°F (Immunol Treated Tube Sample).

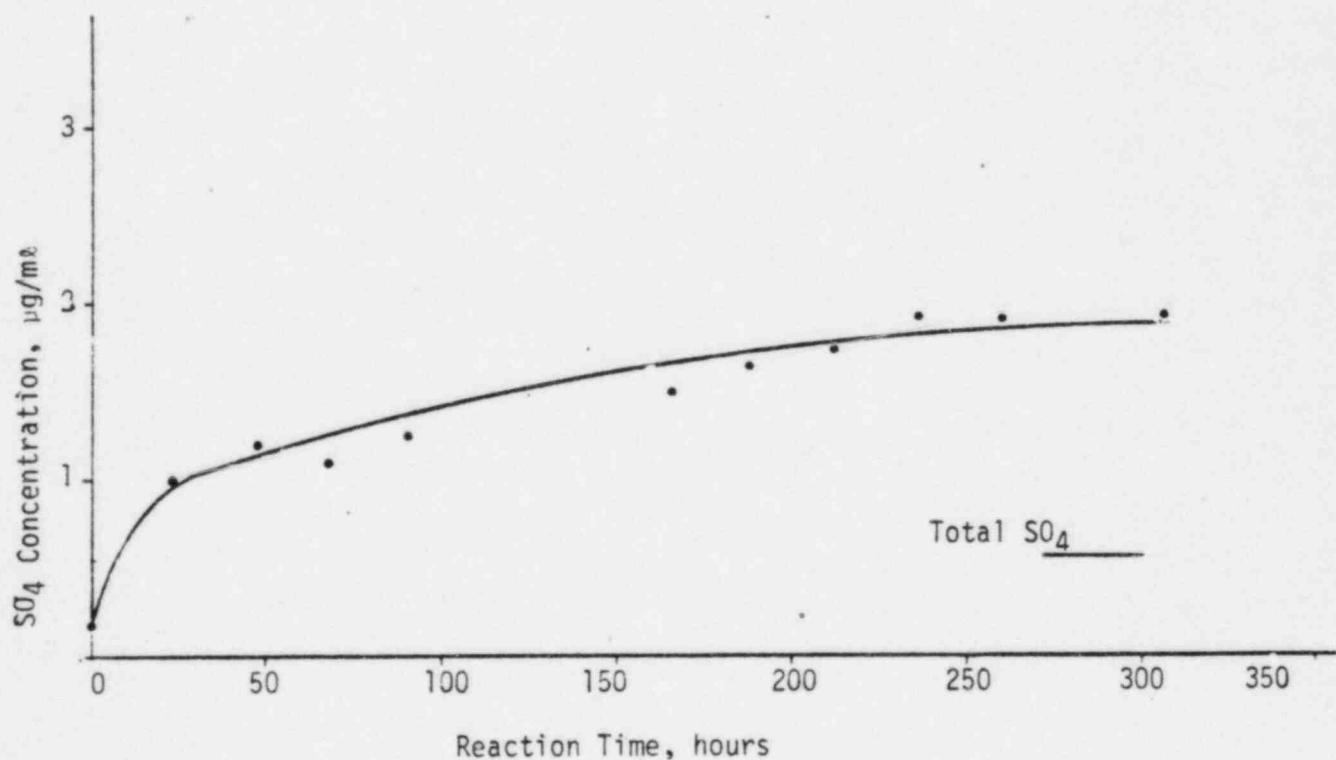
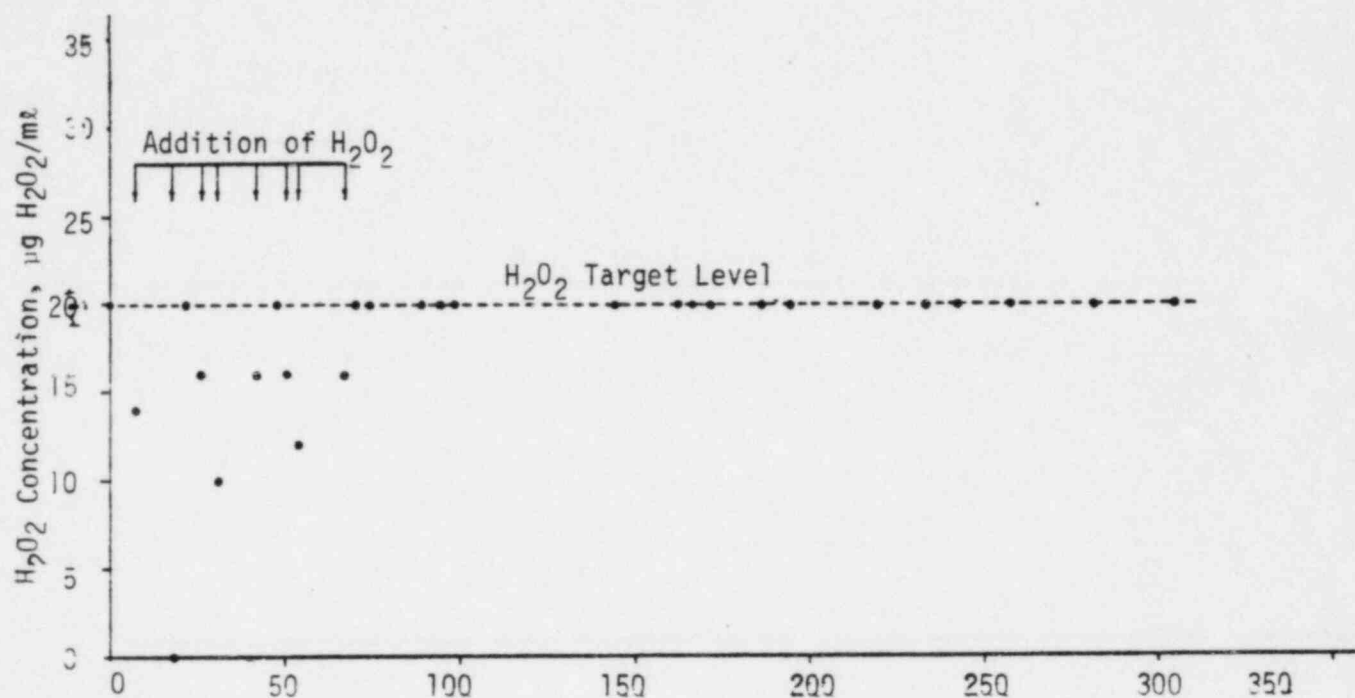


FIGURE 15. HYDROGEN PEROXIDE AND SULFATE CONCENTRATIONS AS A FUNCTION OF REACTION TIME FOR IMMUNOL RUN-2 OF pH 8 AND 130°F (IMMUNOL TREATED TUBE SAMPLE).

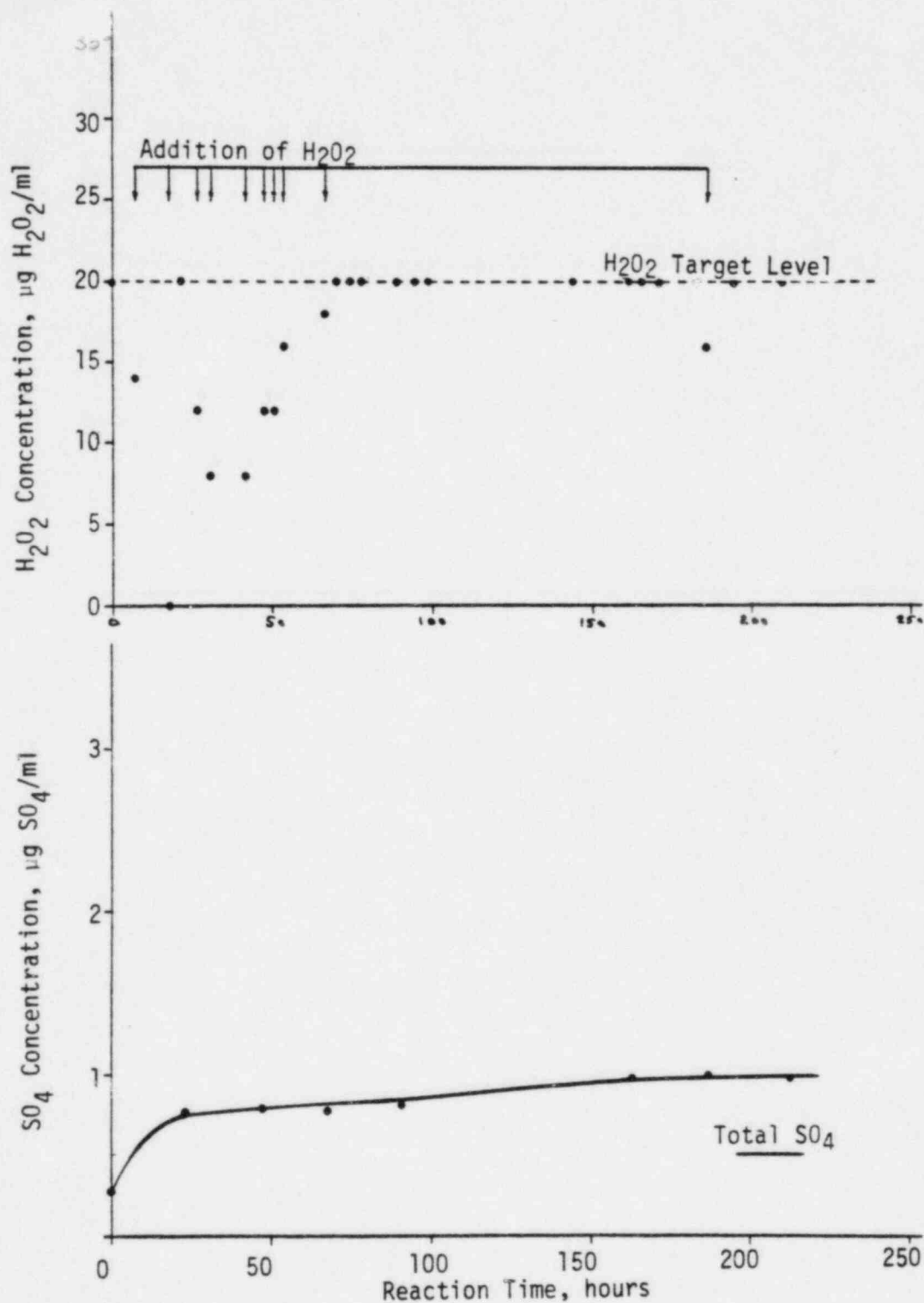


FIGURE 16. HYDROGEN PEROXIDE AND SULFATE CONCENTRATIONS AS A FUNCTION OF REACTION TIME FOR IMMUNOL RUN-3 AT pH 8 AND 130°F (IMMUNOL TREATED TUBE SAMPLE).

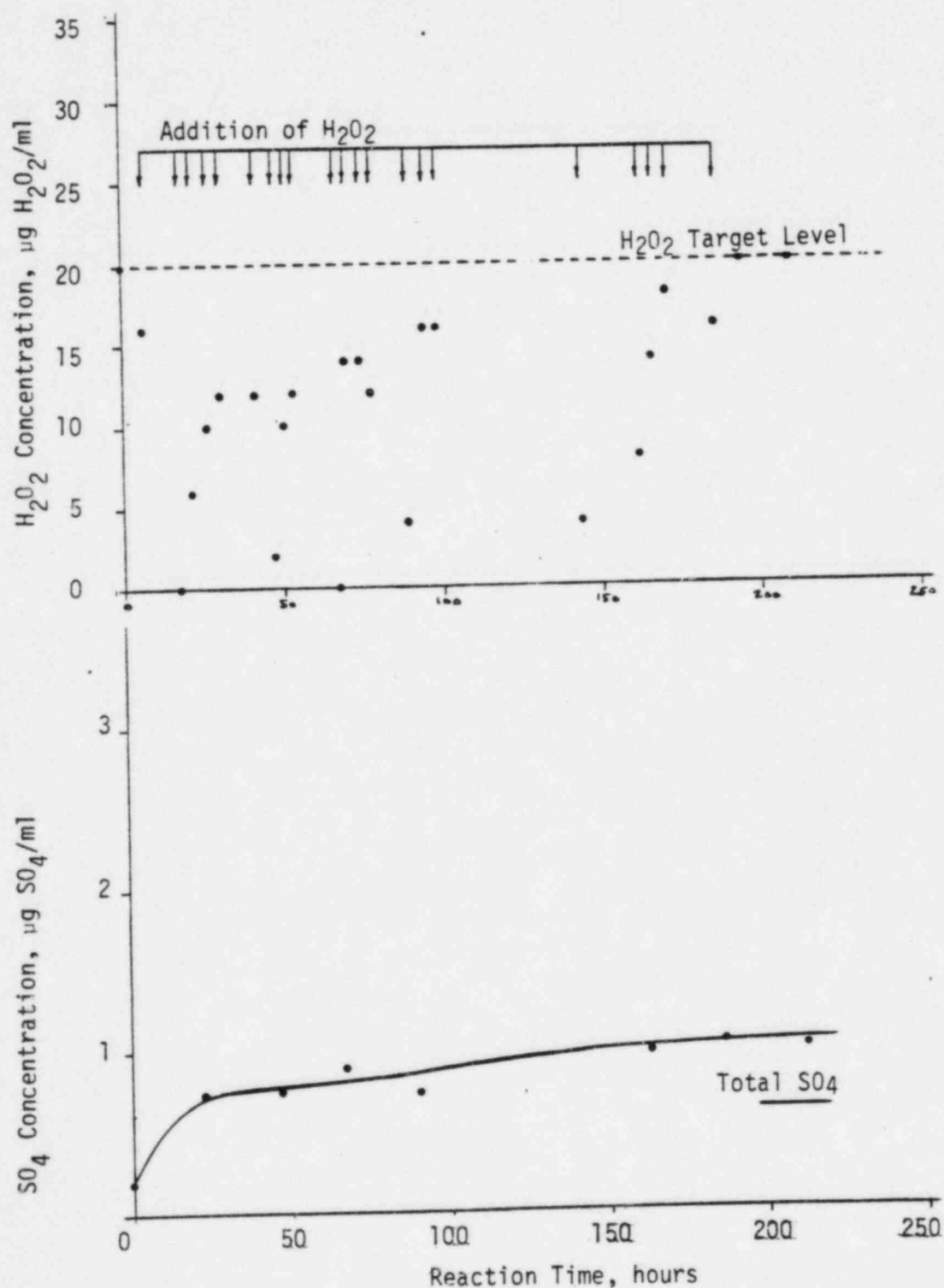


FIGURE 17. HYDROGEN PEROXIDE AND SULFATE CONCENTRATIONS AS A FUNCTION OF REACTION TIME FOR IMMUNOL RUN-4 AT pH8 AND 130°F (UNTREATED TUBE SAMPLE).

