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DEVELOPMENT OF SAMPLING AND ANALYTICAL METHODS OF LIME/LIMESTONE WET SCRUBBING TESTS

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DEVELOPMENT OF SAMPLING AND ANALYTICAL METHODS OF LIME/LIMESTONE WET SCRUBBING TESTS

by

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ABSTRACT

This study was carried out to develop appropriate sampling and analytical methods to be used at OAP's test facility at Shawnee. The three problem areas encountered in analyzing thermodynamically unstable slurry streams as encountered in lime/limestone based SO_2 wet scrubbing processes are sampling, sample handling and chemical analysis. A positive pressure filtration was found to minimize the mass transfer phenomena during the filtration step to an acceptable level. Quenching of the filtered liquid was chosen to avoid change in sample composition. Two sets of analytical methods were selected for application at Shawnee. The back-up methods are based on atomic absorption and wet chemical procedures. The rapid field methods are based on X-ray fluorescence, atomic absorption, and wet chemical analyses.

The X-ray fluorescence spectrometer was automated by interfacing it with a NOVA 1200 minicomputer. Additional peripheral devices have the function of processing all raw data. The raw data are input to the system with a card reader, a teletype, or a CRT. The final results are stored on a magnetic tape. A hard copy is provided by a printer.

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VOLUME III

1.0 INTRODUCTION

The Office of Research and Development has sponsored several approaches for sulfur dioxide removal from flue gases emitted by coal and oil-fired power stations in the past years. One of the most advanced control strategies is SO_2 removal based on lime/limestone wet scrubbing techniques. Since the summer of 1972, three different scrubbing units were tested at Shawnee - a venturi scrubber, a turbulent contact absorber, and a marble bed. The goal of these tests was to demonstrate the long term reliability of these units and the extraction of engineering design information such as:

- vapor-liquid mass transfer characteristics in the scrubbers,
- solid-liquid mass transfer rates throughout the system, and
- scaling potential.

The mathematical description of these problem areas depends on the knowledge of equilibrium partial pressures and important activity products. These quantities can be calculated from the chemical composition of the scrubber solutions obtained by chemical analysis.

Radian was granted a contract in 1970 to select appropriate referee and field chemical analysis methods to be used at Shawnee. This final report consists of three volumes. Volume I summarizes the major findings of the literature and experimental results in broad terms. It starts with a short process description and problem definition. The problem areas

encountered in sampling and sample handling are then discussed. Analytical methods selected for the liquid and solids analyses are described in the following sections. The data collected at TVA's Colbert Steam Plant are presented as an example of methods testing in the field. The analytical results obtained from the scrubber effluent are further processed to demonstrate the extraction of equilibrium partial pressures and important activity products necessary for process evaluation.

X-ray fluorescence proved to be a rapid and accurate procedure for the determination of sulfur in aqueous scrubber samples. Calcium, chlorine, and potassium are additional elements that are detectable by X-ray fluorescence. The X-ray spectrometer was interfaced with a minicomputer and several peripheral devices such as teletype, CRT, card reader, disk, magnetic tape, etc., to automate the fluorescence analysis and to facilitate the data handling problem associated with data reduction.

Volume II is a detailed description of the literature findings and experimental effort leading to the methods of choice. Details of the automated X-ray fluorescence unit and the data handling systems are presented in Volume III.

2.0 PROBLEM DEFINITION

The basic equipment arrangement for limestone injection wet scrubbing (LIWS) processes is shown in Figure 2-1. The three streams entering the system are flue gas, particulates and make-up water. Three streams leaving the unit are cleaned stack gas, solid waste products, and scrubbing liquor. The composition of the incoming streams provides a means of predicting the liquor composition on a qualitative basis. The important species in the LIWS process are:

Group I	Group II	Group III
Calcium	Sodium	Trace elements
Sulfite	Potassium	Iron
Sulfate	Magnesium	Cobalt
	Chloride	Nickel
	Nitrate	Copper
	Nitrite	Manganese
	Carbonate	

The components listed in Group I are the most important. They dominate the process by participating in the gas-liquid and liquid-solid mass transfer steps. The species listed under Group II contribute to the process performance in three ways. First, they influence solubilities which are dependent on the ionic strength of the solution. Second, they form ion pairs with Group I compounds. Finally, they influence the driving force for the mass transfer rates. The components in this group form very soluble compounds with the exception of magnesium hydroxide and calcium carbonate. In a closed loop operation there is a buildup of the soluble compounds, since the only

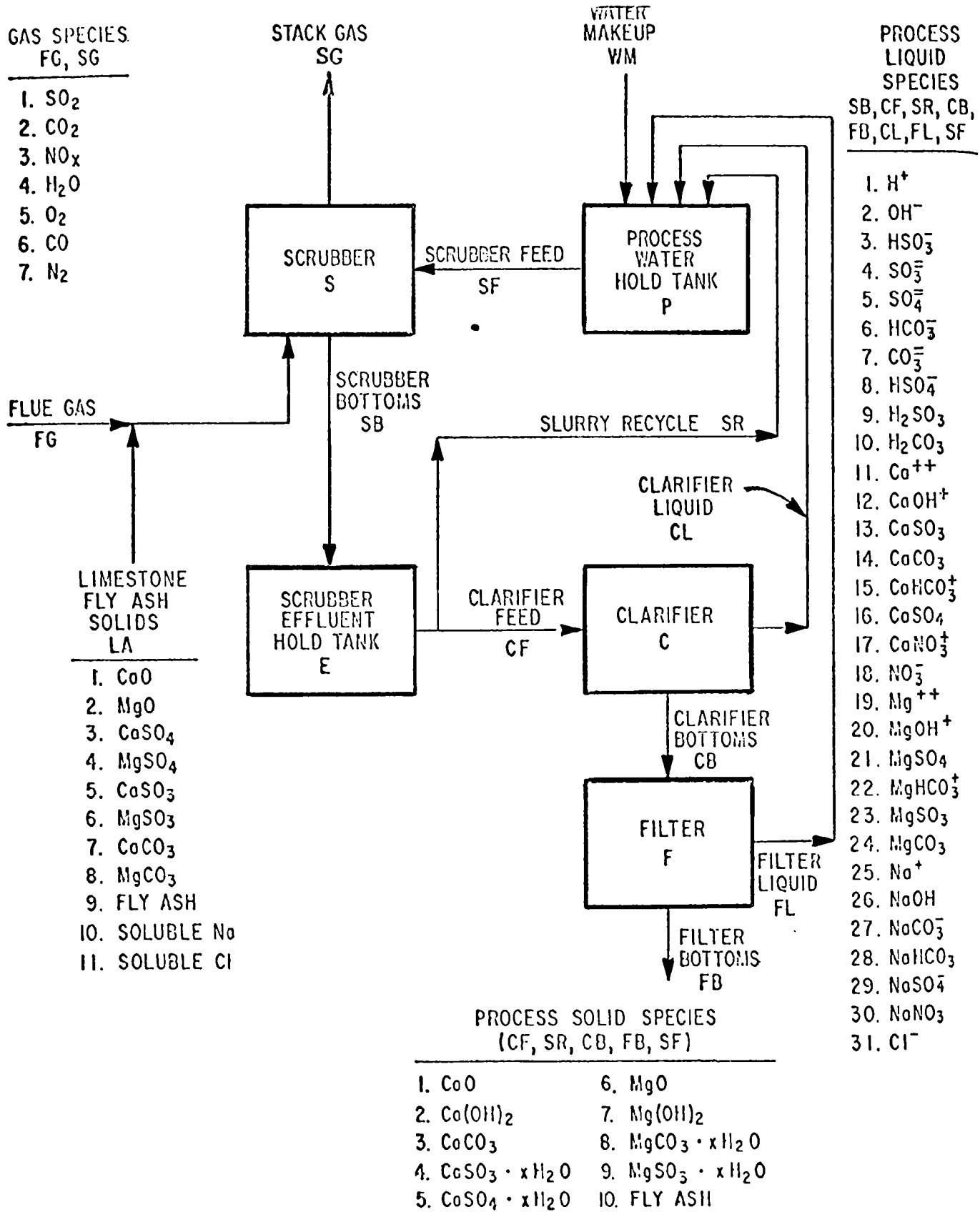

FIGURE 2-1 - WET SCRUBBING SCHEME

stream in which they can leave the scrubbing unit is the liquor adherent to the solids. This fact must be kept in mind when selecting analytical methods. The procedures must give accurate results in those cases where the soluble species build up to a high level. The implications for the selection of methods for sulfate and sulfite will be discussed later.

The third group is comprised of species leached from the fly ash and impurities in the limestone. The concentration of these elements is never very high, since it is limited by the solubility of the hydroxides in the alkaline parts of the scrubbing unit. Their importance is based on the fact that they are catalysts for sulfite oxidation, even if present in the parts per billion range.

The process simulations, performed under CPA Contract No. 70-45, "Study of the Limestone Injection Wet Scrubbing Process," gave a valuable basis for estimating anticipated concentration ranges. Estimation was necessary since no data on a closed loop system operated over an extended period of time were available at the time of analytical method development.

As a general rule, the higher the accuracy demand of an analysis, the higher are its costs. This fact raises the question as to the ultimate use of the analytical results. The accuracy requirements for routine, day-to-day operation are less stringent than the requirements for process analysis. One key objective of the tests at Shawnee is the collection of engineering design information. From an engineering point of view the following areas are of ultimate interest:

- gas-liquid mass transfer rates in the scrubber

- dissolution and precipitation rates as function of liquor composition

- scaling potential

The driving force term in the mass transfer equations describing these rates is a function of the difference of the actual process conditions and the equilibrium conditions of the system. In other words, the rates are a function of the difference of two activity expressions. The closer the system approaches equilibrium the more severely analytical errors will influence rate correlations. For LIWS processes the analyses of the species listed in Group I are, therefore, the most important. Error propagation calculations showed that the error in these analyses should not be greater than about 2%. The concentration of the species influencing the ionic strength (Group II) must be known within about 4%. The accuracy requirements for the trace elements effective as catalysts are still less stringent. Twenty to fifty percent is considered to be sufficient.

An example of how to calculate partial pressures and important solubility (activity) products from chemical analysis data is shown in Chapter VIII of this volume. These data are necessary inputs to evaluate scrubber performance from a chemical engineering point of view.

The analytical results are influenced by three steps:

- solid-liquid separation

- sample handling

actual analysis

These problem areas will be discussed next.