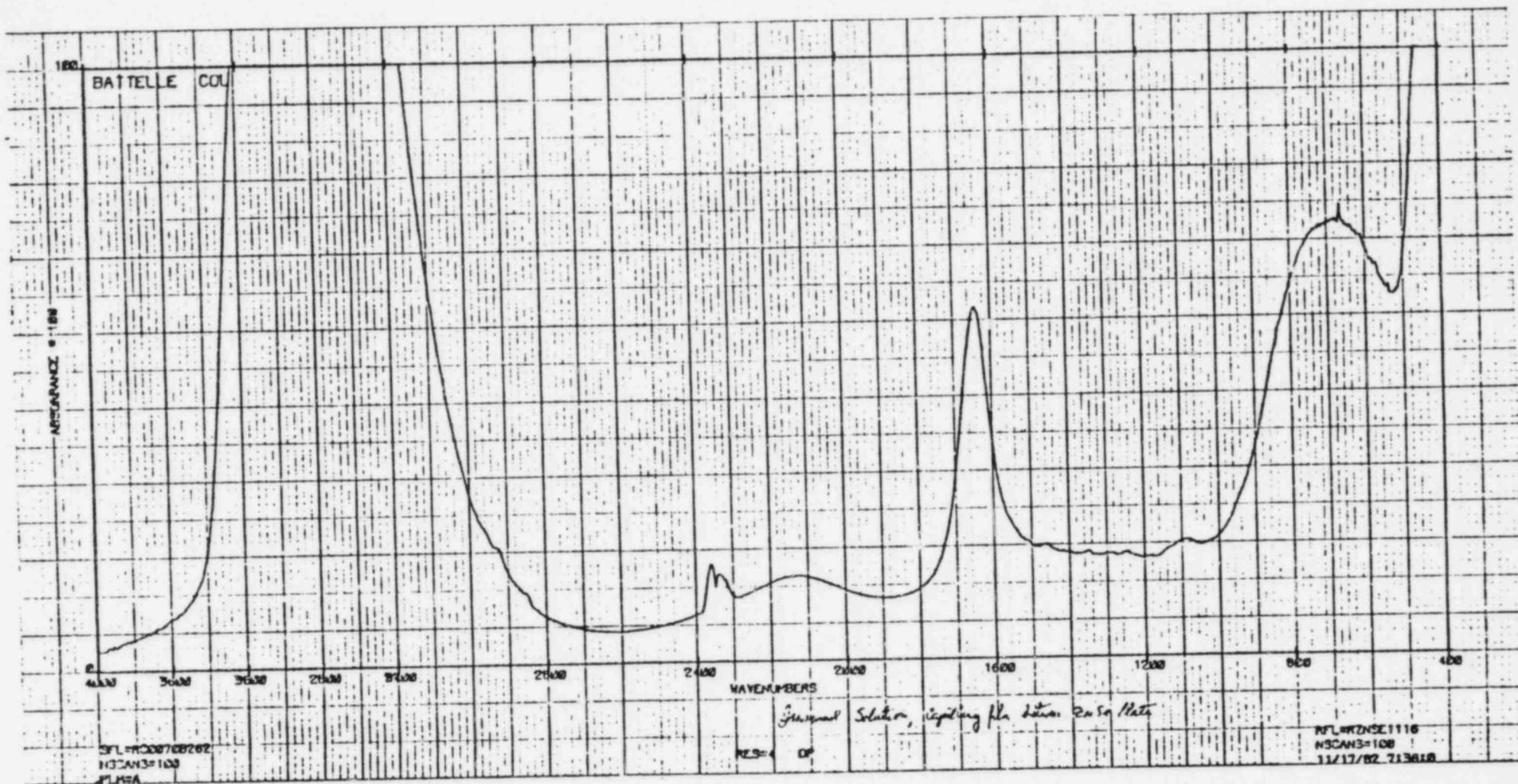


FIGURE 18. INFRARED TRANSMISSION SPECTRUM OF DYED IMMUNOL SOLUTION LOT B-2-62 (THIS MATERIAL USED TO PREPARE TUBE SAMPLES SUPPLIED TO BATTELLE BY B&W).

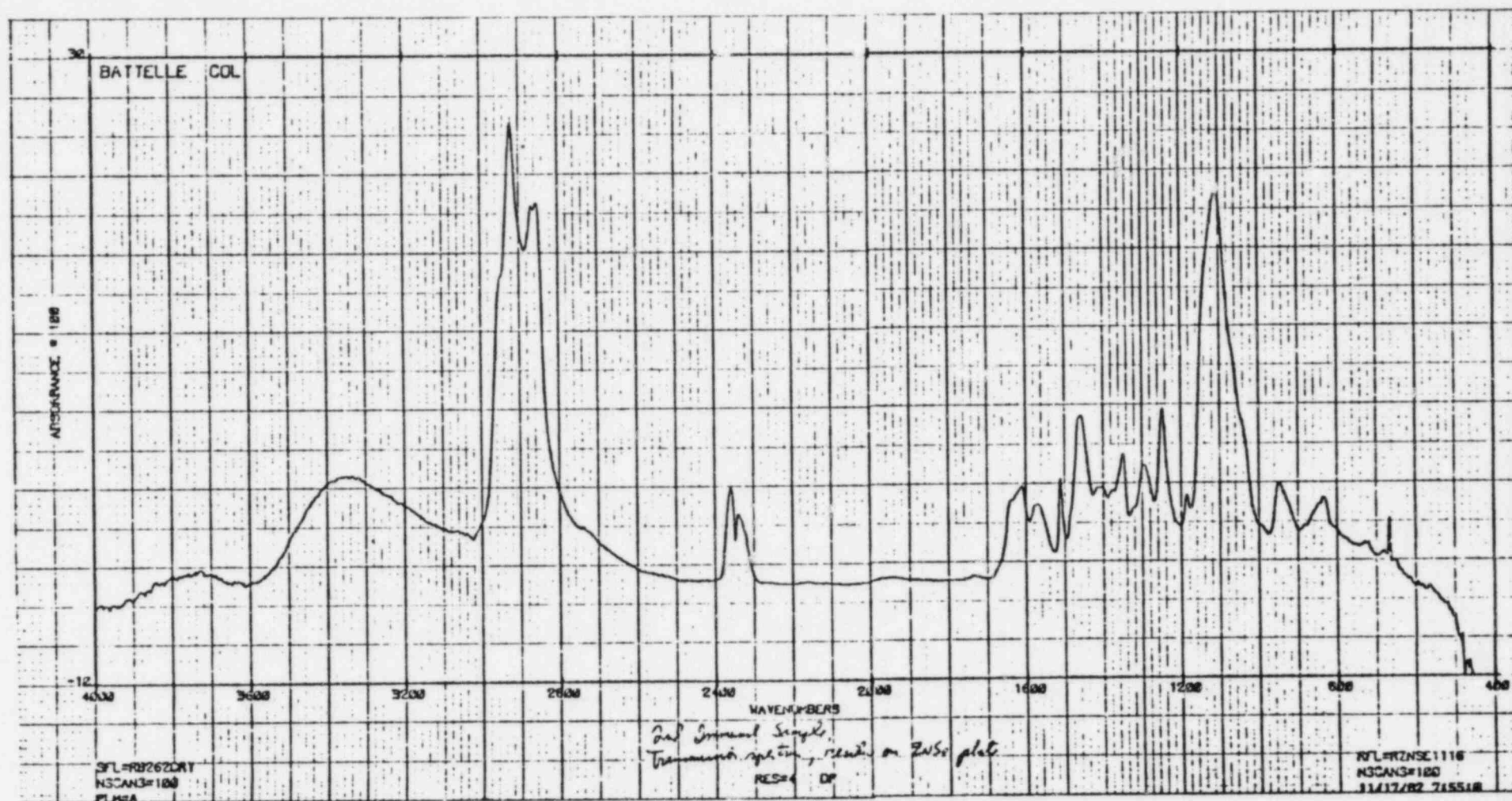


FIGURE 19. INFRARED TRANSMISSION SPECTRUM FOR RESIDUE FROM DYED IMMUNOL LOT NO. B-2-62. SAMPLES EVAPORATED ON ZeSe PLATE. (THIS MATERIAL USED TO PREPARE TUBE SAMPLES SUPPLIED TO BATTELLE BY B&W).

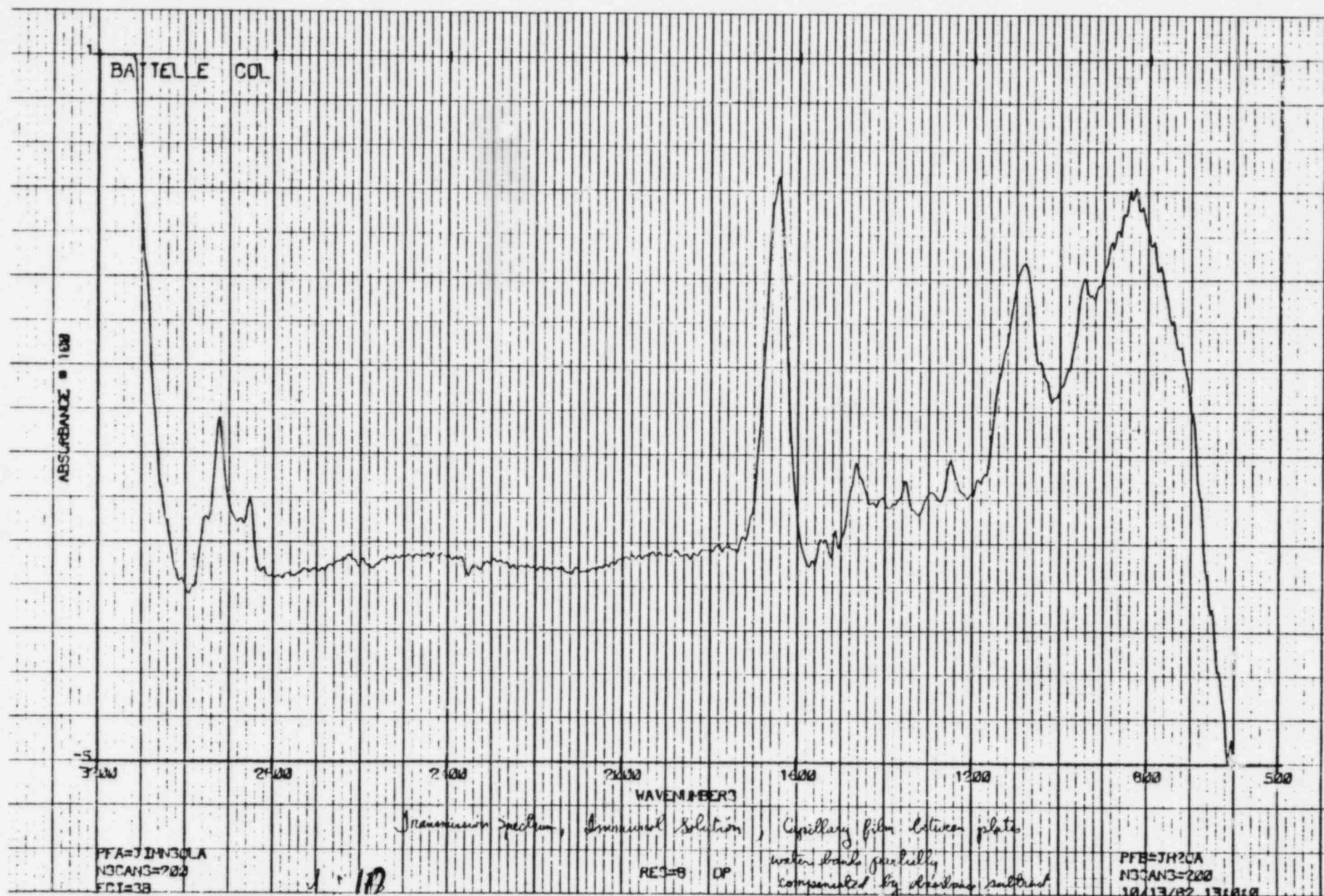


FIGURE 20. INFRARED TRANSMISSION SPECTRUM OF DYED IMMUNOL SOLUTION LOT NO. B-46-99 (THIS MATERIAL SUPPLIED TO BATTELLE BY SANDY POTTERTON OF B&W).

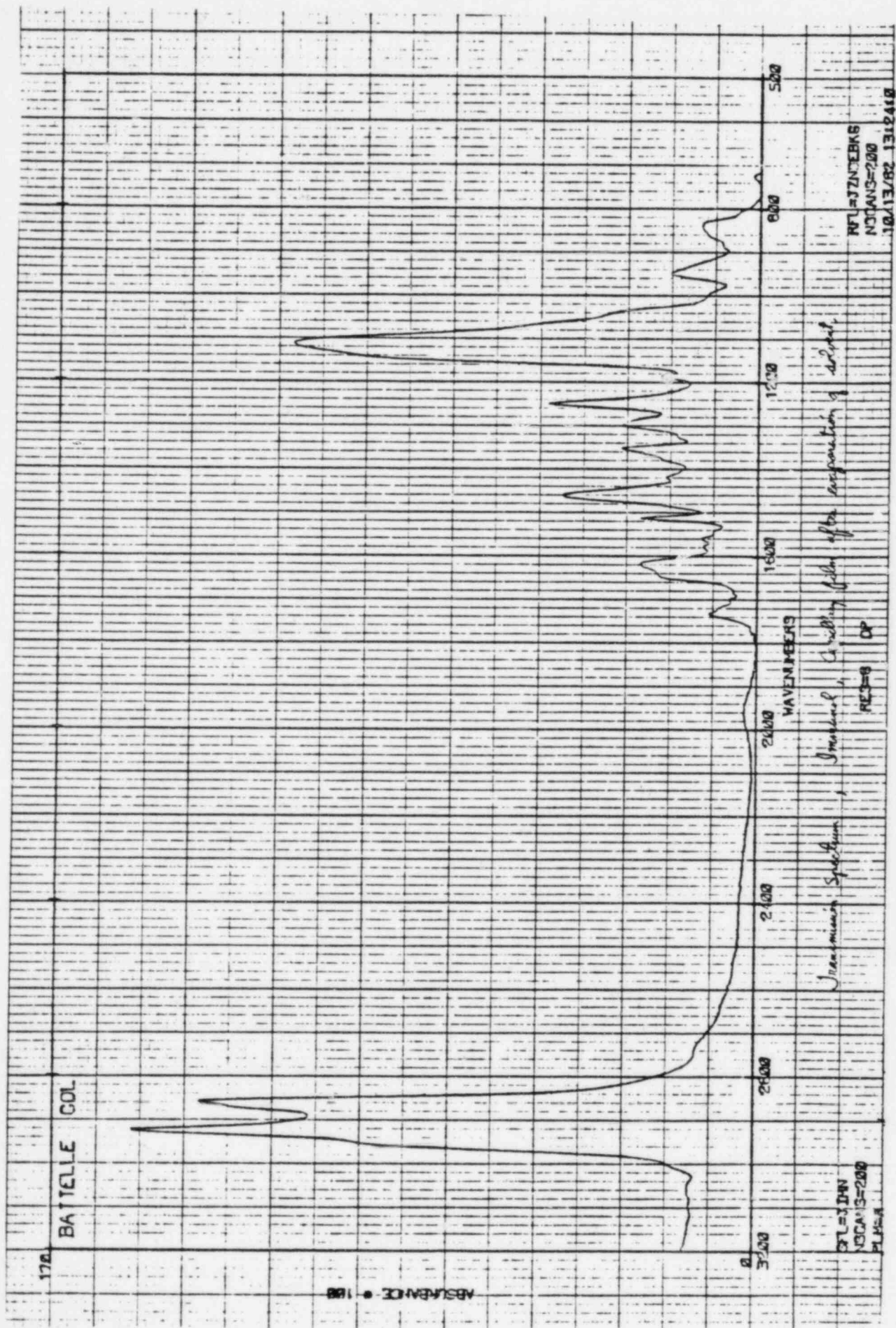


FIGURE 21. INFRARED TRANSMISSION SPECTRUM FOR RESIDUE FROM DYED IMMUNOL LOT NO. B-46-99. SAMPLE EVAPORATED ON ZeSe PLATE. (THIS MATERIAL SUPPLIED TO BATTELLE BY SANDY POTTERTON OF B&W).

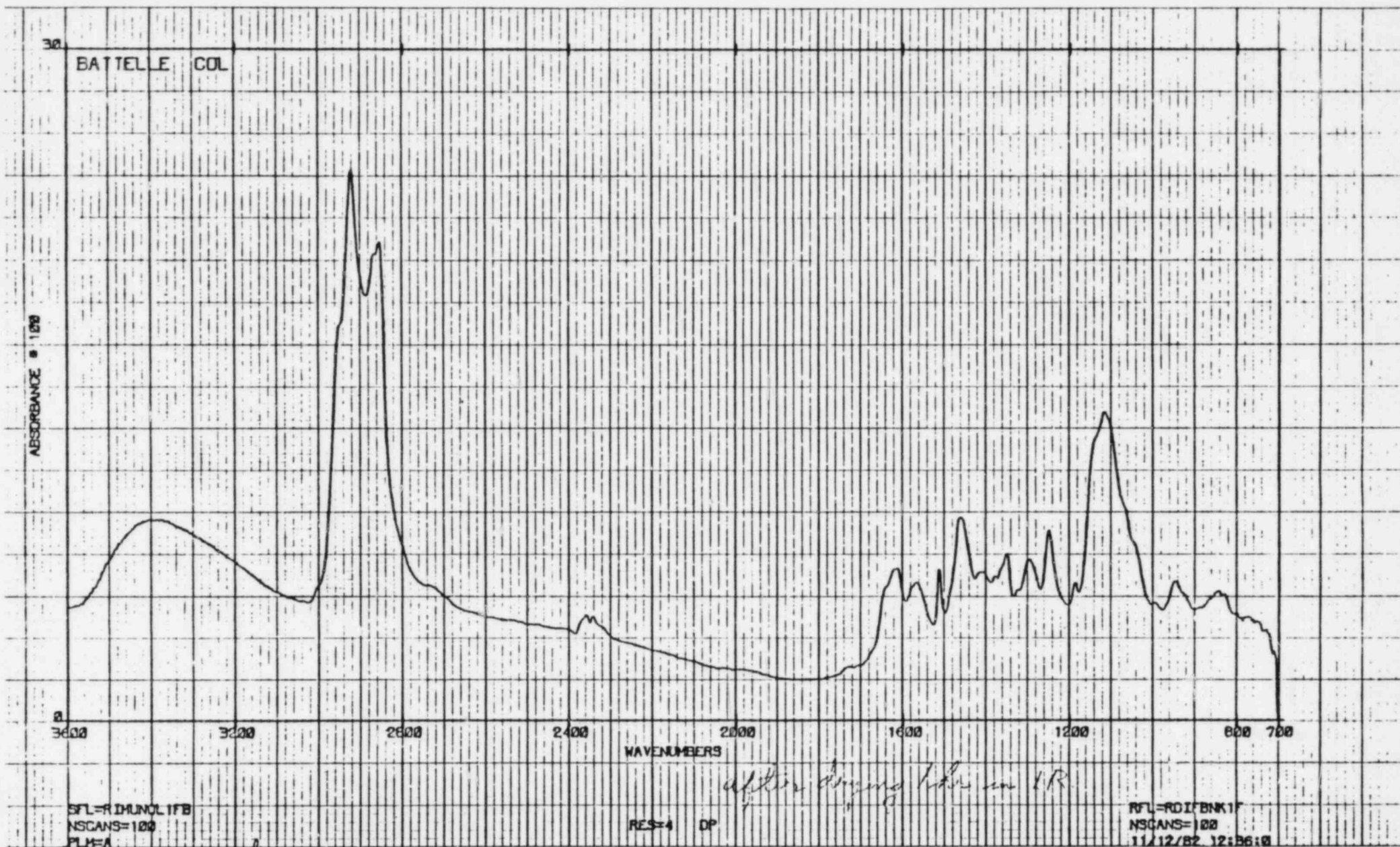


FIGURE 22. INFRARED DIFFUSE REFLECTANCE SPECTRUM FOR DYED IMMUNOL FILM (LOT NO. B-49-99) ON INCONEL-600 SURFACE AFTER DRYING FILM FOR 1 HOUR WITH INFRARED HEAT LAMP (THIS MATERIAL SUPPLIED TO BATTELLE BY SANDY POTTERTON OF B&W).

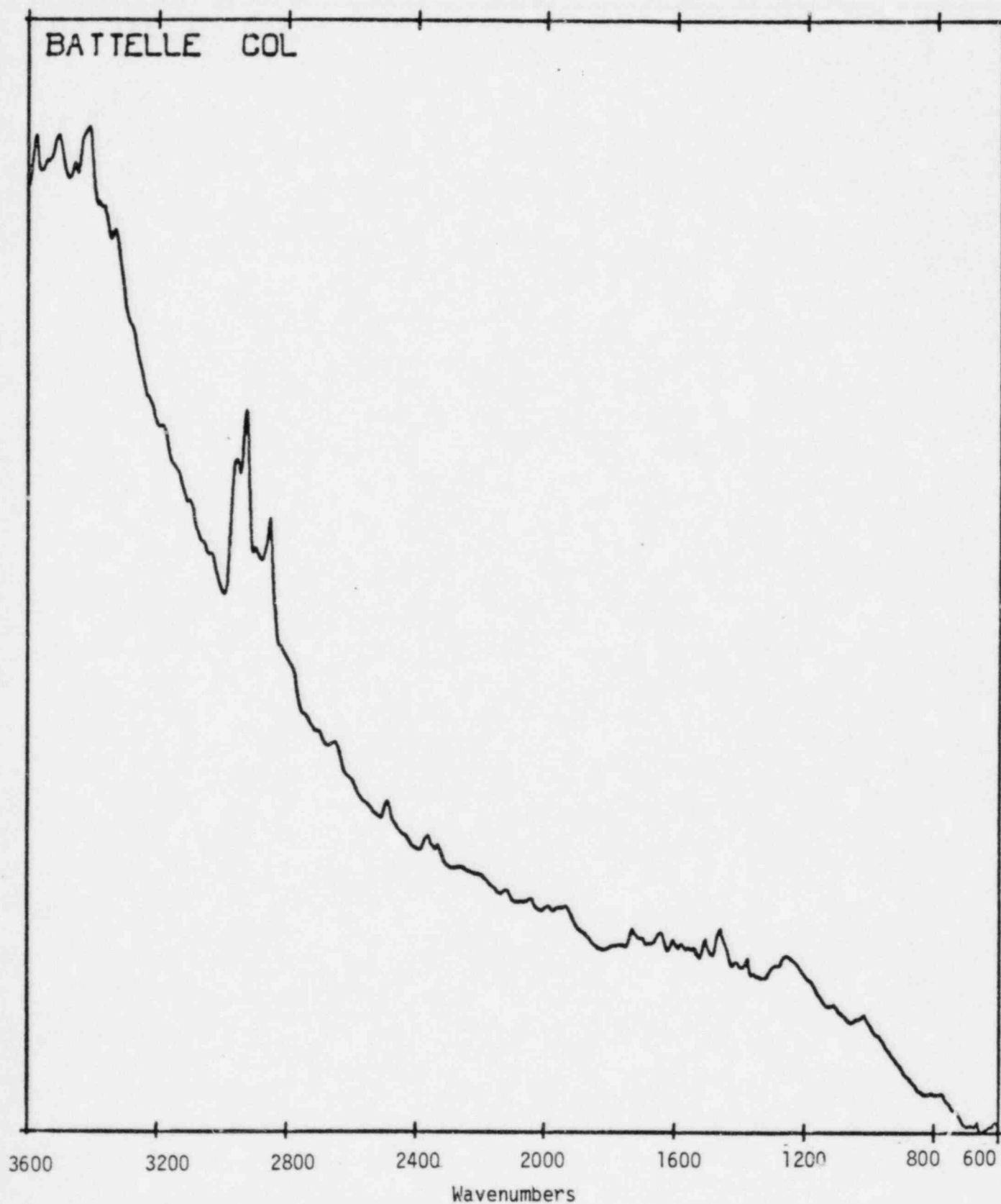


FIGURE 23. INFRARED DIFFUSE REFLECTANCE SPECTRUM FOR ID SURFACE OF TUBE SAMPLE 3-1 AFTER PEROXIDE CLEANING (IMMUNOL RUN-1).

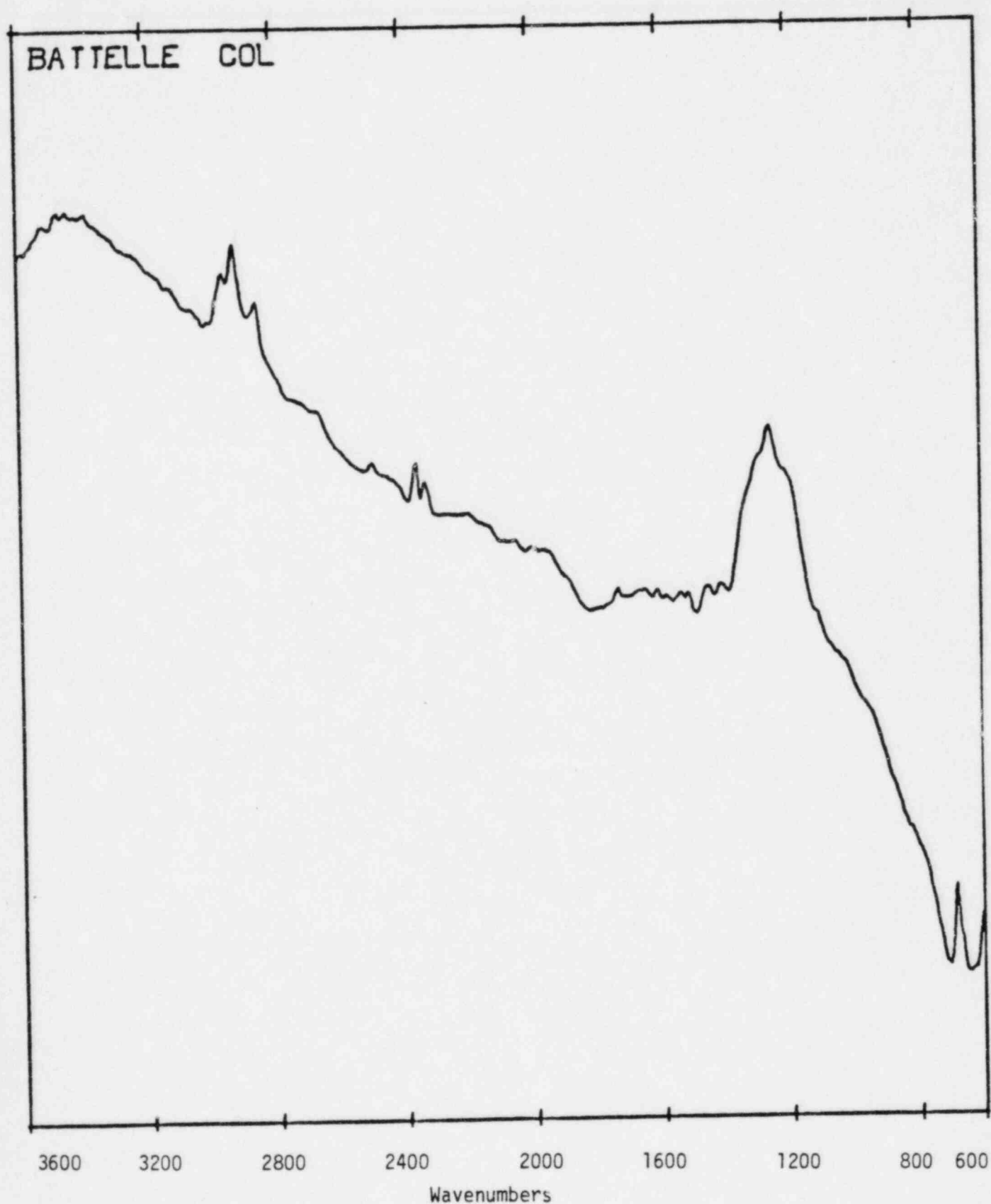


FIGURE 24. INFRARED DIFFUSE REFLECTANCE SPECTRUM FOR DARK SPOT ON ID SURFACE OF TUBE SAMPLE 3-3 AFTER PEROXIDE CLEANING (IMMUNOL RUN-1).

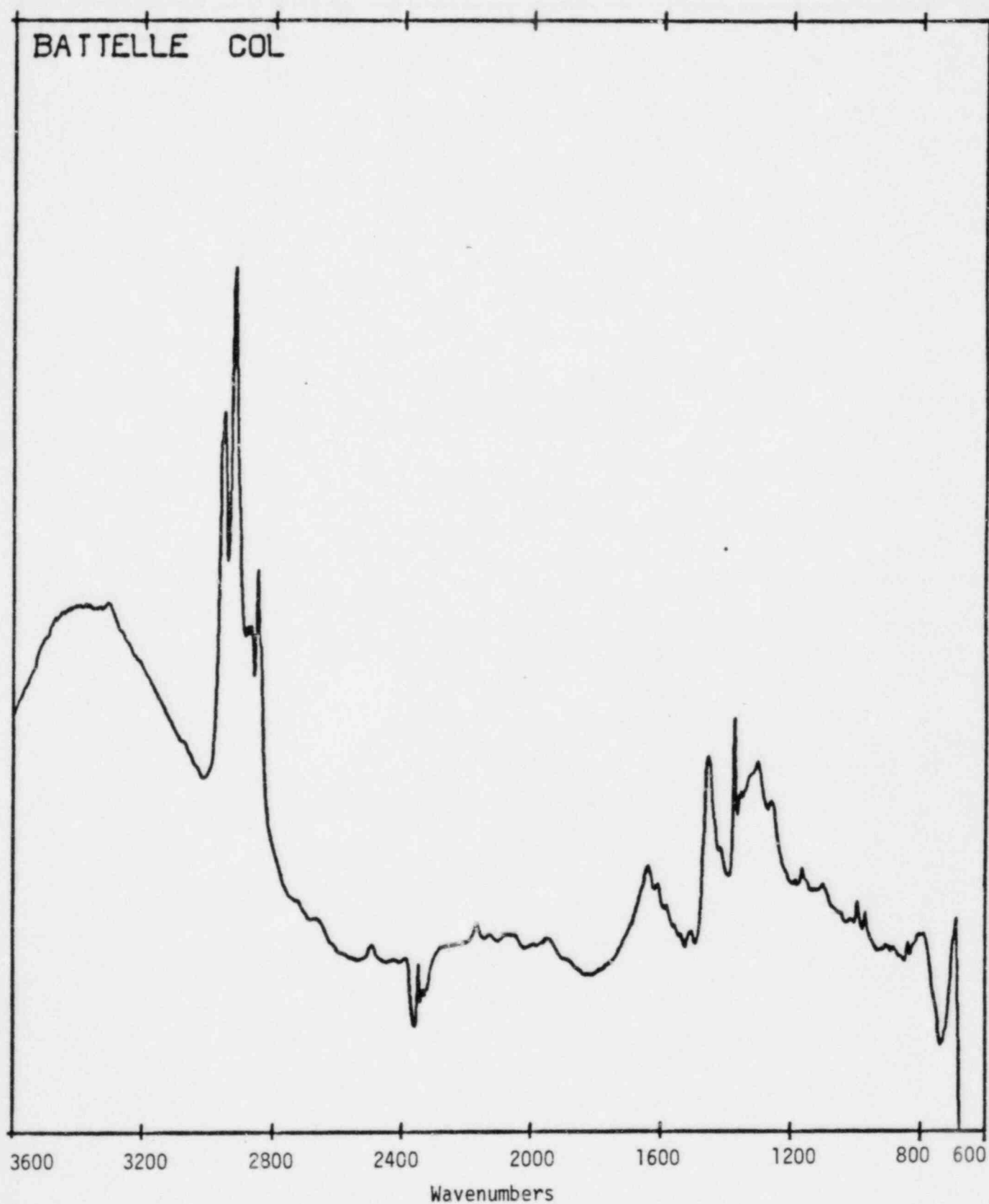


FIGURE 25a. INFRARED DIFFUSE REFLECTANCE SPECTRUM FOR UNCLEARED ID SURFACE OF SAMPLE FROM PIECE 4 OF TUBE NO. AS 111-13.