3.0 SAMPLING

The scrubbing system can be divided into an acidic and a basic part. The environment is acidic in the scrubber itself and in the pipe between the scrubber and the effluent hold tank. The solutions circulated in the rest of the system are alkaline. For sampling purposes it should be noted that the scrubbing slurry, especially in the acidic part of the system, is not in thermodynamic equilibrium. The sorbent tends to dissolve and sulfite and sulfate tend to precipitate. The technique often used to sample this stream is collection of a slurry sample in a beaker and filtration through a Buchner funnel. This technique results in only semi-quantitative results for the follow-on chemical analysis for three reasons:

1. Loss of acidic gases (SO_2, CO_2) especially if a vacuum is used.

2. Solid-liquid mass transfer during the sampling procedure.

3. Sulfite oxidation by air oxygen.

Because of these sources of error much of the pilot plant data collected using this method must be considered to be qualitative in nature and not suitable for the extraction of engineering design information. In-line, positive pressure filtration was the sampling method selected after field tests at several pilot units (see Figure 3-1). The sampling apparatus consists of a positive pressure pump, a membrane filter holder and lines and valves to control sampling and purge rates. Flow rates used in the tests were about 1300 ml/min. The residence time of the slurry is about 2.3 seconds in the filter and approximately seven seconds in the entire sampling equipment.

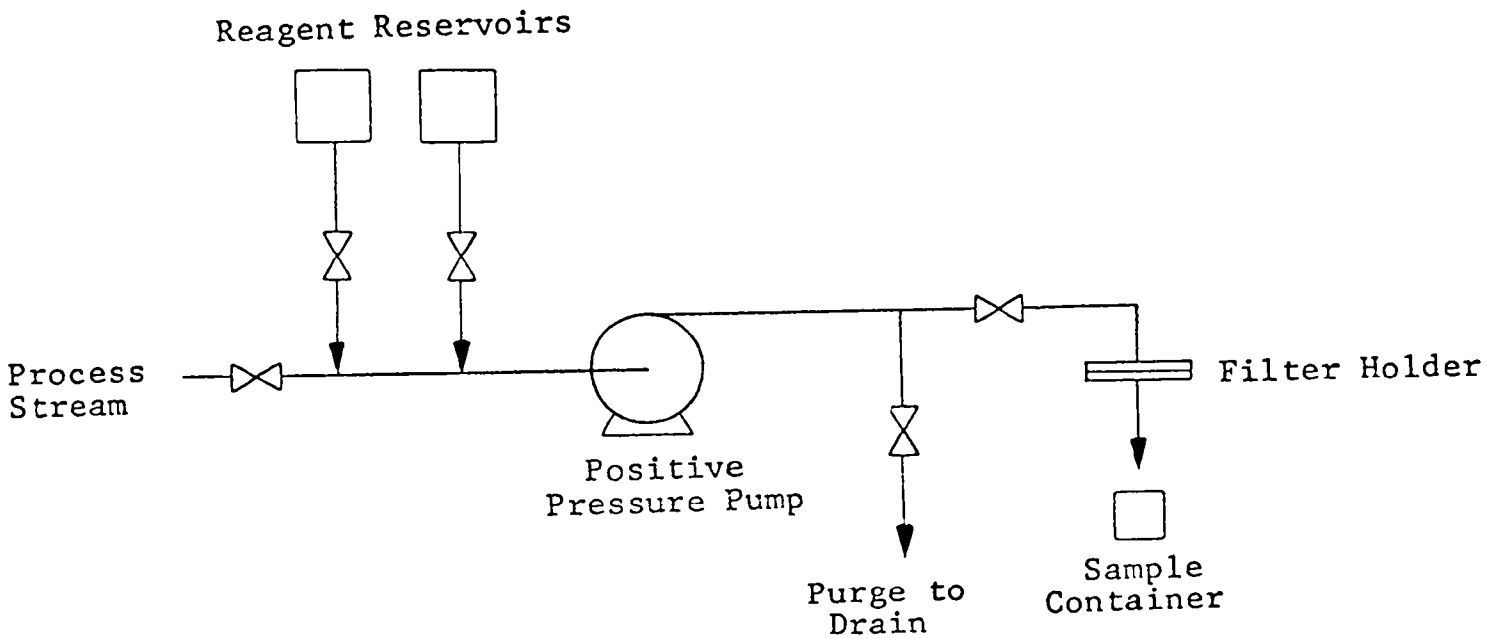

FIGURE 3-1 - TYPICAL SLURRY SAMPLING TRAIN

The degree of mass transfer in the filter cake, which is by nature a good contacting device, was checked by taking consecutive samples and plotting the chemical analysis results as a function of the filtered volume. Extrapolation to zero volume of filtrate represents the true aqueous phase composition. With the exception of carbonate, the amount of solids dissolved or precipitated in the filter cake was within the experimental error of the chemical analyses.

Loss of acidic gases is avoided by the positive pressure filtration, and air oxidation of sulfite is prevented by fixing the sample immediately.

4.0 SAMPLE HANDLING

After filtration care must be taken that the liquid samples do not undergo further change. This is especially true for the sulfite analysis. Sulfite losses can occur by:

- Evaporation from acidic samples
- Oxidation by air oxygen
- Interaction with nitrites

All three sulfite losses can be avoided by quenching the sample in a solution of pH = 6 with known iodine content (see Chapter 5.3.2 of Volume II). Nitrites can be formed by absorption of NO and NO_2 from the flue gas. The degree of NO_x absorption was unknown at the time of method selection.

Carbonate losses from acidic liquid can be avoided by quenching the sample in a solution of pH = 10. EDTA must be added to the buffer in order to avoid calcium carbonate precipitation at this pH (see Chapter 5.3.1 of Volume II).

Sulfate in the presence of sulfite is determined as the difference between the total sulfur and the sulfite sulfur. In order to avoid sulfite losses and sulfate precipitation, the sample for total sulfur analysis is quenched in a H_2O_2-water solution. Hydrogen peroxide oxidizes the sulfite. Dilution with distilled water prevents sulfate precipitation in the sample bottle (see Chapter 5.3.3 of Volume II).

5.0 LIQUID PHASE CHARACTERIZATION

The literature was surveyed through 1970 for analytical methods which might be applicable to the solutions of interest. The sources consulted were:

1. Kolthoff and Elving, "Treatise on Analytical Chemistry"
2. Biannual Reviews on Analytical Chemistry
3. 1969 Book of ASTM Standards
4. FWPCA Methods for Chemical Analysis of Water and Wastes
5. Chemical Abstracts
6. Pertinent Original Articles

The present chapter discusses the wet chemical procedures for the determination of chloride, CO_2 in aqueous solution, sulfite in aqueous solution, total sulfur as sulfate, total nitrogen and for the analysis of nitrite and nitrate. The methods chosen are applicable for highly concentrated scrubber solution as encountered in closed loop operation.

Atomic absorption proved most suitable for the analysis of calcium, magnesium, sodium, and potassium. The catalytically active transition elements, iron, manganese, cobalt, nickel, and copper, are determined after chelation with diethyl-dithiocarbamate and extraction into methyl isobuthyl-ketone.

X-ray fluorescence proved to be an accurate and rapid procedure for the determination of total sulfur, which is a very critical analysis in limestone based wet scrubbing solutions. In addition, calcium, chlorine, and potassium in the aqueous phase can be analyzed by this approach.

The methods selected are described in this chapter in a succinct form. The results of the literature survey and a detailed description of the interference studies performed experimentally are presented in Volume II of this final report.

5.1 Wet Chemical Procedures

5.1.1 Chloride Determination

A summary of the relevant methods for determination of chloride ion in aqueous solution, based on the literature survey, is given in Table 3.1-6 of Volume II. The methods covered in this table fall into one of the following broad categories.

1. Gravimetric as silver chloride
2. Volumetric (visual end point)
3. Spectrophotometric
4. Nephelometry
5. Flame Photometry
6. Potentiometric measurements

7. Amperometric (current) measurements

8. Coulometric measurements

Most chloride determinations are based on the reaction of chloride ion with either silver (I) or mercury (II). The methods proposed by Volhard, the mercurimetric titration for chloride and the potentiometric method described by Shiner and Smith (SH-014, FI-019) were tested in the laboratory. The Volhard method was found to yield good results down to a chloride concentration of 0.02 M (Volume II, page 315). The mercurimetric procedure suffered interferences from iron ion found in some pilot plant samples (Volume II, page 327).

The potentionmetric determination of chloride proved to be the most satisfactory wet chemical procedure (Volume II, page 319). A Fisher Automatic Titralyzer (Model 740) was used to check this procedure. This is an automated potentiometric titrator designed to do volumetric analyses fully automatically. It incorporates into a single, integrated system an electrometer, an automatic buret, a digital data recording system, and an automatic sample changing device.

The potential between a metallic silver indicator electrode and a silver-silver chloride reference electrode is measured as a function of the amount of standard silver nitrate solution added. The reaction of silver nitrate with chloride ion may be represented in the following way.

$$Cl^- + Ag^+ \rightarrow AgCl \text{ (solid)} \qquad (5\text{-}1)$$

The potential of the metallic silver electrode depends on the amount of silver ion in solution.

In practice the potential at the equivalence point is determined by a manual titration or by addition of a known amount of standard silver nitrate solution to a known amount of a standard chloride solution. This known equivalence point potential is then set as the end point potential on the Titralyzer and all other titrations are stopped when this potential is reached.

Interferences

Bromide and iodide will be determined as equivalent chloride concentrations. Ferricyanide causes high results and must be removed. Chromate and dichromate interfere unless reduced to the chromic state. Concentrations of ferric iron, if substantially higher than the amount of chloride, will interfere. Ferrous ion and phosphate do not interfere.

Results of Chloride Titrations

Accuracy and precision are excellent. The relative error using artificial scrubber samples never exceeded .5% in a series of 15 titrations.

This method for determining chloride was also applied to field samples. For the Key West series of samples, triplicate titrations were run for each sample. Recovery tended to run a little low ranging from 98.2% to 99.8% for 22 samples.

For the Colbert Test Series one unspiked aliquot and one spiked aliquot were run for each sample. The results of the recovery studies are given in Table 5-1. Recoveries ranged from 99.4% to 101.8% for 15 samples.

TABLE 5-1

RECOVERY STUDIES ON COLBERT CHLORIDE DETERMINATIONS

Sample Name	(1) Titration of Unspiked Aliquot ml $AgNO_3$	(2) Titration of Spiked Aliquot ml $AgNO_3$	Difference (2)-(1)	Percent Recovery
Scrubber Effluent	2.22	7.26	5.04	100.8
Scrubber Spray	.32	5.32	5.00	100.0
F-12 Overflow	1.91	6.92	5.01	100.2
F-13 Recycle	1.88	6.95	5.07	101.4
Clarifier Overflow	2.15	7.12	4.97	99.4
Limestone Feed	1.81	6.82	5.01	100.2
Make Up Water	.05	5.06	5.01	100.2
Scrubber Effluent	2.38	7.44	5.06	101.2
Scrubber Spray	.53	5.50	4.97	99.4
F-12 Overflow	2.30	7.32	5.02	100.4
F-13 Recycle	2.18	7.19	5.01	100.2
Scrubber Effluent	2.30	7.36	5.06	101.2
Scrubber Spray	.49	5.49	5.00	100.0
F-12 Overflow	4.86	9.90	5.04	100.8
F-13 Recycle	4.56	9.65	5.09	101.8

The recoveries are all well within the accuracies required for chloride determinations and indicate that no serious interferences for this method of chloride determination were found in these sets of field samples.

5.1.2 CO_2 Determination

The literature findings on methods used for measuring CO_2 content in liquid and solid samples are summarized in Chapter 3.1.8 of Volume II. The procedures described can be grouped into one of the following categories:

- Volumetry
- Colorimetry
- Gravimetry
- Evolution techniques

An instrument based on CO_2 evolution in an acid pool with subsequent CO_2 detection by a nondispersive infrared analyzer was found to be suitable for CO_2 determinations in aqueous solutions (Total Carbon System, Oceanography International). Interferences caused by nitrates, nitrites, and sulfite could be overcome by using a 10% KH_2PO_4 solution in the reactor.

Accuracies of better than two percent were obtained in analyzing synthetic scrubber solutions. Table 5-2 gives supporting data. The analysis time per sample ranges from five to six minutes.

TABLE 5-2

INFLUENCE OF NITRITE, NITRATE AND SULFITE ON THE TOTAL CO_2 ANALYSIS USING THE "TOTAL CARBON SYSTEM" (Oceanography International)

Run No.	µℓ Injected	NO_2^- Concentration Moles/Liter	NO_3^- Concentration Moles/Liter	$SO_3^=$ Concentration Moles/Liter	Actual CO_2 Concentration mg/Liter	Experimental CO_2 Concentration mg/Liter	Percent Error
1	46.4	0.5	0.5	0.05	100	102.0	- 2.0
2	96.1	0.5	0.5	0.05	100	100.6	- 0.6
3	146	0.5	0.5	0.05	100	100.2	- 0.2
4	146	0.5	---	---	100	102.0	- 2.0
5	146	---	0.5	---	100	100.5	- 0.5
6	146	---	---	0.05	100	101.0	- 1.0
7	146	0.5	---	---	---	0.0	0.0
8	146	---	0.5	---	---	0.0	0.0
9	146	---	---	0.05	---	0.0	0.0
10	146	0.5	0.5	0.05	---	0.4	- 0.4

5.1.3 Sulfur Dioxide Determination

The literature finding concerning methods for SO_2 determination are summarized in Volume II, page 113. The procedures are based on:

- Polarography
- Atomic absorption spectroscopy
- Fluorescence
- Visible and ultraviolet spectrophotometry
- Amperometry

The amperometric procedure was found to be the most straightforward approach. The sample is added to an excess iodine solution buffered to pH = 6.0 - 6.2 to inhibit sulfite-nitrite and nitrite-iodine interaction (DE-029, SE-015). Iodine remaining after stoichiometric SO_2 oxidation is titrated with standard sodium arsenite solution. An amperometric dead stop method for end point detection is used. The error is 2-4% in the presence of 20 mmoles nitrite.

5.1.4 Total Sulfur Determination

The methods described in the literature for the determination of sulfate in aqueous solutions are summarized in Volume II, Chapter 3.1.10.

The published procedures can be divided into five groups:

1. Gravimetric procedures
2. Direct titrimetric procedures
3. Indirect titrimetric methods
4. Colorimetric techniques
5. Acidimetric methods

The most elegant method is the titrimetric approach using thorin as end point indicator (AM-002, MA-039, FR-003, FR-009). Unfortunately, this method is subject of severe anion interference caused by the presence of phosphate, fluoride, nitrate, and chloride.

The barium chloranilate spectrophotometric procedure was extensively checked (BE-024, PR-007, FE-004). It is based on the precipitation of barium sulfate upon interaction of barium chloranilate with sulfate ion. The intensity of the colored chloranilate is measured at 530 nm. This procedure is amenable to automation (Volume II, page 366). Nitrate and chloride showed interferences if present in high concentrations. The method showed, in addition, pH-sensitivity and problems in the removal of the very fine precipitate.

Barium sulfate precipitation and backtitration of excess barium using EDTA and Eriochrome Black T as indicator gave satisfactory results (Volume II, page 358). Interfering cations (Fe^{3+}, Al^{3+}, Ca and Mg) are removed using a cation

exchange resin in the sodium form. A disadvantage of the procedure is the long digestion time (KO-015, TH-007, SI-005, SH-006).

The titrimetric procedure proposed by Dollman (DO-006) was finally accepted (Volume II, page 383). A sample aliquot is passed through a strong acid type ion exchange resin in the hydrogen form. Sulfate and other anions are converted to the corresponding acids. The column effluent is quantitatively retained. All acids except H_2SO_4 and H_3PO_4 are volatilized at 75°C. Titration with a standard base completes the determination. Phosphate, if present, interferes. It can be determined by the same technique by volatilizing the H_2SO_4. The sulfate value is then corrected. The accuracy of the method, if carefully applied, is better than 1% (see Tables 3.4-13, 3.4-14, 3.4-15 of Volume II).

5.1.5 Total Nitrogen

The nitrogen containing compounds found in lime/limestone based scrubbing solution can be quantitatively reduced to ammonia in the presence of a metallic reducing agent (Volume II, page 138). Devarda's alloy (50% Cu, 45% Al, and 5% Zn) in a strong NaOH solution was found to be satisfactory (EN-020, KO-050, MU-020). The reduction cannot be performed in an acidic medium due to hydrogen sulfide evolution. Ammonia is distilled into hydrochloric acid. Excess HCl is backtitrated.

The error determined in the presence of sulfite was found to be smaller than 1% at nitrate levels of 100 to 160 mg in the aliquot (Volume II, page 399).

5.1.6 Determination of Nitrite and Nitrate

The literature findings for the quantitative analysis of nitrites are presented in Volume II, Chapter 3.1.12. Table 3.1.11 shows examples of the principal types of methods which can be used to determine nitrite in aqueous media. They can be classified in the following categories:

- Ultraviolet
- Manometric
- Amperometric
- Coulometric
- Chemical

Procedures for nitrate determination are similarly numerous. They encompass:

- Nitration
- Reduction
- Ultraviolet
- Electrochemical
- Manometric

- Gravimetric
- Other methods

Key examples are presented in Volume II, Table 3.1-12.

The simultaneous determination of nitrate and nitrite proposed by Wetters and Uglum (WE-008) was found suitable for analysis of scrubber solutions. The method is based on the fact that both nitrate and nitrite absorb in the ultraviolet. Nitrite has an absorbance maximum at 355 nm while nitrate shows a maximum at 302 nm. Calcium, magnesium, sodium, potassium, carbonate, sulfite, sulfate and chloride showed negligible interference. Samples with nitrite concentrations of 100-1000 mg/ℓ can be determined with better than 3% accuracy using 1 cm cells. Samples with nitrate concentrations of 20-500 mg/ℓ and nitrite concentrations of 20-100 mg/ℓ can be determined with better than 5% accuracy using 10 cm cells. Tables 5-3 and 5-4 give supporting data. The experimental results are described in more detail in Volume II, page 400.

Nitrate concentrations at lower levels can be determined using the procedure by West and Ramachandran (WE-012). This method is based on a reaction of nitrate with chromotropic acid. The absorbance is measured at 410 nm. Beer's Law is fulfilled for a nitrate concentration between 0 and 60 ppm. Experimental details of the procedure are presented in Volume II, page 416.

5.2 Atomic Absorption Procedures

The application of atomic absorption procedures for the analysis of scrubber liquors is discussed in detail in

TABLE 5-3

Simultaneous Determination of Nitrate and Nitrite in pH 6 Simulated Filter Bottoms (1 cm cells)

A_{355}	A_{302}	Corrected A_{302}	NO_2^- Added (mg/ℓ)	NO_2^- Found (mg/ℓ)	% Error	NO_3^- Added (mg/ℓ)	NO_3^- Found (mg/ℓ)	% Error
.505	.763	.561	1000	1004	-0.4	5000	4855	+2.9
.505	.219	.117	1000	1004	-0.4	1000	1000	0.0
.504	.225	.024	1000	1002	-0.2	200	200	0.0
.202	.539	.458	400	400	0.0	4000	3924	+1.9
.101	.614	.574	200	198	+1.0	5000	4965	+0.7
.052	.055	.024	100	100	0.0	200	200	0.0

TABLE 5-4

Simultaneous Determination of Nitrate and Nitrite in pH 11.3 Simulated Filter Bottoms (1 cm Cells)

A_{355}	A_{302}	Corrected A_{302}	NO_2^- Added (mg/ℓ)	NO_2^- Found (mg/ℓ)	% Error	NO_3^- Added (mg/ℓ)	NO_3^- Found (mg/ℓ)	% Error
.505	.762	.560	1000	1010	-1.0	5000	4870	+2.6
.501	.317	.117	1000	1002	-0.2	1000	1000	0.0
.499	.223	.0234	1000	998	+0.2	200	199	+0.5
.201	.536	.456	400	404	-1.0	4000	3974	+0.7
.100	.609	.569	200	204	-2.0	5000	4950	+1.0
.048	.079	.060	100	100	0.0	500	508	-1.7
.025	.388	.288	500	500	0.0	2500	2483	+0.7

*All runs were made using deionized water as a reference and $NaNO_2$ and $NaNO_3$ as standards.

Volume II, Section 3.2. This method was found suitable for the analysis of calcium, magnesium, sodium, potassium, and trace elements.

5.2.1 Determination of Ca, Mg, K, and Na

The experimental studies to define optimum concentration ranges and interferences encountered in lime/limestone based wet scrubber solutions are described in detail on pages 181-233 of Volume II. A Perkin-Elmer Model 403 Atomic Absorption instrument was used.

The calcium line at 4227 Å was measured. Interferences, mainly from sulfate, could be suppressed by using a 1% $LaCl_3$, 5% HCl solution in the final dilution step. The absorbance is a linear function of calcium concentration in the range 0-7 mg/ℓ Ca. The accuracy in synthetic scrubber solutions was found to be about 2%.

Magnesium was measured at the 2852 Å line. Interferences could also be suppressed by using a 1% $LaCl_3$, 5% HCl solution in the final solution step. Absorbance is a linear function of concentration in the 0-0.7 mg Mg/ℓ range. The error in analyzing wet scrubbing solutions is approximately 2%.

The absorbance of sodium at 5890 Å is linear up to a sodium concentration of about 1.5 mg/ℓ. Interferences are suppressed by 1% $LaCl_3$, 5% HCl, with the exception of potassium interference. The standards should contain approximately the same amount of potassium than the test solution for accurate determinations. Accuracies using synthetic scrubber solutions were found to be approximately 3%.

Sulfate, calcium, magnesium, and sodium were found to interfere with the potassium determination at 7665 Å. The addition of 1% $LaCl_3$, 5% HCl suppresses the interference partly. The Mg, Ca, and Na content in the standard must be matched to that in the sample. The optimum potassium concentration ranges up to 6 mg/ℓ. Errors in analyzing artificial scrubber solutions using matched standards were approximately 4%.

5.2.2 Determination of Catalytically Effective Trace Elements

Cobalt, copper, iron, manganese, and nickel are reported to catalyze sulfite oxidation by oxygen even if present in the ppb range. These elements can be determined by atomic absorption once they are extracted from the original phase. The elements of interest are concentrated in the extraction step. In addition, the instrument sensitivity is increased two to five-fold (PE-037) when an organic, instead of an aqueous phase, is aspirated into the atomic absorption spectrophotometer.