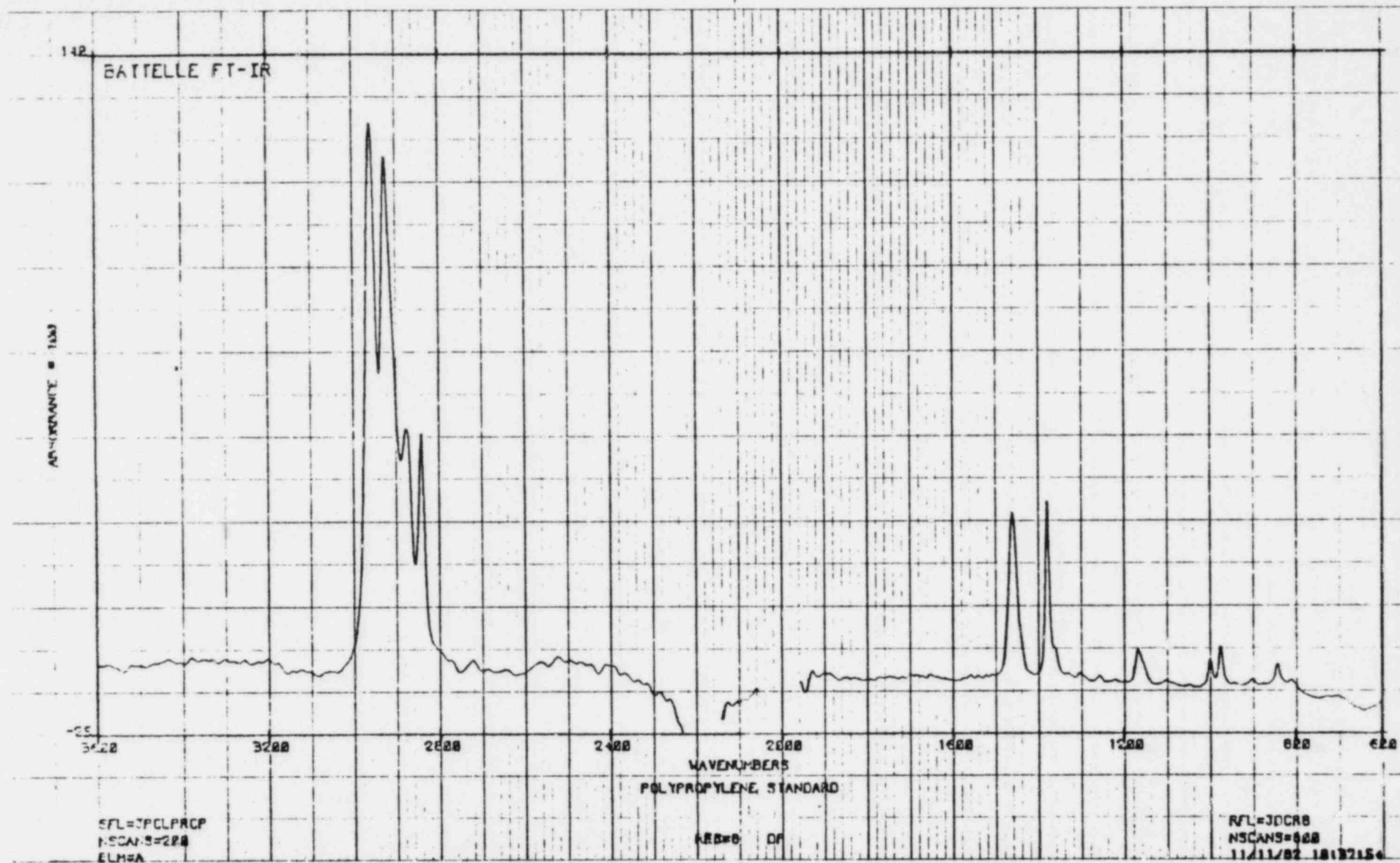


FIGURE 25b. INFRARED TRANSMISSION SPECTRUM FOR POLYPROPYLENE STANDARD

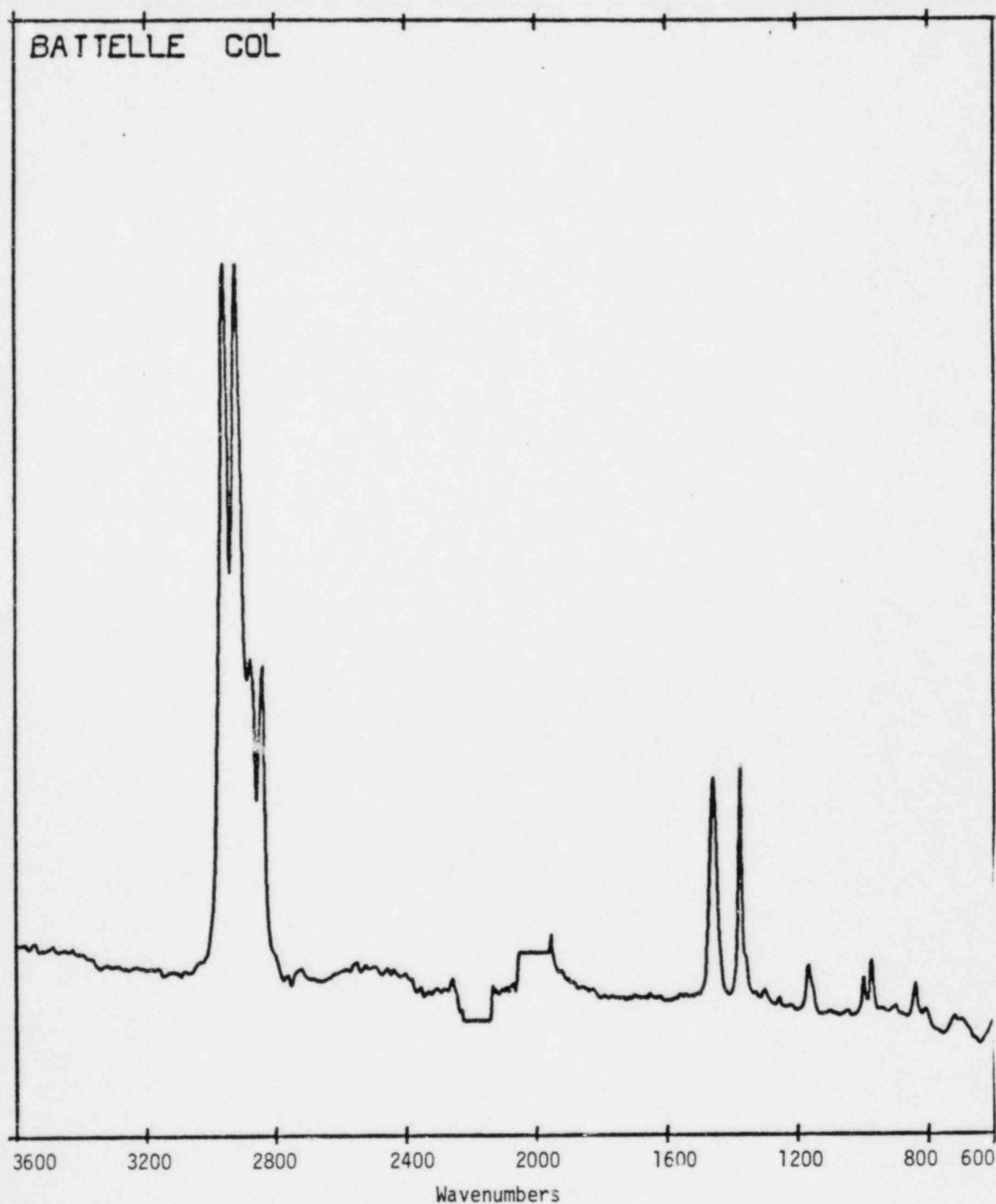


FIGURE 26. INFRARED TRANSMISSION SPECTRUM FOR PARTICLE REMOVED FROM ID SURFACE OF  
PIECS 4 FROM TUBE NO. A 111-13.

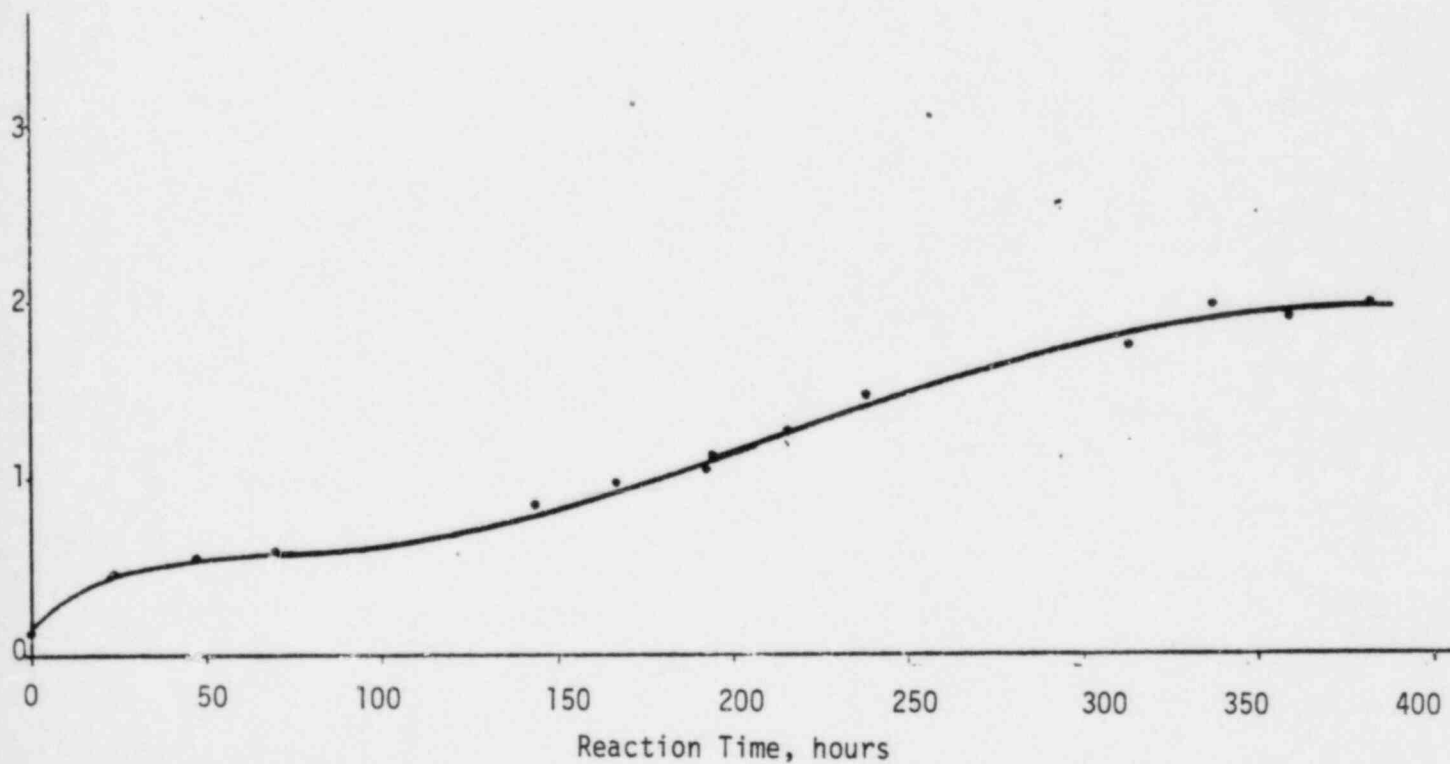
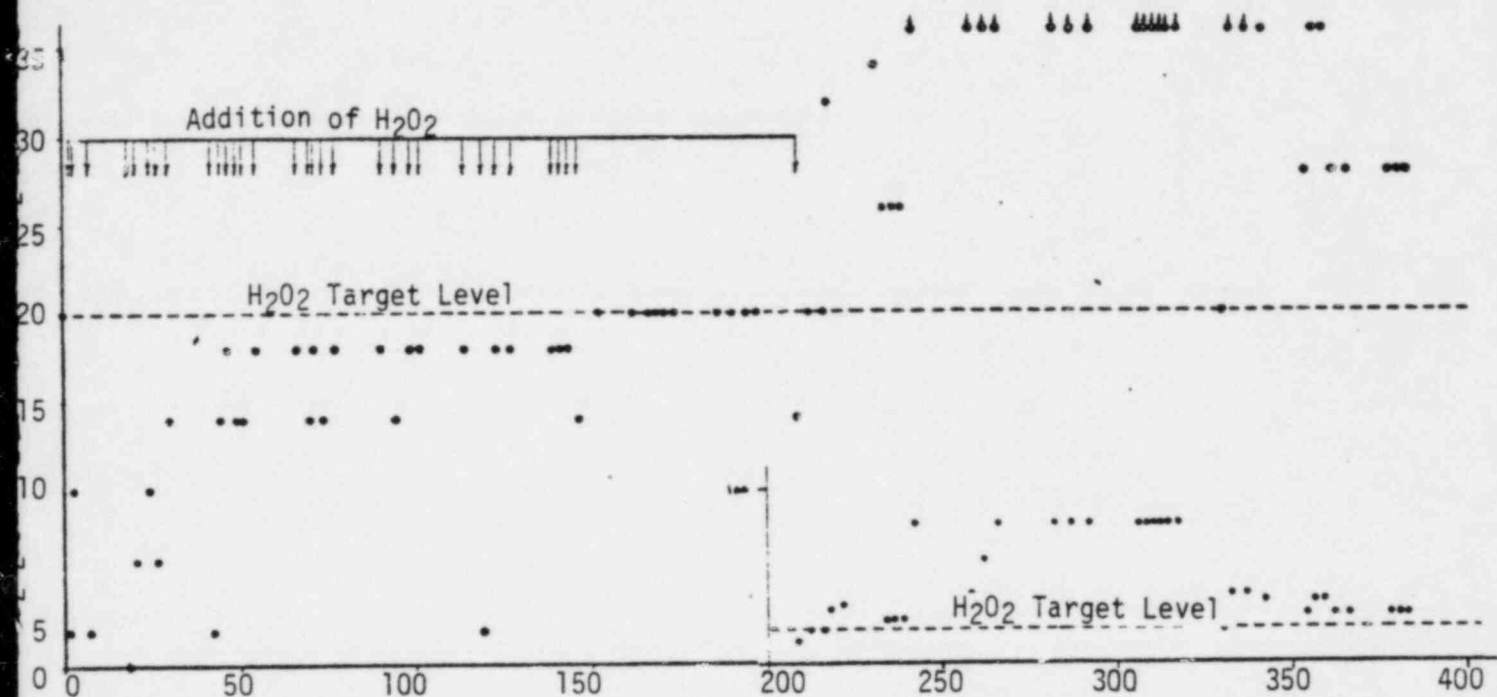


FIGURE 27. HYDROGEN PEROXIDE AND SULFATE CONCENTRATIONS AS A FUNCTION OF REACTION TIME FOR IMMUNOL EXPANSION RUN-1 AT pH8 AND 130°F (UNTREATED TUBE SAMPLE 14 in. FROM EXPANSION TRANSITION ZONE).

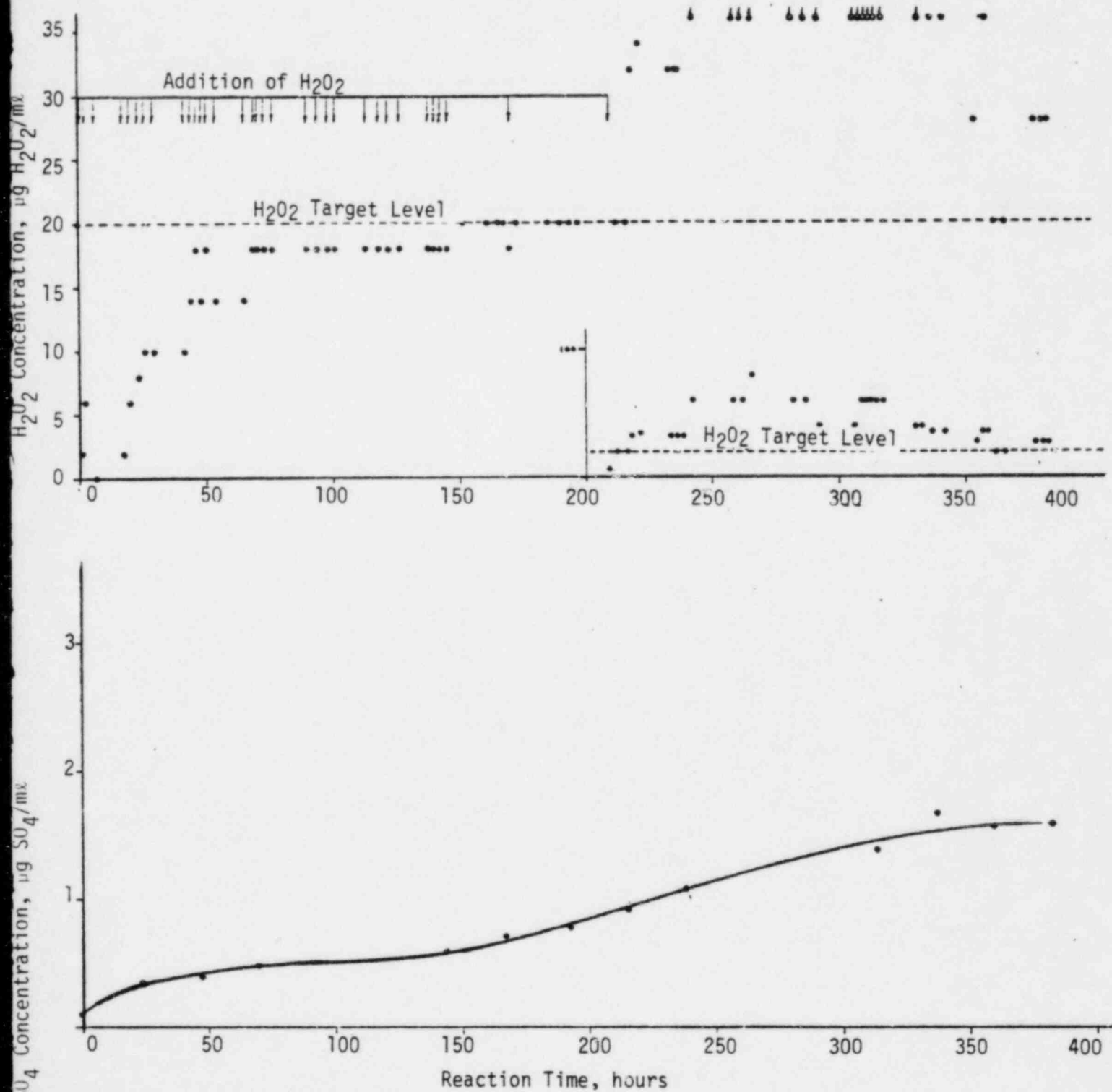


FIGURE 28. HYDROGEN PEROXIDE AND SULFATE CONCENTRATIONS AS A FUNCTION OF REACTION TIME FOR IMMUNOL EXPANSION RUN-2 AT pH8 AND 130°F (UNTREATED TUBE SAMPLE FROM EXPANSION TRANSITION ZONE).

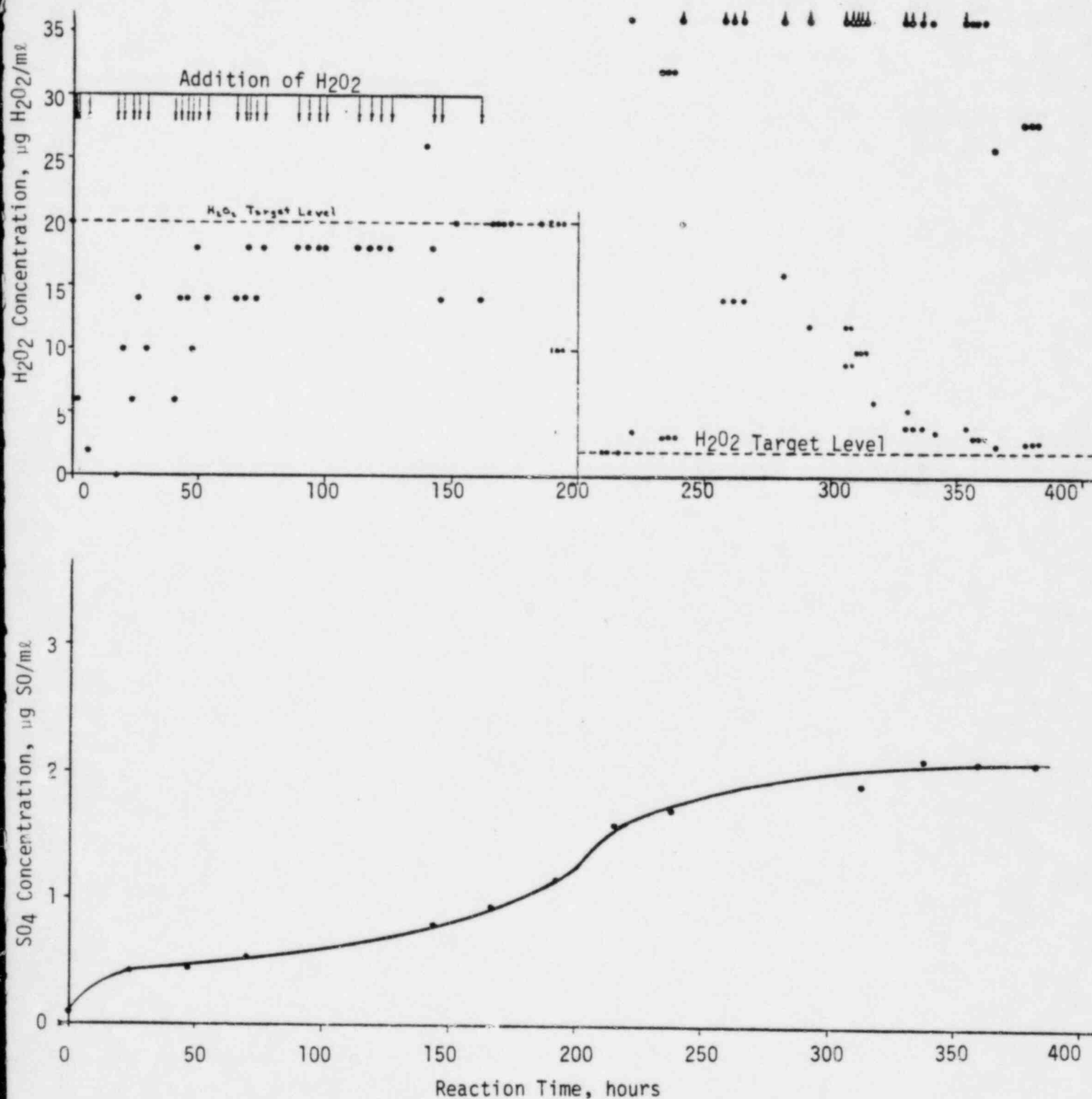


FIGURE 29. HYDROGEN PEROXIDE AND SULFATE CONCENTRATIONS AS A FUNCTION OF REACTION TIME FOR IMMUNOL EXPANSION RUN-3 AT pH8 AND 130°F (IMMUNOL TREATED TUBE SAMPLE 14 in. FROM EXPANSION TRANSITION ZONE).

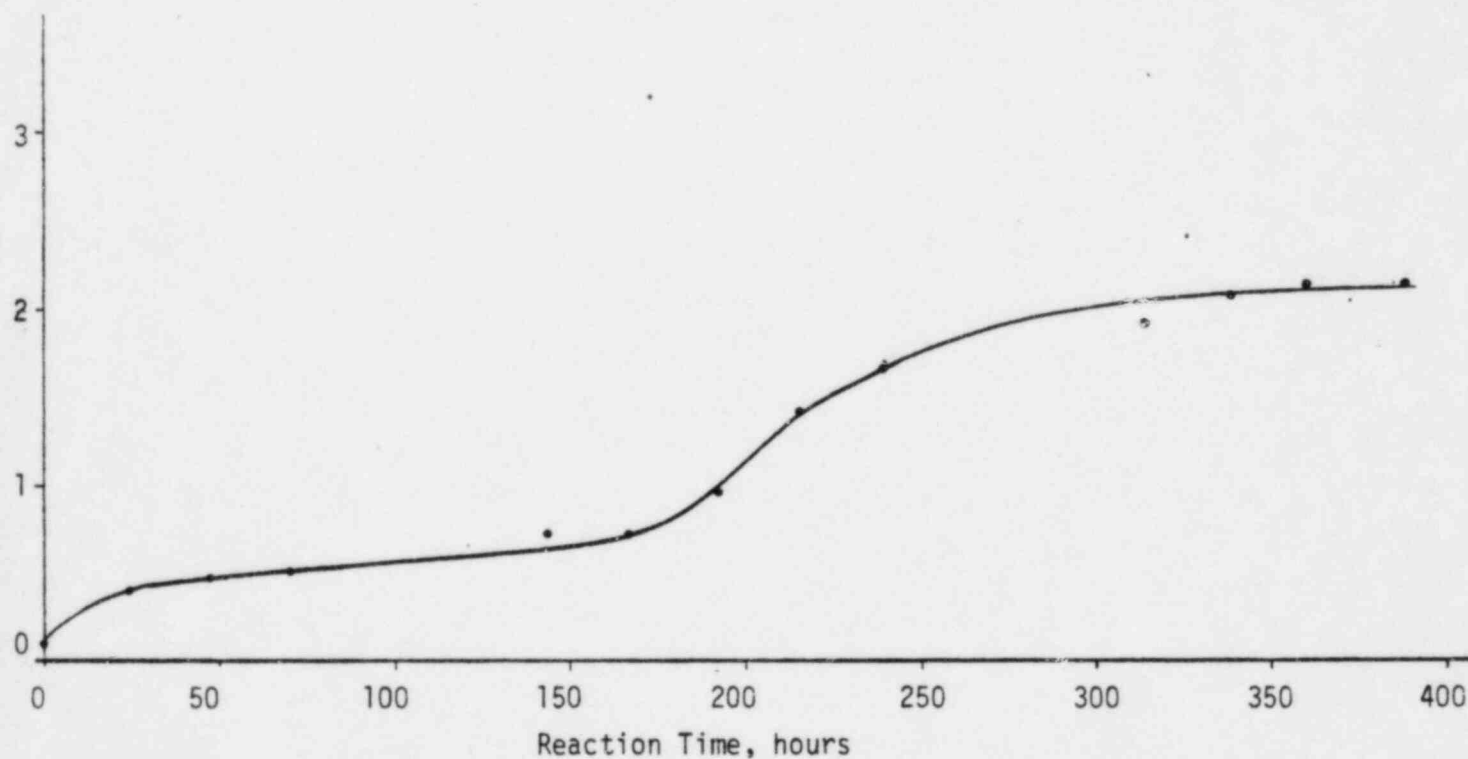
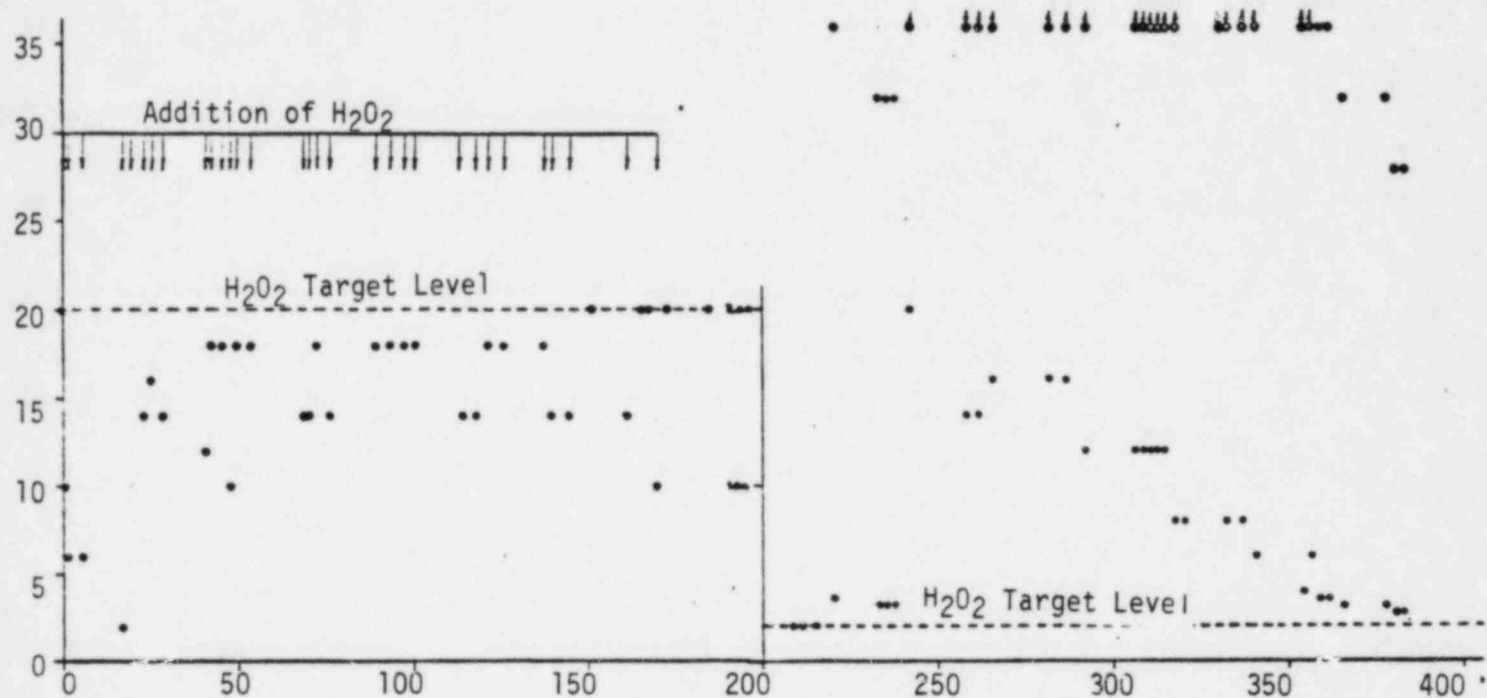


FIGURE 30. HYDROGEN PEROXIDE AND SULFATE CONCENTRATIONS AS A FUNCTION OF REACTION TIME FOR IMMUNOL EXPANSION RUN-4 AT pH8 and 130°F (IMMUNOL TREATED TUBE SAMPLE FROM EXPANSION TRANSITION ZONE).