The system dithizone, 8-quinolinol and acetyl acetone (chelating agent)-ethyl propionate (solvent) extracted Co, Cu, Fe, and Ni but not Mn. It was abandoned in favor of methyl isobutyl ketone (solvent) and diethyldithiocarbamate (chelating agent) (JO-012).

Using this method cobalt, copper, iron, and manganese can be determined at approximately the 10 ppb level to better than ± 25%. Nickel can only be determined to 100 ppb with this accuracy due to flame emission effects at the low wavelength at which nickel is measured. Chapter 3.2.3 in Volume II gives more details.

5.3 X-Ray Fluorescence

The evaluation of the literature on methods to determine total sulfur (in the form of sulfate) revealed that no rapid field method existed giving accuracies of better than 3%. X-ray fluorescence spectrometry was investigated as a possible means to determine sulfur rapidly and accurately. No literature could be found describing the application of X-ray fluorescence to the analysis of liquid samples of composition comparable to samples taken from SO_2 removal processes. In addition to sulfur, calcium, potassium, and chlorine may be determined rapidly using X-ray fluorescence spectrometry.

This section of the report presents a brief discussion of the physical basis for X-ray fluorescence spectrometry and a description of the types of instrumentation available. This section also contains the report of the experimental measurement of relevant matrix interference coefficients and the mathematical description of their application to calibration and measurement procedures. Chapters 3.3 and 4.1 of Volume II discusses the application of X-ray fluorescence in more detail.

5.3.1 Physical Phenomena

If a material is bombarded with X-rays of sufficiently high energy (short wavelength), the atoms of the material will give off characteristic X-rays. The wavelength of the emitted (fluorescent) X-rays will be characteristic of the kinds of atoms (elements) in the material, and the intensity of a given wavelength will indicate the concentration of that particular element. Then by measuring the intensity of the fluorescent X-radiation at different wavelengths it is possible to determine the elements present in a given material and their

concentrations. Absorption of the fluorescent radiation by the sample or secondary fluorescent effects are potential sources of error and are discussed later.

5.3.2 Description of Available Equipment

In conventional X-ray fluorescence instruments, the fluorescent radiation is dispersed so that the angle of dispersion is dependent upon the wavelength. X-ray detectors are used to determine the intensity of the radiation at each angle. X-ray dispersion is usually accomplished by directing the X-rays onto a crystal which acts in the same way as a diffraction grating.

Energy dispersive X-ray fluorescence utilizes a semiconductor detector which responds linearly to the energy of the incoming X-ray and a multichannel analyzer which sorts the resulting voltage pulses according to height and counts the number of pulses in each energy band to produce a complete energy spectrum of the X-rays. Such systems do not have as much resolution as wavelength dispersive instruments, and if radioactive elements are used as sources of existing radiation, they are not as sensitive to low concentrations of elements in the sample. This type of instrument was not tested for this application.

5.3.3 Preliminary Tests

Wavelength dispersive instruments are available which measure one element after another (sequential) or which measure several elements simultaneously (multichannel).

Instruments of both types were tested in the manufacturers' laboratories using simulated scrubbing liquors. The multi-channel instrument yielded more precise analyses for chlorine. The sequential instrument yielded more precise analyses for sulfur and calcium. The precision of potassium analyses was comparable on the two instruments. Sulfur and calcium were the elements for which the more accurate analyses were required; therefore, the sequential instrument was chosen as being more suitable for this particular application.

5.3.4 Description of Sequential Instrumentation

The spectrometer arrangement for the sequential X-ray spectrometer chosen is shown in Figure 5-1. The sample to be analyzed is irradiated from below; the excited characteristic X-radiation is collimated by a Soller slit and reflected at the analyzer crystal at various angles, depending on the wavelength (Bragg reflection condition). The intensity of a spectral line is measured by the proportional counters and the associated electronics. The wavelength to be counted is set for each element in a given sample in sequence. A given analyzing crystal can cover only a finite wavelength range so for large wavelength changes one crystal must be replaced by another. The angle setting mechanism is continuously variable and by careful choice of crystals a large number of elements may be determined.

The system chosen was operated manually for determination of matrix interference coefficients (described below). Before installation at Shawnee a minicomputer and data acquisition system were interfaced with the X-ray fluorescence spectrometer system so that operation of the spectrometer system was controlled by the computer and data reduction was automatic.

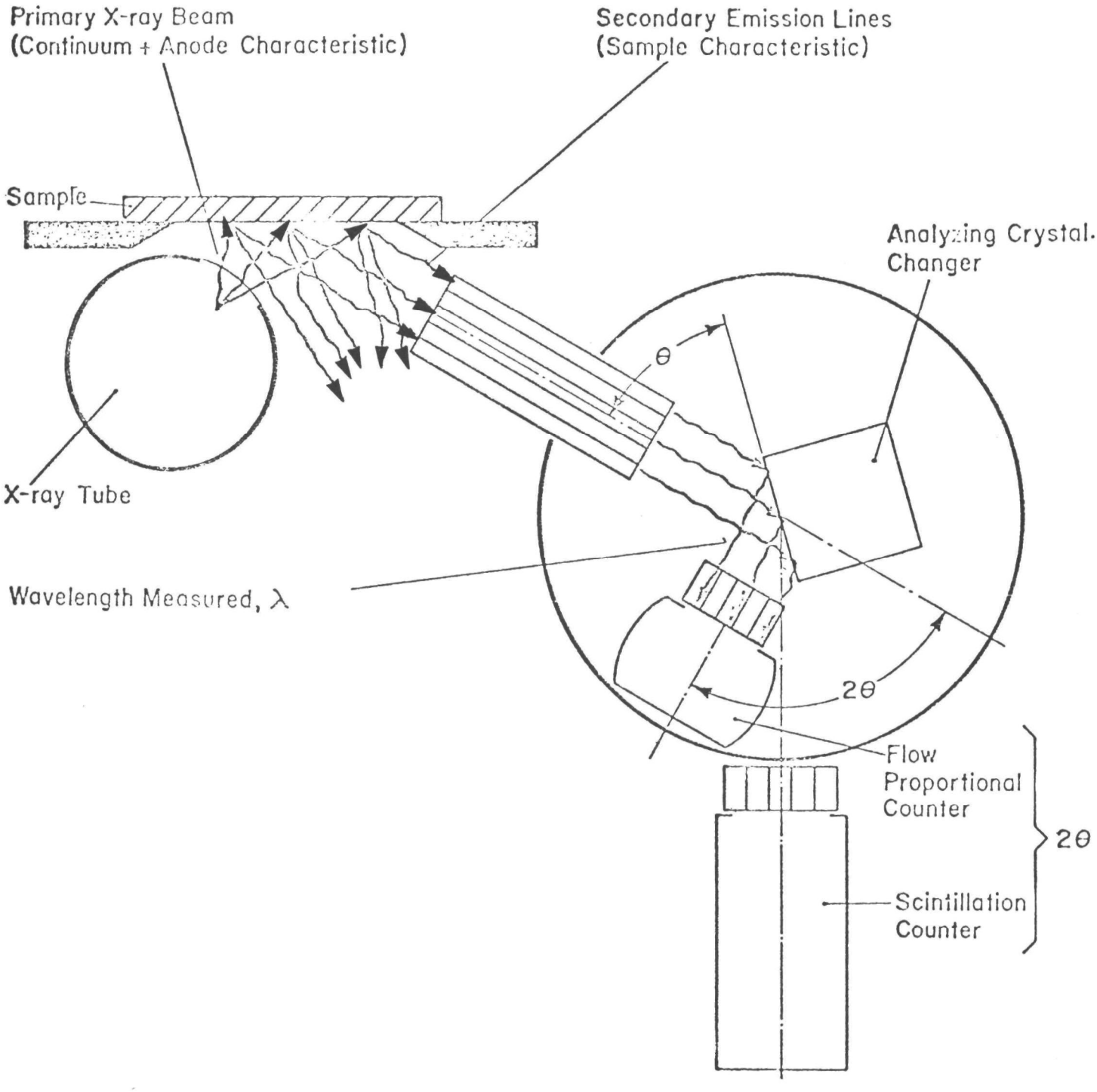

FIGURE 5-1 - BEAM PATH IN THE SEQUENTIAL X-RAY SPECTROMETER

5.3.5 Matrix Interference Corrections

Quantitative X-ray fluorescence analysis, as with most other analytical procedures, is subject to interferences. The intensity of the fluorescent radiation of element i can be reduced or increased by another element j present in the sample. Reduction of intensity is caused by absorption effects and increased intensity is observed if secondary excitation occurs. In the analysis of SO_2 scrubbing liquors, absorption effects are the dominant interfering phenomena and secondary excitation effects can be neglected if they are present at all.

Figure 5-2 is a plot of counting rate versus concentration of chlorine in the presence of varying amounts of sulfur. The error bars represent counting errors for individual measurements. The equations for the lines were obtained using the non-linear least squares program outlined later in this section.

The general equation relating concentrations of interfering elements to the observed intensities may be written:

$$N_i = a_i + b_i c_i \exp^{-\sum_j k_{ij} c_j} \qquad (5\text{-}2)$$

where the i subscripts refer to the element being measured and the j subscripts to the interfering elements. The definitions of the terms in this equation are listed below.

N_i = the counting rate for fluorescent radiation for the element i as calculated from number of counts and the time required to obtain those counts (counts/sec). The counting rate is the instrumental measure of the intensity of the fluorescent radiation.