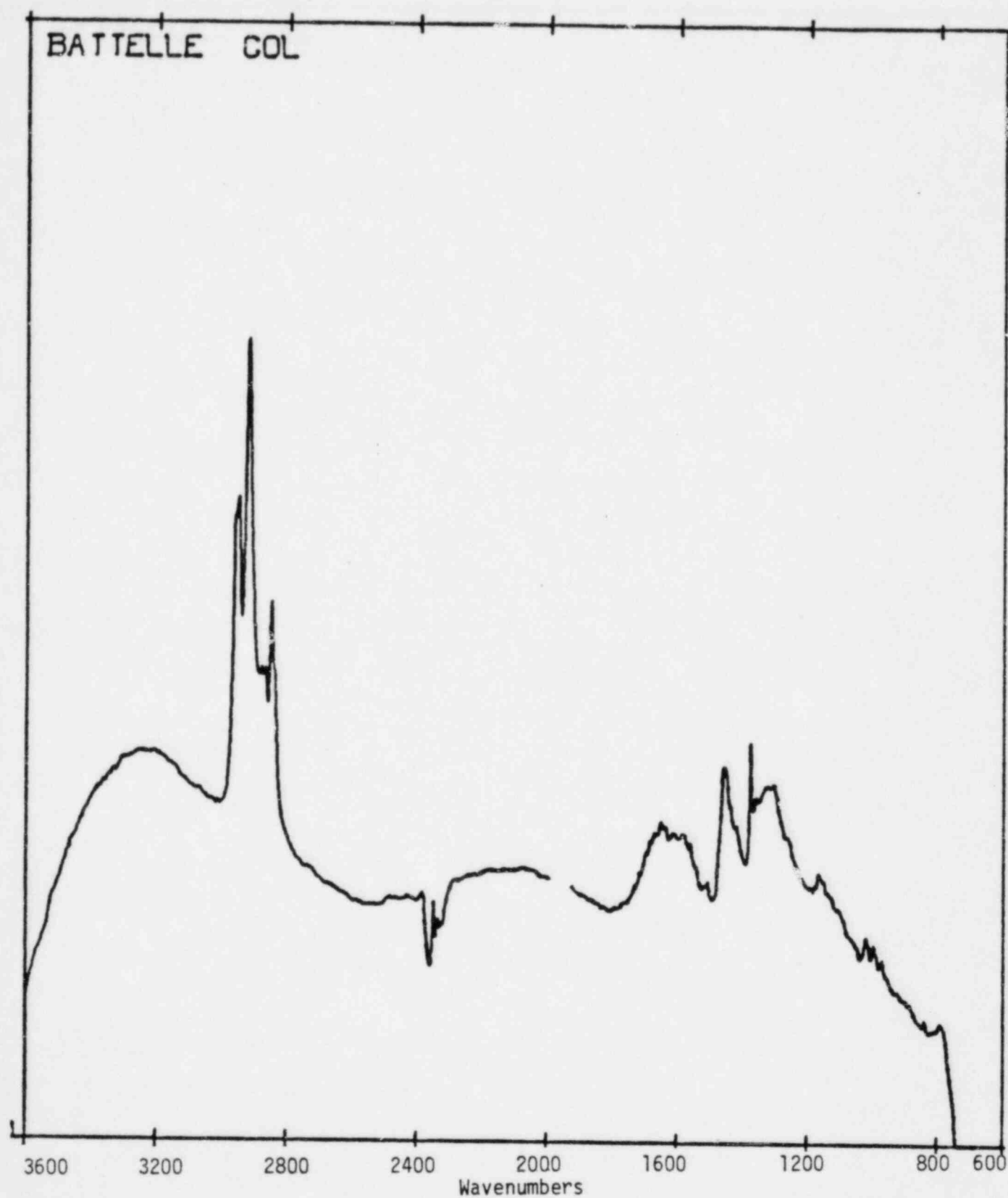


FIGURE 31. INFRARED DIFFUSE REFLECTANCE SPECTRUM FOR SAMPLE NO. 2-10 AFTER PEROXIDE CLEANING (IMMUNOL EXPANSION RUN-2).

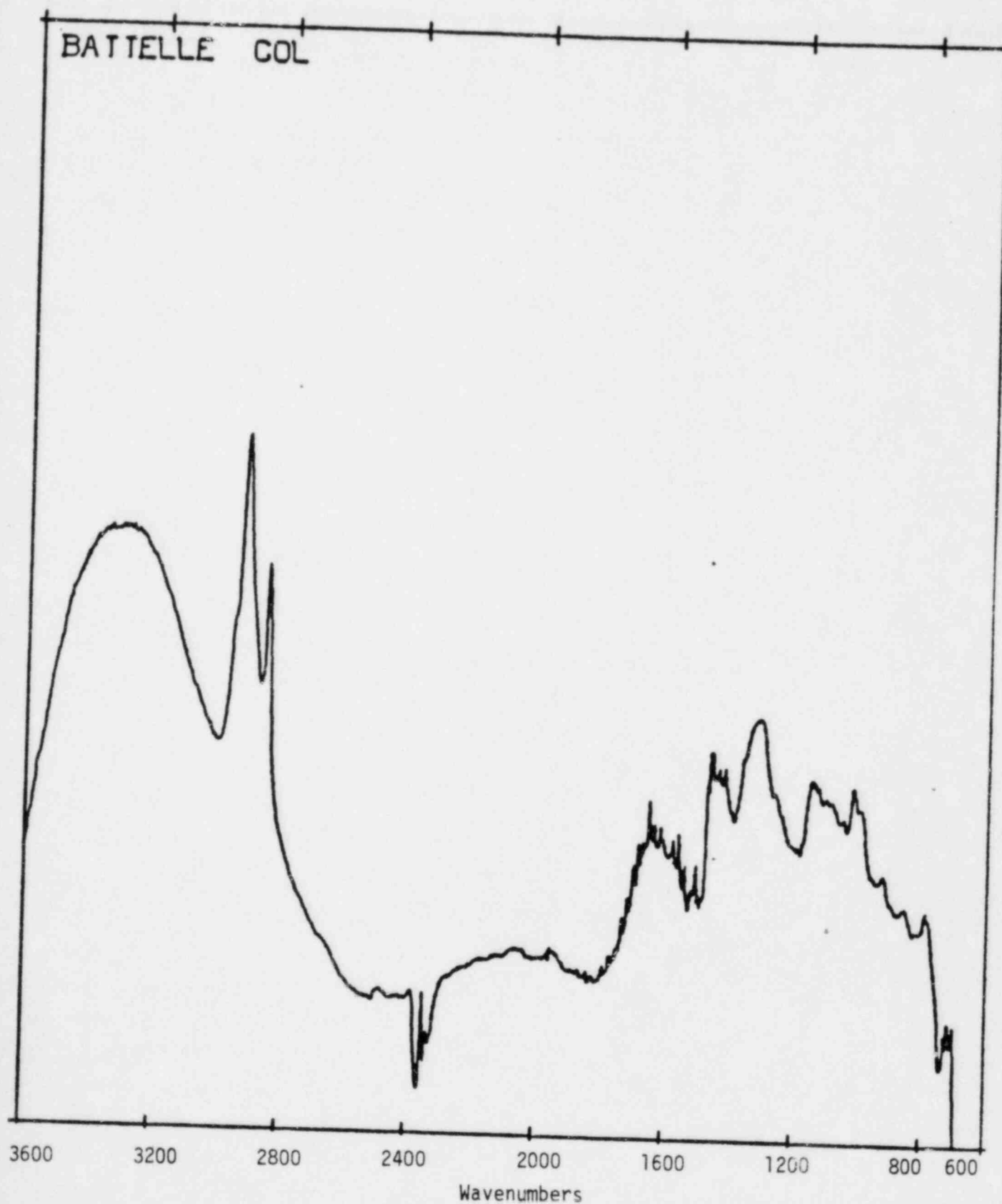


FIGURE 32. INFRARED DIFFUSE REFLECTANCE SPECTRUM FOR SAMPLE NO. 2-2 AFTER PEROXIDE CLEANING (IMMUNOL EXPANSION RUN-1).

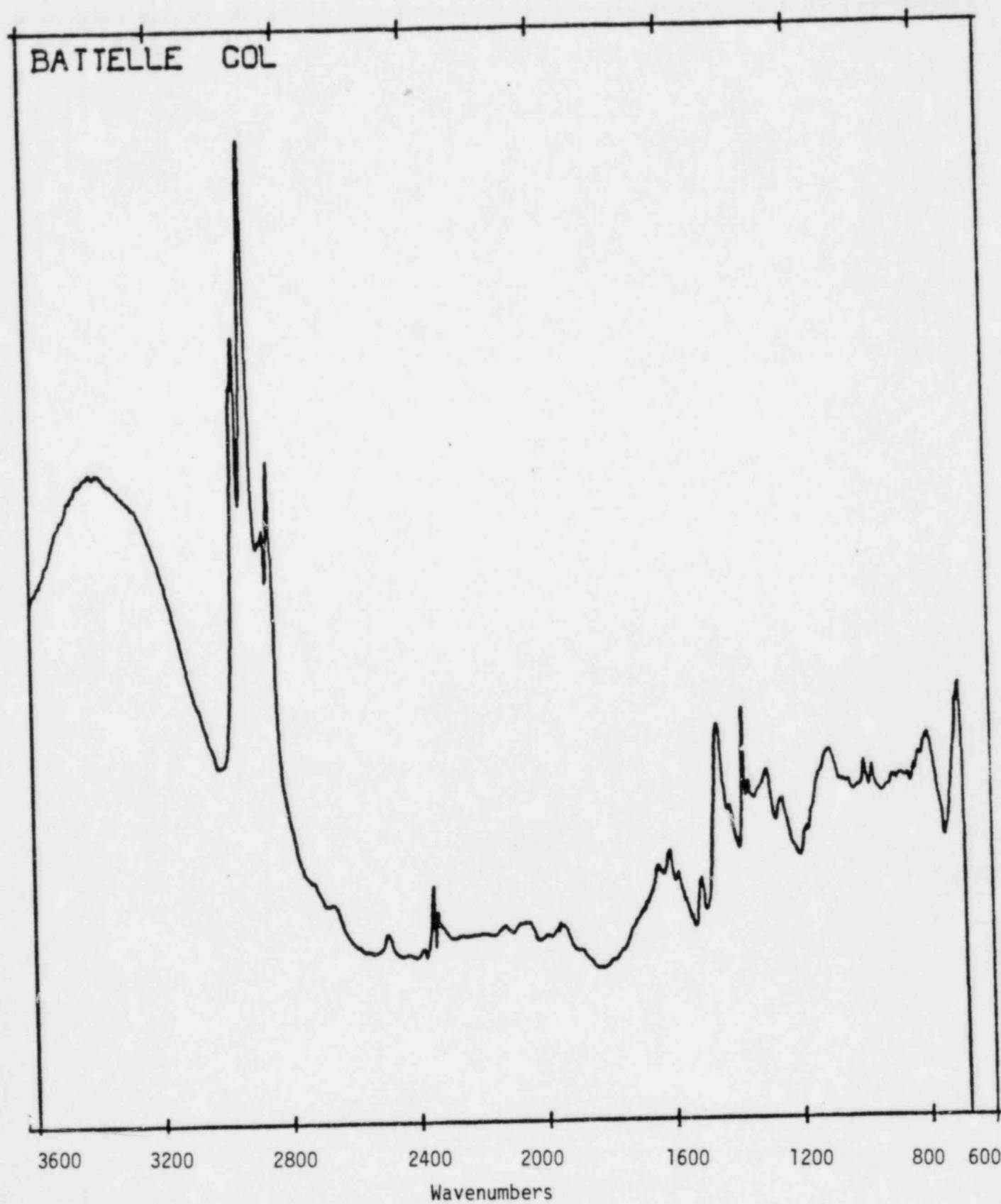


FIGURE 33. INFRARED DIFFUSE REFLECTANCE SPECTRUM FOR UNCLEARED SAMPLE NO. 5-7.

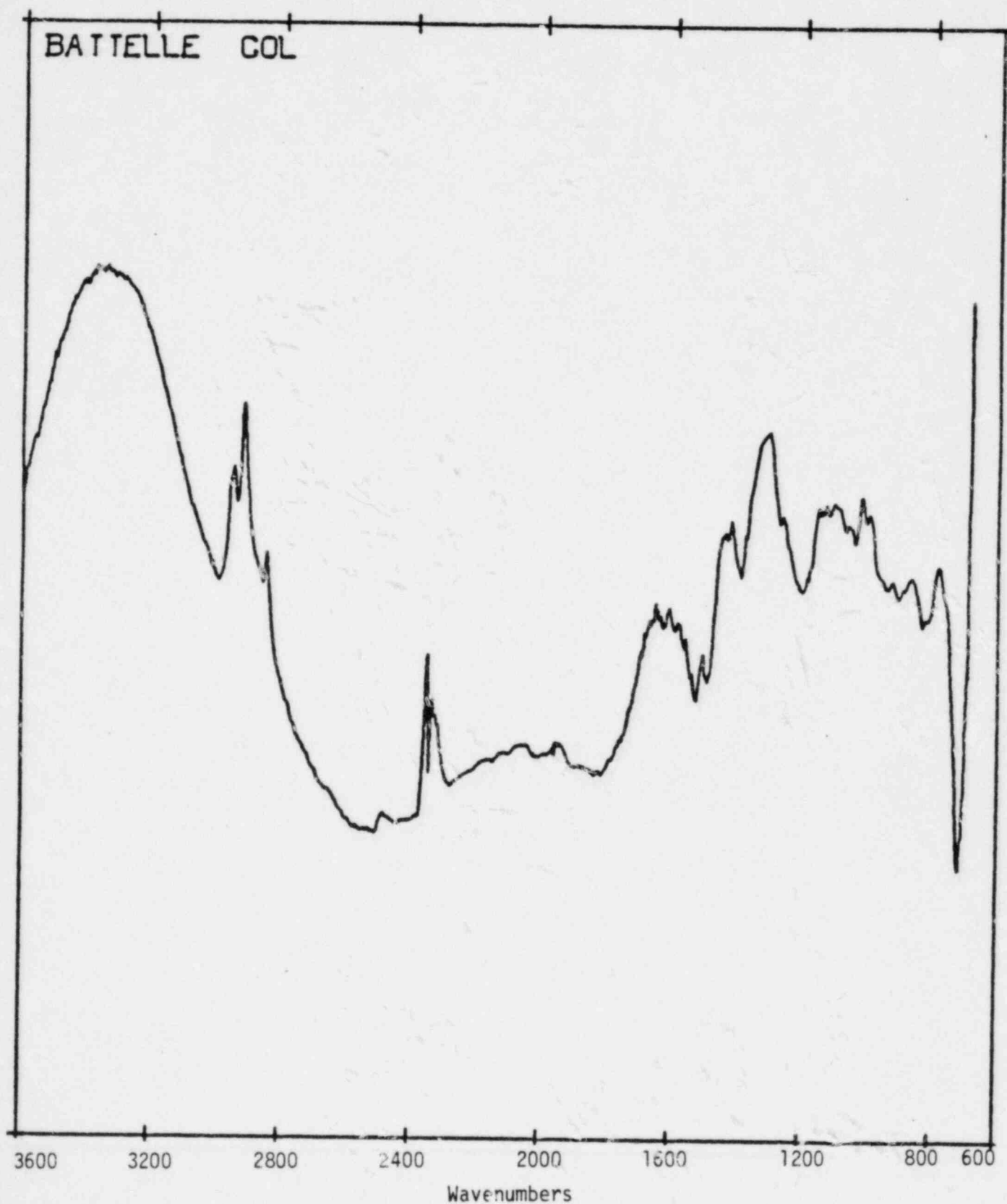


FIGURE 34. INFRARED DIFFUSE REFLECTANCE SPECTRUM FOR SAMPLE NO. 5-2 AFTER PEROXIDE CLEANING (IMMUNOL EXPANSION RUN-3).

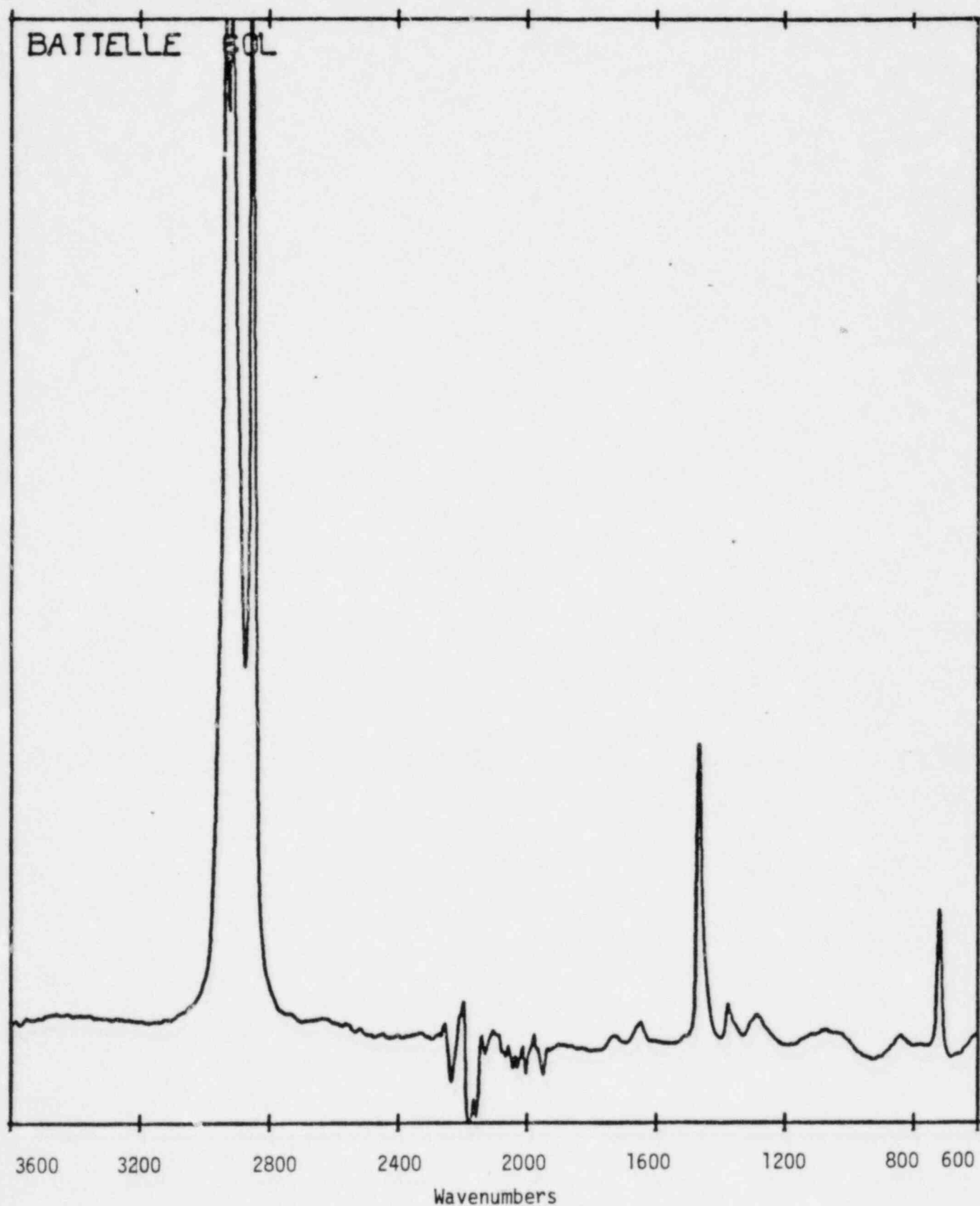


FIGURE 35. INFRARED TRANSMISSION SPECTRUM OF POLYETHYLENE PARTICLE REMOVED FROM ID SURFACE OF SAMPLE NO. 5-10 BEFORE CLEANING.

## PRELIMINARY CONCLUSIONS

Results from the tube cleaning experiments are summarized below:

### TUBE CLEANING SERIES 1

These samples were in the same condition as when they were removed from the TMI-1 steam generator.

- Sulfate production leveled off after approximately 150 hours.
- Total sulfur analyses and SFM/EDAX examinations indicate nearly complete removal of sulfur from tube samples.
- The results from the FTIR diffuse reflectance measurement showed a small amount of organic contamination on the ID surfaces of the tube samples, as evidenced by the CH<sub>2</sub> and CH<sub>3</sub> bands at 2925 and 2960 cm<sup>-1</sup>, respectively.
- There appeared to be no difference in cleaning rate between pH 8 and pH 10.

### TUBE CLEANING SERIES 2

These tests involved Immulon treated and untreated TMI-1 tube samples that had been exposed to debris from the explosive expansion process. These tube sections were connected to the expanded tube during the explosive expansion by means of a Swagelok fitting containing a restrictive orifice.

- Immulon treated tube samples in Run -3 gave the same sulfate production rate as the untreated samples in Run -4. Sulfate production appeared to be at completion after 50 hours. The Immulon treated tube samples from Run -1 and -2 followed roughly the same profiles as Run -3 and -4, except the sulfate started increasing again after about 150 hours and plateaued at about 230 hours.

- Hydrogen peroxide concentration was more stable for the Immunol treated samples.
- The infrared results showed that the tube samples not treated with Immunol retained a polypropylene material. The presence of the polypropylene did not appear to affect the peroxide cleaning process. Debris particles found on the tubes were identified as polypropylene. No evidence of Immunol on the sample surfaces were observed.
- Evaluation of SEM/EDAX and total sulfur data still in progress.

### TUBE CLEANING SERIES 3

The tubes used in this series of cleaning experiments were explosively expanded with and without Immunol treatment. Samples involved in these tests were from the expansion transition zone and from a distance about 14 inches from the transition zone.

- The sulfate concentration/time curves were essentially the same for all four beaker tests. The sulfate concentration leveled off after about 50 hours but increased again after about 150 hours, becoming constant after 330 hours.
- Hydrogen peroxide concentration levels as measured by the peroxide color test increased anomalously without any peroxide addition after about 200 hours, then decayed slowly to about 30 ppm by the end of the runs at 400 hours.
- SEM/EDAX and ESCA studies still in progress.
- The infrared results showed presence of polypropylene on tube sample ID surfaces. Debris particles were found to consist of both polyethylene and polypropylene. Analysis of spectra is continuing.

The detailed interpretation of the data covered in this report is still in progress, and along with additional data will be presented in the final report on this program. The additional data will also include another series of tube cleaning experiments. The tubes involved in the next series will be expanded tube samples with thicker Immunol coatings that are more representative of the coatings that will be used in the actual cleaning of the TMI-1 steam generator tubes. In these next experiments, blanks will be run with clean Inconel-600 samples with no sulfur contamination and with only the peroxide cleaning solution without any Inconel.

An important feature of future cleaning studies will be to direct more attention to the intermediate sulfur species that are formed. A number of the possible intermediates formed in the oxidation chain going from sulfide to sulfate are shown in Figure 36. The tetrathionate, thiosulfate, and possibly other species can severely attack Inconel. A better understanding of the concentrations of these intermediates and their influence on the cleaning process is advisable.

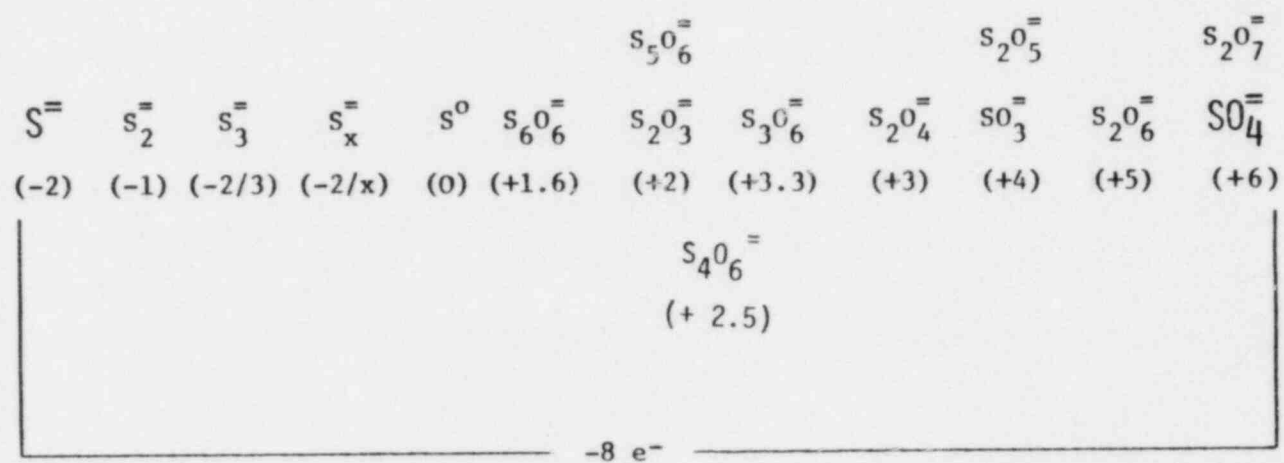


Figure 36. Reaction Intermediate, for Oxidation of Sulfide to Sulfate.

#### APPENDIX A

The following figures and tables present the results of the total sulfur analyses on the tube samples and summarize the results in terms of sulfur cleaning efficiencies.

TABLE A-1. SUMMARY OF SULFUR CLEANING RESULTS FOR TMI-1 TUBE SAMPLE

Beaker Cleaning Series	Beaker Test No.	(A) Sulfur In Unclean Sample, $\mu\text{g SO}_4/\text{in.}^2$	(B) Sulfur Removed By cleaning, $\mu\text{g SO}_4/\text{in.}^2$	(C) Sulfur in Sample after Cleaning, $\mu\text{g SO}_4/\text{in.}^2$	Cleaning Efficiency, Percent $B \div (B+C) \times 100$ $(A-C) \div A \times 100$	
1	Tube Run-1	28.6	51.0	8.2	86.1	71.3
	Tube Run-2	22.8	39.1	6.9	85.0	69.7
	Tube Run-3	38.5	66.3	10.2	86.7	73.5
	Tube Run-4	53.7	70.1	5.7	92.5	89.4
2	Immuno1 Run-1	20.6	105.6	55.6	65.5	-
	Immuno1 Run-2	20.6	125.7	25.3	83.2	-
	Immuno1 Run-3	20.6	64.8	14.0	82.2	32.0
	Immuno1 Run-4	20.7	67.4	7.6	89.9	63.3
3	Imm. Exp. Run-1	4.5	56.9	12.3	82.2	-
	Imm. Exp. Run-2	7.8	48.0	9.7	83.2	-
	Imm. Exp. Run-3	7.0	60.8	12.4	83.3	-
	Imm. Exp. Run-4	10.0	62.3	12.5	83.3	-