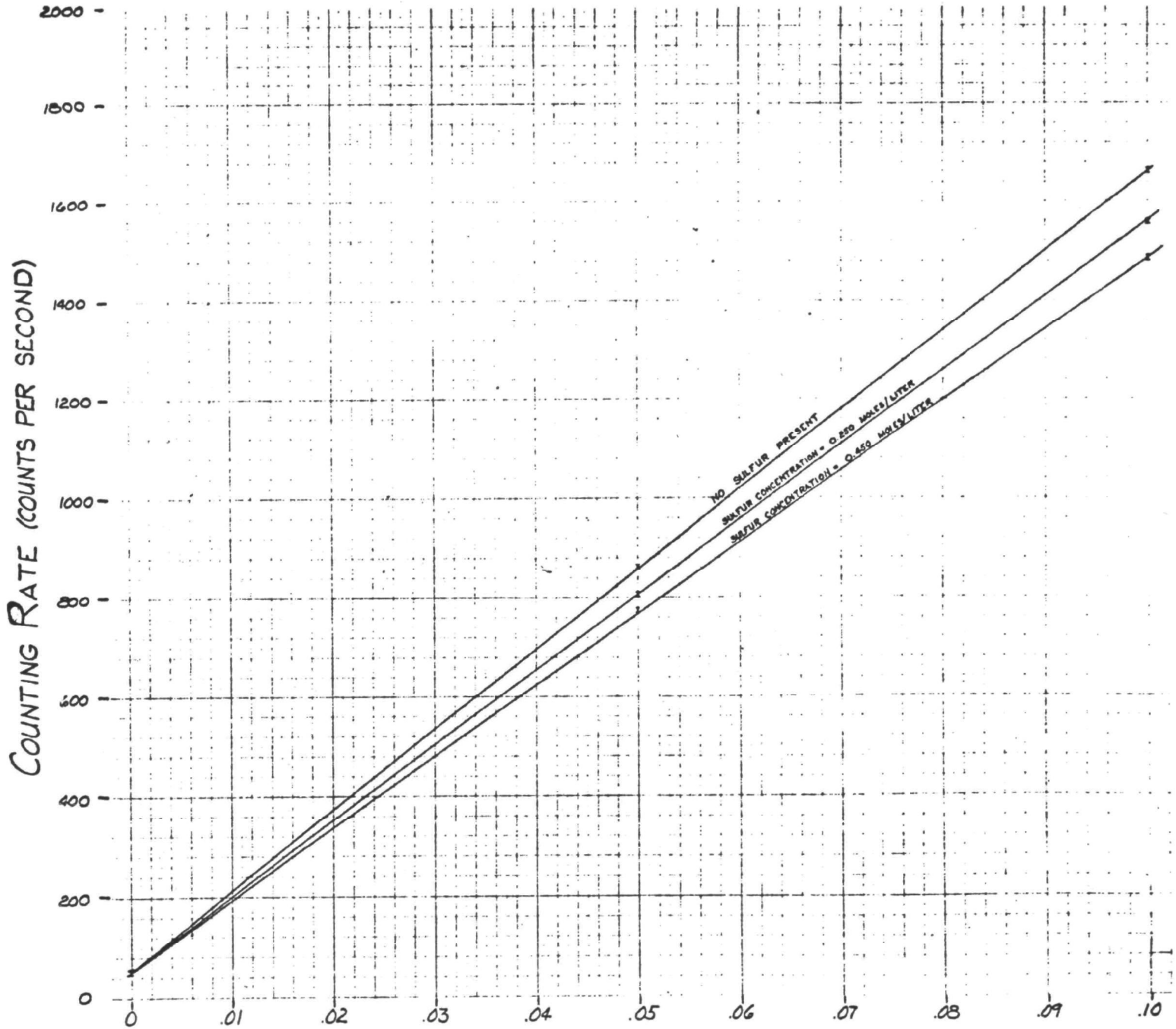

FIGURE 5-2 - CONCENTRATION OF CHLORINE (MOLES PER LITER)

a_i = the intercept of the calibration line. It is the counting rate at the setting for measuring element i when no element i is present in the sample (counts/sec).

b_i = the slope of the calibration line for element i when no interfering elements are present $\left(\frac{\text{counts/sec}}{\text{moles/liter}}\right)$

c_i = the concentration of element i in the sample measured (moles/liter).

k_{ij} - matrix interference coefficient for j as the interfering element when element i is being measured (liters/mole).

c_j = The concentration of interfering element j (moles/liter).

Reliable literature values for the matrix interference coefficients (k_{ij}) were not available. Matrix interference coefficients of importance in analyzing lime/limestone scrubber liquors were determined as part of the in-house testing and preparation of the sequential X-ray fluorescence system.

Matrix interference coefficients were determined using solutions containing known concentrations of interfering elements as well as known concentrations of the element being measured. In the simplest case, three solutions were used which had the following concentration specifications. One solution would contain no element i. Measurement of the fluorescent

intensity of this solution would determine a_i. The other two solutions would contain equal amounts of element i but different amounts of element j, the interfering element. Practical considerations (prevention of the formation of a precipitate or a volatile species) dictated that in some cases more than one interfering element had to be present. In practice there were never more than three interfering elements present. We now let the subscript j stand for the element, the effect of which we are trying to measure, and the subscripts ℓ and p indicate other interfering elements which may be in solution. If appropriate substitutions are made into Equation (5-2), the resulting equations solved simultaneously and rearranged we obtain:

$$k_{ij} = \frac{\ln\left(\frac{N_{i1} - a_i}{N_{i2} - a_i}\right) - k_{i\ell}\left(c_{\ell 2} - c_{\ell 1}\right) - k_{ip}\left(c_{p2} - c_{p1}\right)}{c_{j2} - c_{j1}} \qquad (5\text{-}3)$$

Equation (5-3) is the basic equation used to calculate all the values of k_{ij} which were obtained by measurements on three solutions.

Matrix interference coefficients were determined for the four elements to be measured by X-ray fluorescence, sulfur, chlorine, potassium, and calcium as element i. Interfering elements were taken to be nitrogen, sodium, magnesium, sulfur, chlorine, potassium, calcium. The self-interference of an element (k_{ii}) was found to be zero in the concentration range of interest. Typically, three determinations of each matrix interference coefficient were made by the method outlined above.

In order to obtain more accurate data for certain key interactions and for those systems which for practical reasons did not contain large excesses of the interfering element,

several sets of data were taken using 10-16 known solutions. The data for these solutions were correlated using a computer to perform a non-linear least squares program which calculated the coefficients a_i, b_i, and k_{ij} (Equation 5-2) iteratively so as to minimize the error between observed counting rates and counting rates calculated using the coefficients and known concentrations. Mathematical details and computer printouts are given in Section 3.3.4.4, Volume II of this report.

5.3.6 Summary of Selected Values for Matrix Interference Coefficients and Associated Uncertainties

The selected values of k_{ij} are listed in Table 5-5. In cases where least squares values are available, they are used. In some cases the average of two least squares calculations was chosen. If sets of least squares data were not available, then averages of the values obtained on sets of three solutions were selected. These are the values which are used in the Shawnee data handling computer program to calculate matrix corrections.

Table 5-5 lists the errors to be expected for a solution of a composition which might reasonably be found at Shawnee. The sixth column lists the errors if matrix interference corrections are neglected at all, and the last column the uncertainties of the results caused by errors of the k_{ij}'s.

5.3.7 Calibration Procedures for X-Ray Fluorescence Spectrometry

Referring back to Equation (5-2), we note that counting rates that are measured, N_i, are related not only to the

TABLE 5-5

SUMMARY OF ERRORS TO BE EXPECTED IN CONCENTRATION MEASUREMENTS IF MATRIX INTERFERENCES ARE IGNORED AND OF UNCERTAINTIES IN CONCENTRATION MEASUREMENTS DUE TO UNCERTAINTY IN VALUES OF k_{ij}

Element Measured i	Interfering Element j	Concentration of Measured Element i (moles/liter)	Concentration of Interfering Element j (moles/liter)	Value of k_{ij} Used	% Relative Error in Concentration Measurement if Matrix Correction is Ignored	Uncertainty in Value of k_{ij}	% Relative Uncertainty in Concentration Measurement of Element i Due to Uncertainty in k_{ij}
Limestone System							
S	N	.025	.002	.03*	.008	.01	.003
S	Na	.025	.001	.05	.005	.01	.001
S	Mg	.025	.017	.10*	.17	.02	.04
S	Cl	.025	.025	.009*	.025	.005	.01
S	K	.025	.001	.01	.001	.01	.001
S	Ca	.025	.020	.1**	.2	.1	.2
Totals for Sulfur					.4		.3
Cl	N	.025	.002	.02	.004	.02	.004
Cl	Na	.025	.001	.08	.008	.01	.001
Cl	Mg	.025	.017	.11	.2	.04	.008
Cl	S	.025	.025	.26*	.65	.01	.02
Cl	K	.025	.001	.03	.003	.01	.001
Cl	Ca	.025	.020	.2*	.4	.2	.4
Totals for Chlorine					1.3		.4
K	N	.001	.002	.03	.006	.01	.002
K	Na	.001	.001	.08	.008	.02	.002
K	Mg	.001	.017	.11	.2	.04	.11
K	S	.001	.025	.28	.8	.01	.03
K	Cl	.001	.025	.26	.65	.01	.025
K	Ca	.001	.020	.08	.18	.04	.08
Totals for Potassium					1.8		.3
Ca	N	.020	.002	.03*	.006	.01	.002
Ca	Na	.020	.001	.08	.008	.01	.001
Ca	Mg	.020	.017	.09*	.15	.03	.05
Ca	S	.020	.025	.3**	.9	.2	.6
Ca	Cl	.020	.025	.29**	.72	.03	.05
Ca	K	.020	.001	.41	.04	.06	.006
Totals for Calcium					1.8		.7
Sodium Carbonate System							
S	Na	.015	.035	.05	.18	.01	.03

* Obtained by non-linear least squares calculation using at least 10 data points. (Tables 3.3-8 - 3.3-20)

** Average of 2 values obtained from non-linear least squares calculations on 2 sets of data points.

(Estimated concentrations for limestone runs were obtained from data for Colbert Steam Plant Pilot Unit - October, 1971. The concentrations listed are approximately ½ the maximum concentration found for a given element. Thus, a dilution of approximately 1:1 is assumed in line with the standard procedure for obtaining type X samples.)

concentration of the element for which the analysis is run, c_i, the concentration of interfering species, c_j, and the matrix interference coefficient, k_{ij}, but also to a_i and b_i which are respectively the intercept and slope of the calibration line. These last two parameters are dependent not only on the settings and characteristics of the entire X-ray excitation and measuring system but also on the characteristics of the individual plastic membrane used as a window on the bottom of the sample cup.

Measurements on sulfuric acid solutions using a set of nine hostaphane membranes revealed significant variation from one membrane to the next. The necessity of calibrating each plastic membrane was established.

Calibration will also be required if any change is made in the settings of the X-ray excitation and measuring system. In normal field operation this is likely to occur when the P-10 gas used in the flow proportional counter is changed or in the instances of instrumental failure and subsequent repairs.

The following calibration procedure is recommended. For a given membrane all elements will be calibrated at once. Two to four calibrating solutions each containing different amounts of sulfur, chlorine, potassium, and calcium will be used. The counts obtained in analyzing deionized water determine a_i. The minimum total number of calibration solutions is three so that the calibration line may be calculated by the least squares program outlined below. Five solutions including deionized water are a practical number to establish the calibration constants.

5.3.8 Mathematical Background for Computer Calculation of Calibration Parameters for XRF System

The computer program is designed to calculate the intercept and slope of the best straight line as fitted by a least squares calculation through three to five data points. It is anticipated that each datum point will represent the counting rate for a different concentration of the element under consideration.

The program optimizes the intercept and slope in an iterative manner by minimizing the difference between the measured counting rates and those calculated from trial values of a_i and b_i and the known concentrations. Matrix interference corrections are made for the interfering elements in the calibrating solutions.

The mathematical basis for the program is given in more detail in Section 3.3.5.1 of Volume II. Details of the computer program are given in Volume III.

Detailed instructions for the preparation of suitable calibrating solutions are given in Volume II, Section 3.6, "Selected Field Methods and Data Analysis System."

5.3.9 Fluorescence Counting Rate Measurements

Referring again to Equation (5-2), we have listed the values of k_{ij} (in Table 5-5) and have outlined the method for obtaining a_i and b_i from the calibration procedure. N_i is obtained directly from the output of the X-ray measuring system, and if we can obtain values of c_j we will be in a position to calculate c_i.

The concentrations of interfering elements (the c_j's) come from two different sources. The concentrations of nitrogen, sodium, and magnesium are determined by methods other than X-ray fluorescence. These concentrations, when available, may be put into the computer and the corrections calculated directly. The concentrations of sulfur, chlorine, potassium, and calcium will usually be determined by X-ray fluorescence and their concentrations must be calculated simultaneously by an interative process. For computational purposes the interfering elements are divided into two groups. The group j = 1 through J are elements determined by XRF. The elements ℓ = j+1 through L are determined externally. The logarithm of Equation (5-2) is taken and the above definitions used.

$$\ell n \left(\frac{N_{is} - a_{is}}{b_{is}}\right) = \ell n\, c_i - \sum_j k_{ij}\, c_j$$

$$= \ell n\, c_i - \sum_{j=1}^{J} k_{ij}\, c_j - \sum_{\ell=J+1}^{L} k_{i\ell}\, c_\ell \qquad (5\text{-}4)$$

The s subscripts for N, a, and b refer to a particular sample membrane.

The set of non-linear equations obtained when known values are substituted into Equation (5-4) is solved iteratively by assuming that the corrections are small to obtain initial values, then defining an error function and minimizing it. Mathematical details are given in Section 3.3.5.2 of Volume II.

6.0 SOLID PHASE CHARACTERIZATION

The characterization of solids comprises two steps, namely (1) determination of the chemical composition and (2) crystalline phase identification. The first task is achieved by chemical analysis after dissolution of the solids, the second by use of X-ray diffraction. The problem area is discussed in detail in Section 4.0 of Volume II on pages 491-547.

6.1 Chemical Composition

The components of interest in the solids include calcium, magnesium, total sulfur, carbon dioxide, and sulfur dioxide. Total sulfate is calculated as the difference of total sulfur and sulfite sulfur.

Approximately 1 g of solid sample (dried at 75°C) is dissolved in a hydrogen peroxide, hydrochloric acid solution. The dissolution step is carried out in a stoppered flask to avoid loss of SO_2. Sulfate, sulfite, and carbonate dissolve completely under these conditions. Sulfite sulfur is oxidized to sulfate sulfur. The solution is brought to volume. Total sulfate is determined by the ion exchange alkalimetric procedure or by X-ray fluorescence. Calcium is determined by X-ray fluorescence or atomic absorption. Atomic absorption is the method of choice for magnesium.

Carbon dioxide in solids is determined by an evolution technique (see Sections 3.4.4 and 4.3.2 of Volume II). CO_2 from solids is liberated by acidifying the sample with sulfuric acid in a closed system, which includes a carbon dioxide absorber, a gas scrubber, an expansion baldder and a circulating pump.

The carbon dioxide combines with barium hydroxide solution of known normality content to form $BaCO_3$ precipitate. The excess hydroxide is titrated with standard hydrochloric acid to the phenolphthalein end point.

About 0.1 to 0.4 g of original sample is dissolved in a buffered iodine solution for sulfite determination. Excess iodine is back titrated with arsenite solution using the dead stop technique for end point determination. The procedure is described in more detail in Sections 3.5.4 and 4.3.3 of Volume II.

6.2 Phase Identification

The crystalline phases contained in the solids are identified by X-ray diffraction. The principle of X-ray diffraction techniques are summarized in Section 4.1 of Volume II.

A finely ground powder is irradiated with monochromatic X-radiation. The lattice planes of the fine crystals diffract the X-rays in a discrete direction if the Bragg equation is fulfilled.

$$n\lambda = 2d_i \cdot \sin \theta_i \qquad (6\text{-}1)$$

λ = wavelength of the incident X-ray beam (Å)

n = order of the reflection

d_i = distance between reflecting crystal planes

θ_i = reflection angle from crystal planes of distance d_i

The intensity of the diffracted radiation is a function of the atomic structure of the crystalline phase which is reflected in the atom form and structure factors. The set of lattice spacings d_i and the intensity of the diffracted lines is unique for each distinct crystalline phase and is used for phase identification of unknown material.

The instrumentation used to record the X-ray pattern is either a powder camera (Debye-Scherrer method) or a goinometer.

Section 4.1.3 of Volume II shows the X-ray patterns of the following phases potentially present in solids from lime/limestone wet scrubbing processes.

1. CaO
2. $Ca(OH)_2$
3. $CaCO_3$ (aragonite)
4. $CaCO_3$ (calcite)
5. $CaSO_3 \cdot \frac{1}{2}H_2O$
6. $\gamma CaSO_4$ (soluble anhydride)
7. $\beta CaSO_4$ (insoluble anhydride)
8. $CaSO_4 \cdot 2H_2O$
9. $CaSO_4 \cdot \frac{1}{2}H_2O$
10. MgO
11. $Mg(OH)_2$
12. $MgCO_3 \cdot 3H_2O$
13. $MgSO_3 \cdot 3H_2O$
14. $MgSO_3 \cdot 6H_2O$
15. $CaMg(CO_3)_2$ (dolomite)
16. SiO_2 (from fly ash)

7.0 FIELD STUDIES

The sampling, sample handling, and analytical methods described in previous sections were developed and tested by analyzing data from several pilot units. Samples were collected during

- OAP in-house studies (Volume II, page 569),
- pilot plant runs at the Tidd Plant in Brilliant, Ohio (Volume II, page 573),
- pilot plant runs at Key West (Volume II, page 592),
- pilot plant studies at TVA's Colbert Steam Plant (Volume II, page 613),
- pilot plant studies at Shawnee (Volume II, page 635).

Representative results will be presented here for the pilot studies at TVA's Colbert steam plant (see Volume II for the other systems). The system arrangement at Colbert is shown in Figure 7-1. Samples were taken and analyzed at the scrubber effluent (Sample Point 2), scrubber spray (Sample Point 1), effluent hold tank F-12 overflow (Sample Point 3), and the process liquor tank F-13 (Sample Point 4). The results of the liquid and solid phase analyses are shown in Tables 7-1 through 7-3 for the liquids and Tables 7-4 through 7-6 for the solids analyses. The buildup of inerts is very small in this arrangement since most of the fly ash was removed by the raw water spray. The accuracy of the methods is reflected in the total ionic imbalance.

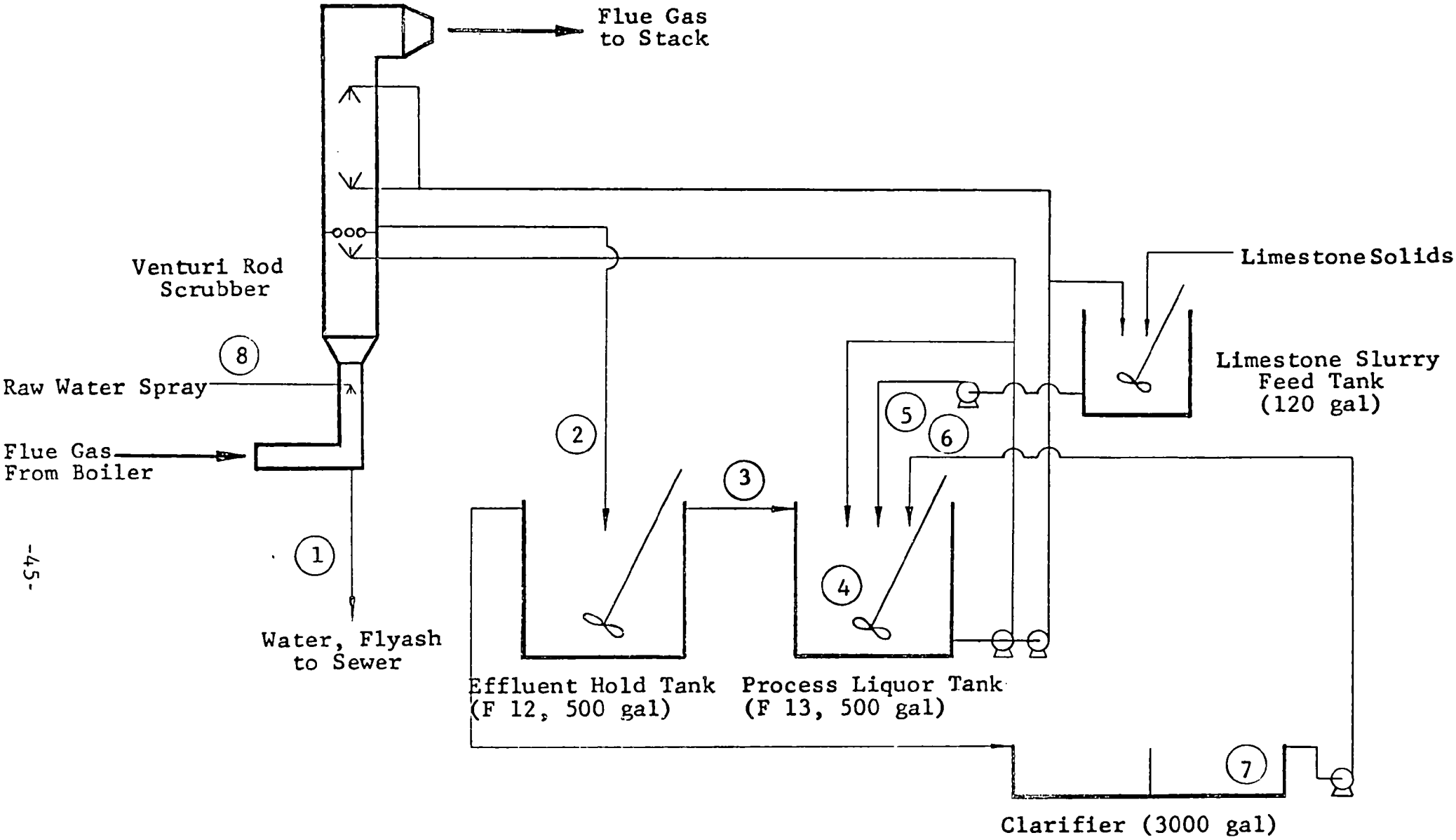

FIGURE 7-1 - TVA LIMESTONE WET SCRUBBER PILOT UNIT

TABLE 7-1

Results of Liquid Sample Analysis
Colbert Plant, Run 1 5-27-71

Sample Designation	Sample Point (See Fig. 2-1)	K	Na	Ca	Mg	Sulfite + Sulfate	Sulfite	Sulfate	CO_3	CL	Total N	NO_3	Imbalance $\Sigma m_{i_{pos}}, Zi - m_{i_{neg}}, Zi$ (m moles)	pH	Temperature (°F)
Scrubber Effluent #1	2	0.31		33.8	10.1	47.7	15.4	32.3	3.18						
Scrubber Effluent #2	2		0.56	36.0	10.5	48.8	15.9	32.9	3.75	9.0	2.73	.614	-3.95	5.31	101
Scrubber Effluent #3	2		0.56	35.2	10.7	49.4	16.2	33.2	3.70						
Scrubber Spray	1	0.11	0.23	6.40	0.26	9.25	7.0	2.25	2.48	1.3	0.67	.036	+1.42	5.42	109
F-12 Overflow #1	3	0.28	0.55	34.3	10.6	47.0	13.3	33.7	3.64						
F-12 Overflow #2	3		0.53	36.1	10.4	46.9	13.3	33.6	4.14	7.7	1.17		-2.72	5.55	101
F-12 Overflow #3	3			36.2	10.6	48.3	12.7	35.6	4.86						
F-13 Recycle #1	4	0.28	0.46	31.4	9.9	43.2	14.0	29.0	3.75						
F-13 Recycle #2	4		0.51	32.4	10.0	44.2	14.1	30.1	4.80	7.7	1.43	.551	-2.66	5.57	98
F-13 Recycle #3	4			32.2	9.7	44.0	14.0	30.0	4.25						
Clarifier Overflow #1	6	0.30	0.62	25.7	10.6	32.4	3.5	28.9	3.61						
Clarifier Overflow #2	6			26.5	11.1	33.9	3.3	30.6	5.95	8.5	1.90	.614	-2.12	6.13	89.5
Clarifier Overflow #3	6			26.2	10.9	33.4	3.3	30.1	4.55						
Limestone Feed	5	0.22	0.55	25.1	10.0	31.1	1.2	29.9	2.75	7.3	2.10	.555	-2.89	6.94	95
Raw Water	8	0.03	0.19	0.55	0.14	0.0		0.0	0.66	0.20	0.30	.025			