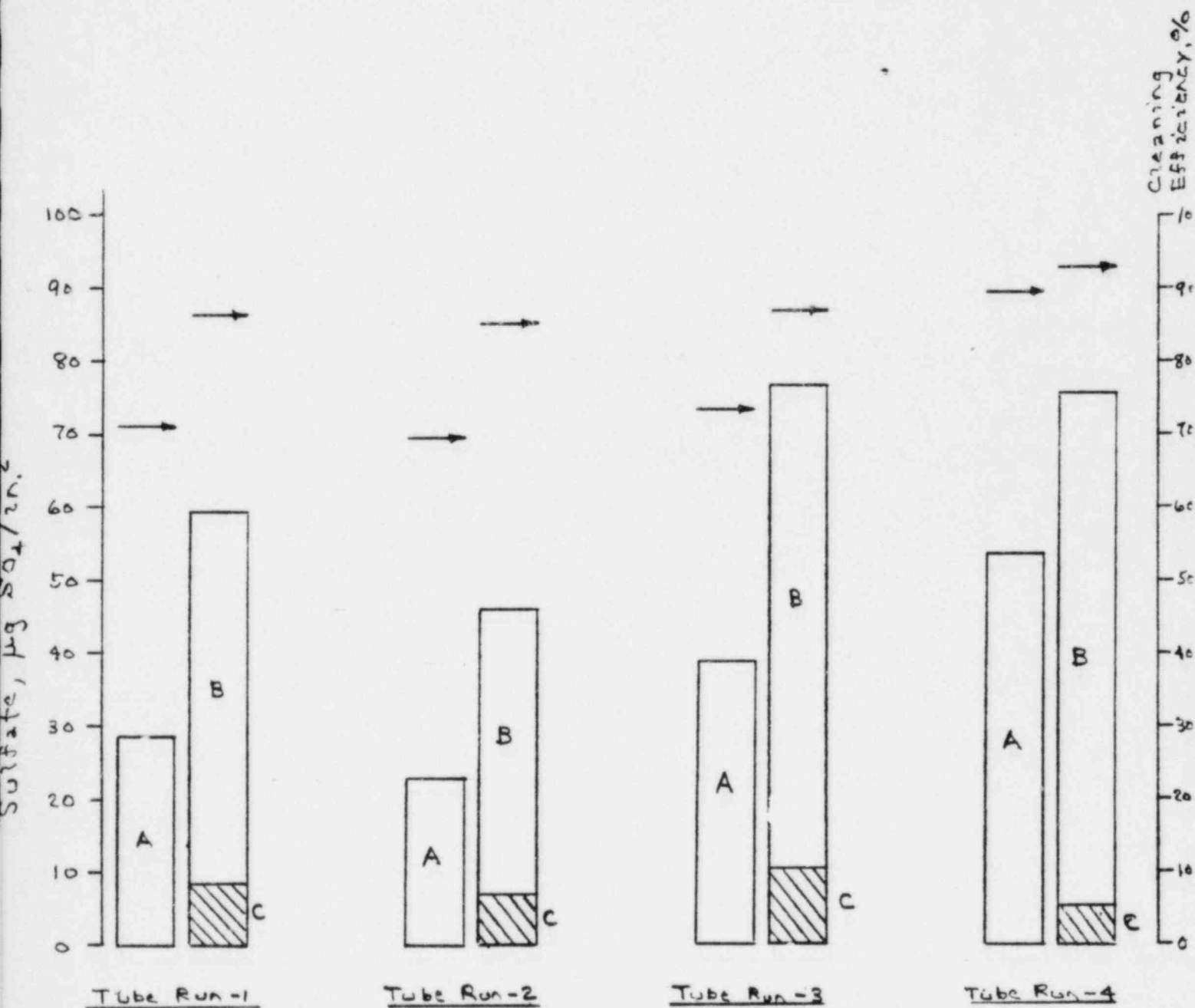


FIGURE A -1. SUMMARY OF SULFUR ANALYSES AND CLEANING EFFICIENCIES FOR BEAKER CLEANING SERIES 1

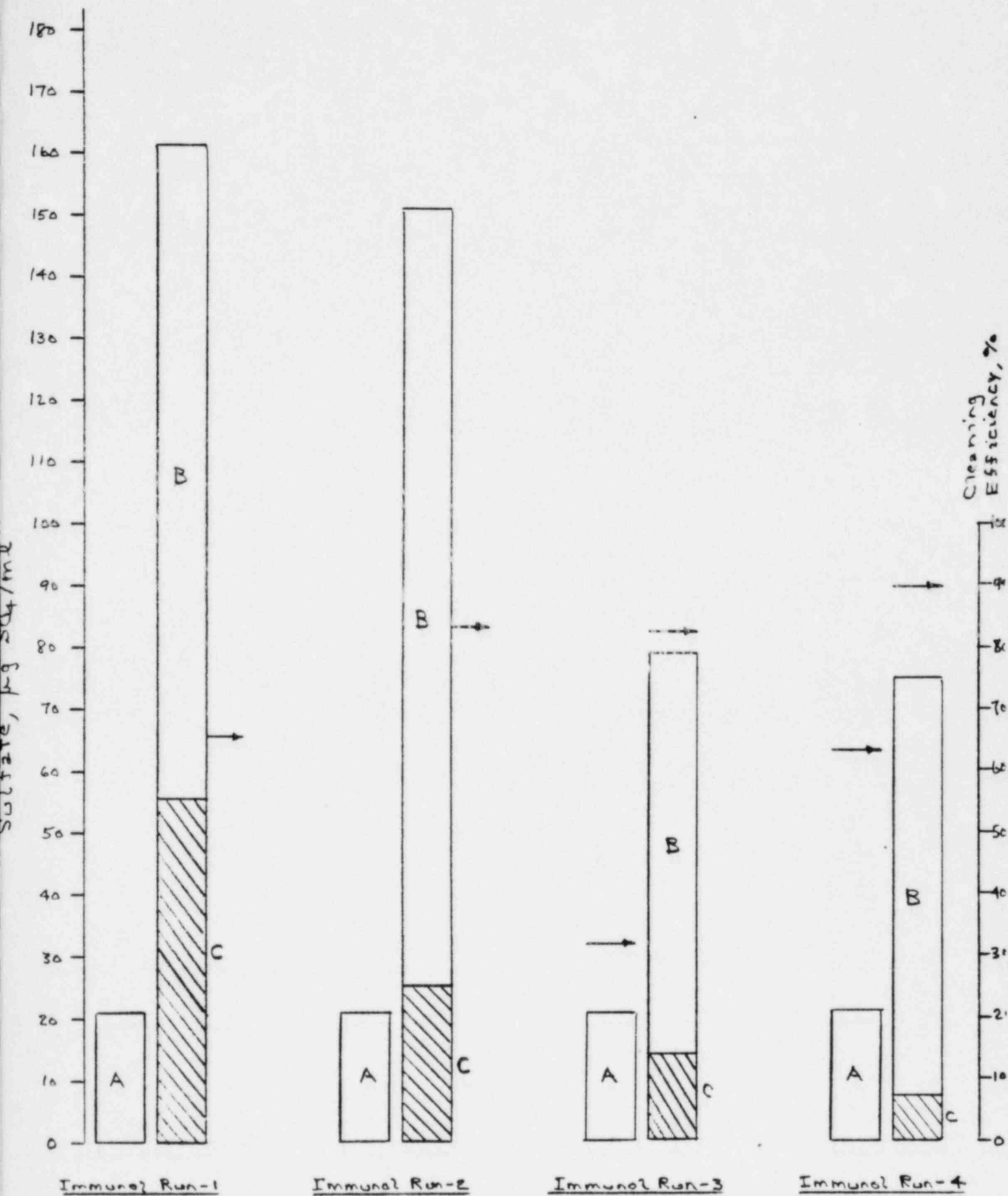


FIGURE A-2 SUMMARY OF SULFUR ANALYSES AND CLEANING EFFICIENCIES FOR BEAKER CLEANING SERIES 2

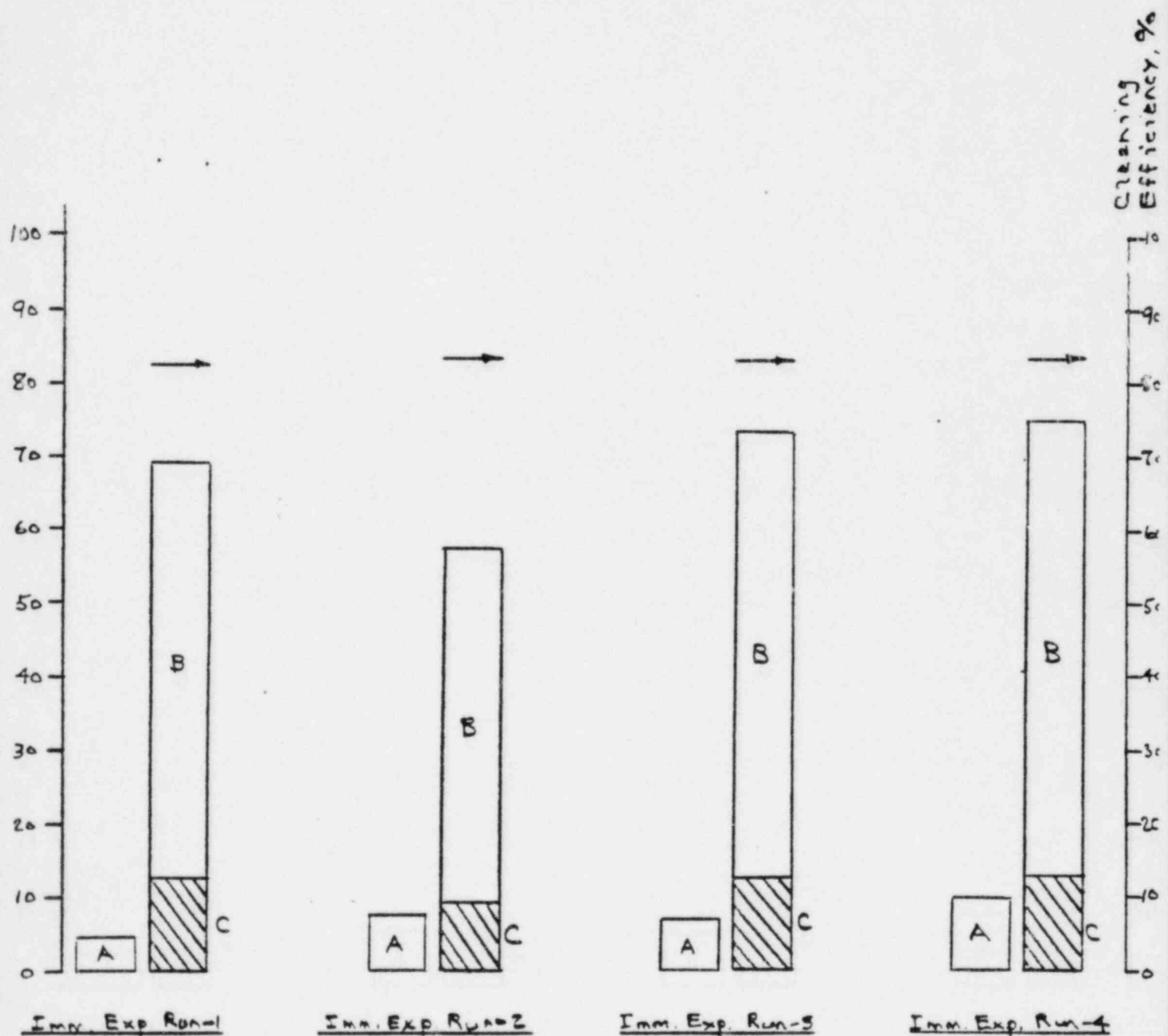


FIGURE A-3 SUMMARY OF SULFUR ANALYSES AND CLEANING EFFICIENCIES FOR BEAKER CLEANING SERIES 3

APPENDIX I

TABLE 3. SPECIMEN ASSIGNMENT

Test No.	Cleaning Solution	Beaker No.	U-bend No.		C-Ring No.	ESCA-Auger Specimen No.
			IN600	304SS		
1	pH 8 ammonium hydroxide	1	6-01 to 6-03	3-01 to 3-03	B11-23 (1-3)	B11-23
		2	6-04 to 6-06	3-04 to 3-06		
	pH 10 lithium hydroxide	3	6-07 to 6-09	3-07 to 3-09	A71-126 (1-2)	A71-126
		4	6-10 to 6-12	3-10 to 3-12	A78-32-2 (1)	
2	pH 8 Immunol treated	5	-	-	A78-32-2 (2-4)	A78-32-2
	pH 8 non-Immunol treated	6	-	-	A11-13-5 (4,6,8)	-
					A111-13-2 (4,6,8)	-
3	Thiosulfate	7	6-24	3-24	A78-32-2 (5)	-

TABLE 4. RESULTS OF THE METALLOGRAPHIC EXAMINATION FOR THE  
RESENCE OF CRACKS ON THE EDGES OF THE STAINLESS  
STEEL TYPE 304 U-BEND SPECIMENS (MAG. = 250 TEST 1)

Figure 8 identifies examined positions 1, 2 and 3  
on the U-bend.

Cleaning Solution	Beaker No.	Specimen No.	Side	Position (0= No Cracks Observed)		
				1	2	3
pH 8 ammonium hydroxide	1	3-01	1	0	0	0
			2	0	0	0
	1	3-02	1	0	0	0
			2	0	0	0
	1	3-03	1	0	0	0
			2	0	0	0
	2	3-04	1	0	0	0
			2	0	0	0
	2	3-05	1	0	0	0
			2	0	0	0
	2	3-06	1	0	0	0
			2	0	0	0
pH 10 lithium hydroxide	3	3-07	1	0	0	0
			2	0	0	0
	3	3-08	1	0	0	0
			2	0	0	0
	3	3-09	1	0	0	0
			2	0	0	0
	4	3-10	1	0	0	0
			2	0	0	0
	4	3-11	1	0	0	0
			2	0	0	0
	4	3-12	1	0	0	0
			2	0	0	0

TABLE 5. RESULTS OF THE METALLOGRAPHIC EXAMINATION FOR  
THE PRESENCE OF CRACKS ON THE EDGES OF THE  
IN600 U-BEND SPECIMENS (Mag. = 250X TEST 1)

Figure 8 identifies examined positions 1, 2 and  
3 on the U-bend specimen.

Cleaning Solution	Beaker No.	Specimen No.	Side	Position (x = No SCC Observed)		
				1	2	3
pH 8 ammonium hydroxide	1	6-01	1	0	0	0
			2	0	0	0
	1	6-02	1	0	0	0
			2	0	0	0
	1	6-03	1	0	0	0
			2	0	0	0
	2	6-04	1	0	0	0
			2	0	0	0
	2	6-05	1	0	0	0
			2	0	0	0
	2	6-06	1	0	0	0
			2	0	0	0
pH 10 lithium hydroxide	3	6-07	1	0	0	0
			2	0	0	0
	3	6-08	1	0	0	0
			2	0	0	0
	3	6-09	1	0	0	0
			2	0	0	0
	4	6-10	1	0	0	0
			2	0	0	0
	4	6-11	1	0	0	0
			2	0	0	0
	4	6-12	1	0	0	0
			2	0	0	0

TABLE 6. RESULTS OF THE METALLOGRAPHIC  
EXAMINATION OF THE LEFT HALF-  
SIDES OF THE C-RINGS (TEST 1)

Cleaning Solution	Beaker No.	Specimen No.	Side	No Cracks Found*
pH 8 ammonium hydroxide	1	B11-23 (1)	1	0
			2	0
	1	B11-23 (2)	1	0
			2	0
	1	B11-23 (3)	1	0
			2	0
	2	B111-62-7A (1)	1	0
			2	0
	2	B111-62-7A (2)	1	0
			2	0
	2	B111-62-7A (3)	1	0
			2	0
pH 10 lithium hydroxide	3	A71-126 (1)	1	0
			2	0
	3	A71-126 (2)	1	0
			2	0
	3	A78-32-2 (1)	1	0
			2	0
	4	A78-32-2 (2)	1	0
			2	0
	4	A78-32-2 (3)	1	0
			2	0
	4	A78-32-2 (4)	1	0
			2	0

\* Small intergranular attack present.

TABLE 7. RESULTS FOR THE RIGHT HALVES OF  
THE C-RINGS, (TEST 1)

Solution	Beaker No.	Specimen No.	No Crack Found*
pH 8 ammonium hydroxide	1	B11-23 (1)	0
	1	B11-23 (2)	0
	1	B11-23 (3)	0
	2	B111-62-7A (1)	0
	2	B111-62-7A (2)	0
	2	B111-62-7A (3)	0
pH 10 lithium hydroxide	3	A71-126 (1)	0
	3	A71-126 (2)	0
	3	A78-32-2 (1)	0
	4	A78-32-2 (2)	0
	4	A78-32-2 (3)	0
	4	A78-32-2 (4)	0

\* Intergranular attack present on all tubes.

TABLE 8. AUGER AND ESCA ANALYSIS OF C-RINGS IN BEAKER 1 (TEST 1)

Depth Below Surface ( m)	Concentration (atomic %)									
	Cu	Ni	Co	Fe	Cr	O	C	Si	Zn	Al
0	3.6	4.2	1.8	1.7	1.3	55.2	14.0	9.0	4.9	4.4
0.005	5.1	11.9	nr	4.8	2.2	46.7	5.0	7.0	4.7	12.6
0.025	6.6	7.2	nr	8.6	5.0	55.5	2.8	6.8	2.3	5.1

nr = not reported

TABLE 9. AUGER AND ESCA ANALYSIS OF C-RINGS IN BEAKER 4 (TEST 1)

Depth Below Surface ( m)	Concentration (atomic %)										
	Cu	Ni	Fe	F	Cr	O	Ag	C	Zn	Si	Al
0	3.3	6.1	5.2	13.2	3.2	38.4	0.2	23.4	3.9	1.2	1.7
0.005	3.5	16.2	6.6	7.4	8.4	35.0	0.4	7.1	2.1	2.3	11.0
0.025	4.0	17.1	6.9	5.8	6.4	32.5	0.2	8.1	1.8	1.8	15.5

TABLE 10. RESULTS OF THE METALLOGRAPHIC EXAMINATION  
OF THE LEFT HALF SIDES OF THE IMMUNOL AND  
NON-IMMUNOL TREATED C-RINGS FROM EXPLAINED  
TUBES (TEST 2)

Cleaning Solution	Beaker No.*	Specimen No.	Side	Stress Corrosion Cracks Found	
				No	Yes
pH 8 Immunol treated	5	A111-13-5 (4)	1	0	
			2	0	
	5	A111-13-5 (6)	1	0	
			2	0	
	5	A111-13-5 (8)	1	0	
			2	0	
pH 8 non-Immunol treated	6	A111-13-2 (4)	1	0	
			2	0	
	6	A111-13-2 (6)	1	0	
			2	0	
	6	A111-13-2 (8)	1	0	
			2	0	

\* No sulfide additions to the solution, cover gas for the  
beakers was air.

TABLE 11. RESULTS FOR THE OPENED UP RIGHT HALVES  
OF THE IMMUNOL AND NON-IMMUNOL TREATED  
C-RINGS (TEST 2)

Cleaning Solution	Beaker No. Beaker No.	Specimen No. Specimen No.	Stress Corrosion Cracks Found	
			No	Yes
pH8 Immunol treated	5	A111-13-5 (4)	0	
	5	A111-13-5 (6)	0	
	5	A111-13-5 (8)	0	
non-Immunol treanted	6	A111-13-2 (4)	0	
	6	A111-13-2 (6)	0	
	6	A111-13-2 (8)	0	

TABLE 12. COMPARISON OF CONCENTRATION OF OXYGEN EXPECTED  
IN OXIDE FORM TO THE TOTAL MEASURED OXYGEN

Probable Oxide	Beaker 1		Beaker 4	
	Atomic % Oxygen	Total Measured Oxygen	Atomic %	Total Measured Oxygen
CuO	3.3		3.6	
Ni(OH) <sub>2</sub>	12.2		8.4	
CoO	-		1.8	
FeOOH	10.4		3.4	
Cr(OH) <sub>3</sub>	9.6		3.9	
SiO	2.4		18	
AgO	0.2		-	
ZnO	3.9		4.9	
Al <sub>2</sub> O <sub>3</sub>	2.6		6.6	
Total	44.6	38.4	50.6	55.2