(Concentrations are given in m moles per liter)

TABLE 7-2

Results of Liquid Sample Analysis
Colbert Plant, Run 2 5-28-71

Sample Designation	Sample Point (See Fig. 2-1)	K	Na	Ca	Mg	Sulfite + Sulfate	Sulfite	Sulfate	CO_3	CL	Total N	NO_3	Imbalance $\sum mi_{pos}, Zi - mi_{neg}, Zi$ (m moles)	pH	Temperature (°F)
Scrubber Effluent #1	2	0.29	0.48	35.5	12.3	47.4	12.2	35.2	3.25						
Scrubber Effluent #2	2			35.3	12.3	48.0	12.2	35.8	3.98	9.6	1.73	.690	-2.21	5.52	99
Scrubber Effluent #3	2		0.48	36.2	12.5	48.5	11.8	36.7	3.39						
Scrubber Spray	1	0.16	0.27	7.10	0.34	8.92	6.2	2.72	1.42	2.1	0.40	.044	+2.36	3.38	104
F-12 Overflow #1	3	0.28	0.47	31.6	11.8	42.3	10.1	32.2	3.75						
F-12 Overflow #2	3		0.48	32.9	12.1	43.6	10.1	33.5	5.25	9.2	1.33	.678	-3.24	5.88	100
F-12 Overflow #3	3			32.0	11.9	43.2	10.1	33.1	4.93						
F-13 Recycle #1	4	0.30	0.48	30.3	11.9	40.0	6.70	33.3	3.41						
F-13 Recycle #2	4			30.5	11.9	39.6	6.40	33.2	3.75	8.7	1.10	.614	-0.66	5.68	100
F-13 Recycle #3	4			30.2	11.9	39.7	6.50	33.2	4.02						
Clarifier Overflow	6										0.95	.560			

(Concentrations are given in m moles per liter)

TABLE 7-3

Results of Liquid Sample Analysis
Colbert Plant, Run 3 5-28-71

Sample Designation	Sample Point (See Fig. 2-1)	K	Na	Ca	Mg	Sulfite + Sulfate	Sulfite	Sulfate	CO_2	CL	Total N	NO_3	Imbalance $\Sigma m_{i_{pos}}, Zi - m_{i_{neg}}, Zi$ (m moles)	pH	Temperature (°F)
Scrubber Effluent #1	2	0.28	0.49	31.6	12.2	42.4	10.3	32.1	3.07						
Scrubber Effluent #2	2		0.51	34.1	12.5	43.8	10.5	33.3	4.55	9.3	3.50	.662	-2.69	5.67	101
Scrubber Effluent #3	2		0.52	32.5	12.4	44.1	9.1	35.0	5.16						
Scrubber Spray	1	0.12	0.25	6.9	0.27	9.23	6.5	2.73	1.45	2.0	0.17		+1.78	3.19	102
F-12 Overflow #1	3	0.30	0.49	31.2	12.7	41.1	8.5	32.6	4.75						
F-12 Overflow #2	3			30.3	12.6	41.4	9.0	32.4	4.95	9.8	1.27	.723	-1.87	5.77	101
F-12 Overflow #3	3		0.50	30.8	12.9	41.7	8.7	33.0	5.75						
F-13 Recycle #1	4	0.29	0.49	29.7	12.4	39.2	5.3	33.9	3.23						
F-13 Recycle #2	4		0.48	29.9	12.7	39.0	5.6	33.4	3.93	9.2	1.23	.649	-1.12	5.96	101
F-13 Recycle #3	4		0.48	30.1	12.6	39.0	5.4	33.6	3.93						
Clarifier Overflow	6										0.94	.588			

(Concentrations are given in m moles per liter)

TABLE 7-4

Results of Solid Sample Analysis
Colbert Plant Run 1 5-27-71

Sample Designation	Sample Point (see Fig. 2.1)	Results of X-Ray Analysis	Weight of Analyzed Sample (mg)	Undissolved Solids (mg)	Slurry Concentration (g/l)	Analyses of Acid Soluble Material Concentration in m moles Per Gram of Solid								Solids Composition	
						Ca	Mg	Sulfite and Sulfate	Sulfate	Sulfite	Carbonate	Ca + Mg	Sulfate + Sulfite + Carbonate		
Scrubber Effluent	2	1. $CaCO_3$ (Calcite) 2. $CaSO_4 \cdot 2H_2O$ (Gypsum) 3. $CaSO_3 \cdot \frac{1}{2}H_2O$	982	29	143	7.97	0.50	3.91	1.07	2.84	4.09	8.47	8.00	$CaSO_3 \cdot \frac{1}{2}H_2O$ $CaSO_4 \cdot 2H_2O$ $MgCO_3$ $CaCO_3$ Insoluble Total	36.6% 18.4% 4.2% 40.6% 3.0% 102.8%
Scrubber Spray	1	1. $CaCO_3$ (Calcite) 5. $Ca(Al_2Si_2O_8) \cdot 4H_2O$ (possible) 6. SiO_2 (possible)	1003	701	12.1	2.79	0.23	.10	0.01	0.09	2.89	3.02	2.99	$CaSO_3 \cdot \frac{1}{2}H_2O$ $CaSO_4 \cdot 2H_2O$ $MgCO_3$ $CaCO_3$ Insoluble Total	1.2% 0.2% 1.9% 26.9% 69.1% 99.3%
F-12 Overflow	3	1. $CaCO_3$ (Calcite) 2. $CaSO_4 \cdot 2H_2O$ (Gypsum) 4. $CaSO_3 \cdot \frac{1}{2}H_2O$ (Also unidentified compound) major peak	993	20	99.6	8.45	0.53	2.35	0.57	1.78	6.24	8.98	8.59	$CaSO_3 \cdot \frac{1}{2}H_2O$ $CaSO_4 \cdot 2H_2O$ $MgCO_3$ $CaCO_3$ Insoluble Total	23.0% 9.8% 4.5% 61.0% 2.0% 100.3%
F-13 Recycle	4	1. $CaCO_3$ (Calcite) 2. $CaSO_4 \cdot 2H_2O$ (Gypsum) 4. $CaSO_3 \cdot \frac{1}{2}H_2O$	990	33	59.4	8.07	0.52	3.36	1.02	2.34	5.20	8.59	8.56	$CaSO_3 \cdot \frac{1}{2}H_2O$ $CaSO_4 \cdot 2H_2O$ $MgCO_3$ $CaCO_3$ Insoluble Total	30.2% 17.5% 4.4% 47.1% 3.3% 102.5%
Clarifier Overflow	6	1. $CaCO_3$ (Calcite) 2. $CaSO_4 \cdot 2H_2O$ (Gypsum) 4. $CaSO_3 \cdot \frac{1}{2}H_2O$	342	4	1.5	7.40	0.19	5.36	1.76	3.60	2.40	7.59	7.76	$CaSO_3 \cdot \frac{1}{2}H_2O$ $CaSO_4 \cdot 2H_2O$ $MgCO_3$ $CaCO_3$ Insoluble Total	46.5% 30.3% 1.6% 20.4% 1.2% 100.0%
Clarifier Bottoms	7	1. $CaCO_3$ (Calcite) 2. $CaSO_4 \cdot 2H_2O$ (Gypsum) 4. $CaSO_3 \cdot \frac{1}{2}H_2O$	1011	71	—	8.18	0.35	1.96	0.79	1.17	6.55	8.53	8.50	$CaSO_3 \cdot \frac{1}{2}H_2O$ $CaSO_4 \cdot 2H_2O$ $MgCO_3$ $CaCO_3$ Insoluble Total	15.1% 13.6% 3.0% 62.2% 7.0% 100.9%
Limestone Feed	5	1. $CaCO_3$ (Calcite) 2. $CaSO_4 \cdot 2H_2O$ (Gypsum) 4. $CaSO_3 \cdot \frac{1}{2}H_2O$ (Unidentified components present)	984	26	141	8.84	0.63	1.67	0.52	1.15	7.73	9.47	9.40	$CaSO_3 \cdot \frac{1}{2}H_2O$ $CaSO_4 \cdot 2H_2O$ $MgCO_3$ $CaCO_3$ Insoluble Total	14.8% 9.0% 5.3% 71.7% 3.0% 103.8%

TABLE 7-5

Results of Solid Sample Analysis
Colbert Plant Run 2 5-28-71

Sample Designation	Sample Point (see Fig. 2.1)	Results of X-Ray Analysis	Weight of Analyzed Sample (mg)	Weight of Undissolved Solids	Slurry Concentration (g/l)	Analyses of Acid Soluble Material Concentration in m moles Per Gram of Solid								Solids Composition	
						Ca	Mg	Sulfite and Sulfate	Sulfate	Sulfite	Carbonate	Ca + Mg	Sulfate + Sulfite + Carbonate		
Scrubber Effluent	2	1. $CaCO_3$ (Calcite) 2. $CaSO_4 \cdot 2H_2O$ 4. $CaSO_3 \cdot \frac{1}{2}H_2O$	991	66	88.0	8.17	0.49	3.06	1.02	2.04	5.43	8.66	8.49	$CaSO_3 \cdot \frac{1}{2}H_2O$ $CaSO_4 \cdot 2H_2O$ $MgCO_3$ $CaCO_3$ Insoluble Total	26.5% 17.5% 4.1% 51.1% 6.7% 105.9%
Scrubber Spray	1	1. $CaCO_3$ (Calcite) 3. $Ca(Al_2Si_2O_8) \cdot 4H_2O$ (possible) 6. SiO_2 (possible)	993	779	15.7	1.46	0.10	0.11	0.03	.08	1.44	1.56	1.55	$CaSO_3 \cdot \frac{1}{2}H_2O$ $CaSO_4 \cdot 2H_2O$ $MgCO_3$ $CaCO_3$ Insoluble Total	1.0% 0.5% 0.8% 13.5% 78.4% 94.2%
F-12 Overflow	3	1. $CaCO_3$ (Calcite) 2. $CaSO_4 \cdot 2H_2O$ 4. $CaSO_3 \cdot \frac{1}{2}H_2O$	1007	41	86.0	8.29	0.48	2.79	1.02	1.77	5.47	8.77	8.26	$CaSO_3 \cdot \frac{1}{2}H_2O$ $CaSO_4 \cdot 2H_2O$ $MgCO_3$ $CaCO_3$ Insoluble Total	22.8% 17.5% 4.0% 55.0% 4.1% 103.4%
F-13 Recycle	4	1. $CaCO_3$ (Calcite) 2. $CaSO_4 \cdot 2H_2O$ 4. $CaSO_3 \cdot \frac{1}{2}H_2O$	987	47	75.0	8.09	0.49	3.30	1.22	2.08	5.30	8.58	8.60	$CaSO_3 \cdot \frac{1}{2}H_2O$ $CaSO_4 \cdot 2H_2O$ $MgCO_3$ $CaCO_3$ Insoluble Total	26.9% 21.0% 4.1% 47.9% 4.8% 103.7%

TABLE 7-6

Results of Solid Sample Analysis
Colbert Plant Run 3 5-28-71

Sample Designation	Sample Point (see Fig. 2.1)	Results of X-Ray Analysis	Weight of Analyzed Sample (mg)	Weight of Undissolved Solids	Slurry Concentration (g/l)	Analyses of Acid Soluble Material: Concentration in m moles Per Gram of Solid								Solids Composition	
						Ca	Mg	Sulfite and Sulfate	Sulfate	Sulfite	Carbonate	Ca + Mg	Sulfate + Sulfite + Carbonate		
Scrubber Effluent	2	1. $CaCO_3$ (Calcite) 2. $CaSO_4 \cdot 2H_2O$ (Gypsum) 4. $CaSO_3 \cdot \frac{1}{2}H_2O$	1003	35	85.2	7.98	0.53	3.11	1.16	1.95	5.41	8.51	8.52	$CaSO_3 \cdot \frac{1}{2}H_2O$ $CaSO_4 \cdot 2H_2O$ $MgCO_3$ $CaCO_3$ Insoluble Total	25.2% 20.0% 4.5% 48.7% 3.5% 101.9%
Scrubber Spray	1	1. $CaCO_3$ (Calcite) 5. $Ca(Al_2Si_2O_8) \cdot 4H_2O$ (possible) 6. SiO_2 (possible)	996	784	17.2	1.52	0.09	.076	.006	0.07	1.57	1.61	1.65	$CaSO_3 \cdot \frac{1}{2}H_2O$ $CaSO_4 \cdot 2H_2O$ $MgCO_3$ $CaCO_3$ Insoluble Total	1.0% 0.1% 0.8% 14.4% 78.6% 94.9%
F-12 Overflow	3	1. $CaCO_3$ (Calcite) 2. $CaSO_4 \cdot 2H_2O$ 4. $CaSO_3 \cdot \frac{1}{2}H_2O$	1006	42	100	8.10	0.59	2.78	1.05	1.73	5.38	8.69	8.16	$CaSO_3 \cdot \frac{1}{2}H_2O$ $CaSO_4 \cdot 2H_2O$ $MgCO_3$ $CaCO_3$ Insoluble Total	22.3% 18.1% 5.0% 53.2% 4.2% 102.8%
F-13 Recycle	4	1. $CaCO_3$ (Calcite) 2. $CaSO_4 \cdot 2H_2O$ 4. $CaSO_3 \cdot \frac{1}{2}H_2O$ Unidentified Component Present in Significant Amounts	1014	44	87.9	7.85	0.51	3.44	1.40	2.04	5.00	8.36	8.44	$CaSO_3 \cdot \frac{1}{2}H_2O$ $CaSO_4 \cdot 2H_2O$ $MgCO_3$ $CaCO_3$ Insoluble Total	26.3% 24.1% 4.3% 44.1% 4.3% 103.1%

$$\text{Imbalance} = \sum (m_i \cdot z_i)_{pos} - \sum (m_i \cdot z_i)_{neg}$$

m_i = molar concentration of charged species

z_i = charge number

The pH measurements and analytical results shown in Tables 7-1 through 7-3 were used to calculate this imbalance. The imbalance should ideally be zero for zero errors in the analytical determinations. Another source of ionic imbalance is the presence of species for which no analysis was made.

The results of the solid phase analyses are presented in Tables 7-4 through 7-6. The concentrations of the solid species add up to nearly 100% with exception of the solids of the scrubber spray which contain most of the fly ash. Compounds leached from the fly ash for which no analysis was made may be responsible for the low values found.

8.0 USE OF THE RAW DATA

It was mentioned earlier that the results of the chemical analyses have no value per se. They gain their value in the chemical engineering framework within which they are used. Dominant points of interest are:

- mass transfer characteristics in the scrubber
- solid-liquid mass transfer rates
- scaling potential

Therefore, analytical results like those presented in the previous chapter must be processed further. As an example, the scaling tendency of the scrubber effluent of Run 3 given in Table 7-3 will be determined. This task is solved by considering the ionic equilibria in the aqueous phase. The results of the chemical analysis listed in Table 7-3, the pH value, and the temperature were used as inputs for computer calculations. This equilibrium program distributes the eight key species into 30 important complexes (see Table 8-1) and calculates the equilibrium partial pressures of sulfur dioxide and carbon dioxide. Individual activity coefficients are calculated using an extended Davies equation. The resulting activities of the individual ionic species for the scrubber effluent are listed in Table 8-1.

The activities of Ca^{++}, $SO_3^{=}$, and $SO_4^{=}$ are given as 7.25×10^{-3}, 1.22×10^{-4}, and 5.84×10^{-3}, respectively. The ratios of activity product to solubility product constant at 38°C for $CaSO_3 \cdot \frac{1}{2}H_2O$ and $CaSO_4 \cdot 2H_2O$ are 10.6 and 1.79, respectively.

TABLE 8-1

DISTRIBUTION ACTIVITIES OF KEY SPECIES

10 June 1971 14:41:52.539 Temperature 38.340 Deg. C

INPUT MOLES

SO_2 = 1.00-02
CO_2 = 3.07-03
SO_3 = 3.34-02 N_2O_5 = 1.75-03 CaO = 3.27-02 MgO = 1.24-02
Na_2O = 3.85-04 HCL = 9.30-03 H_2O = 5.55+01

AQUEOUS SOLUTION EQUILIBRIA

Component	Molality	Activity	Activity Coefficient
H_2O			1.0-00
H^+	2.6-06	2.1-05	8.3-01
OH^-	1.6-08	1.2-08	7.7-01
HSO_3^-	6.8-03	5.2-03	7.7-01
SO_3^{--}	3.5-04	1.2-04	3.4-01
SO_4^{--}	1.9-02	5.8-03	3.0-01
HCO_3^-	7.0-04	5.4-04	7.7-01
CO_3^{--}	4.3-08	1.5-08	3.4-01
NO_3^-	3.4-03	2.4-03	7.0-01
HSO_4^-	2.3-06	1.8-06	7.7-01
H_2SO_3	1.1-06	1.1-06	1.0+00
H_2CO_3	2.2-03	2.3-03	1.0+00
Ca^{++}	2.0-02	7.2-03	3.6-01
$CaOH^+$	3.0-09	2.3-09	7.7-01

Component	Molality	Activity	Activity Coefficient
$CaSO_3$	2.6-03	2.6-03	1.0+00
$CaCO_3$	2.0-07	2.0-07	1.0+00
$CaHCO_3^+$	1.0-04	7.8-05	7.7-01
$CaSO_4$	10.0-03	1.0-02	1.0+00
$CaNO_3^+$	7.0-05	5.4-05	7.7-01
Mg^{++}	8.0-03	2.8-03	3.5-01
$MgOH^+$	2.1-08	1.6-08	7.7-01
$MgSO_3$	3.3-04	3.3-04	1.0+00
$MgHCO_3^+$	1.9-05	1.5-05	7.7-01
$MgSO_4$	4.1-03	4.1-03	1.0+00
$MgCO_3$	1.2-07	1.2-07	1.0+00
Na^+	7.4-04	5.8-04	7.8-01
$NaOH$	1.9-12	1.9-12	1.0+00
$NaCO_3^-$	2.3-10	1.8-10	7.7-01
$NaHCO_3$	1.7-07	1.8-07	1.0+00
$NaSO_4^-$	2.5-05	1.9-05	7.7-01
$NaNO_3$	5.5-07	5.6-07	1.0+00
CL^-	9.3-03	7.1-03	7.6-01

PSO_2 = 1.46-06 ATM
PCO_2 = 9.37-02 ATM

Molecular Water = 9.99-01 KGS

Specified pH = 5.670
Ionic Strength = 1.08-01 Res. E. N. = -2.692-03

This shows that the solution is highly supersaturated with respect to $CaSO_3 \cdot \frac{1}{2}H_2O$ and moderately supersaturated with respect to $CaSO_4 \cdot 2H_2O$. These numbers will be of value in conjunction with scaling studies to define scaling tendency.

Another number of importance for engineering calculations is the partial pressure of SO_2. From Table 8-1, it is seen that P_{SO_2} in the scrubber effluent is 1.46×10^{-6} atm or about 1.5 ppm. This is a necessary input for SO_2 vapor-liquid mass transfer calculations. In similar fashion other activities can be calculated if required for the description of solid-liquid mass transfer rates.

9.0 DATA HANDLING SYSTEM

The Shawnee laboratory data analysis system is designed to perform data storage, laboratory computations, and report generation tasks associated with the laboratory operations. The system is basically a card oriented system using marked-sense card input to ease the problem of converting data to a machine readable format. In addition, the system is designed to provide automatic operation of an X-ray fluorescence spectrometer with automatic calibration and matrix corrections performed upon the results. The X-ray analysis results are entered automatically without operator intervention. The system is represented diagrammatically in Figure 9-1.

For each set of analyses defined by a time, sampling point, sample type (i.e., line out, steady-state, or exception), and run number, a data packet is created on disk to store all raw data and computed results associated with that set of analyses. After all data for that particular set of analyses has been entered into the data processing system and all calculations performed, the completed data packet is transferred by the operator from the disk to magnetic tape and by means of the line printer a hard copy is prepared. The data analysis system may be commanded to prepare sample taking schedules and sample analysis schedules.

Volume III of this report contains a detailed description of the system, including complete operating instructions. The paragraphs below give a very brief description of the hardware and software components of the system.

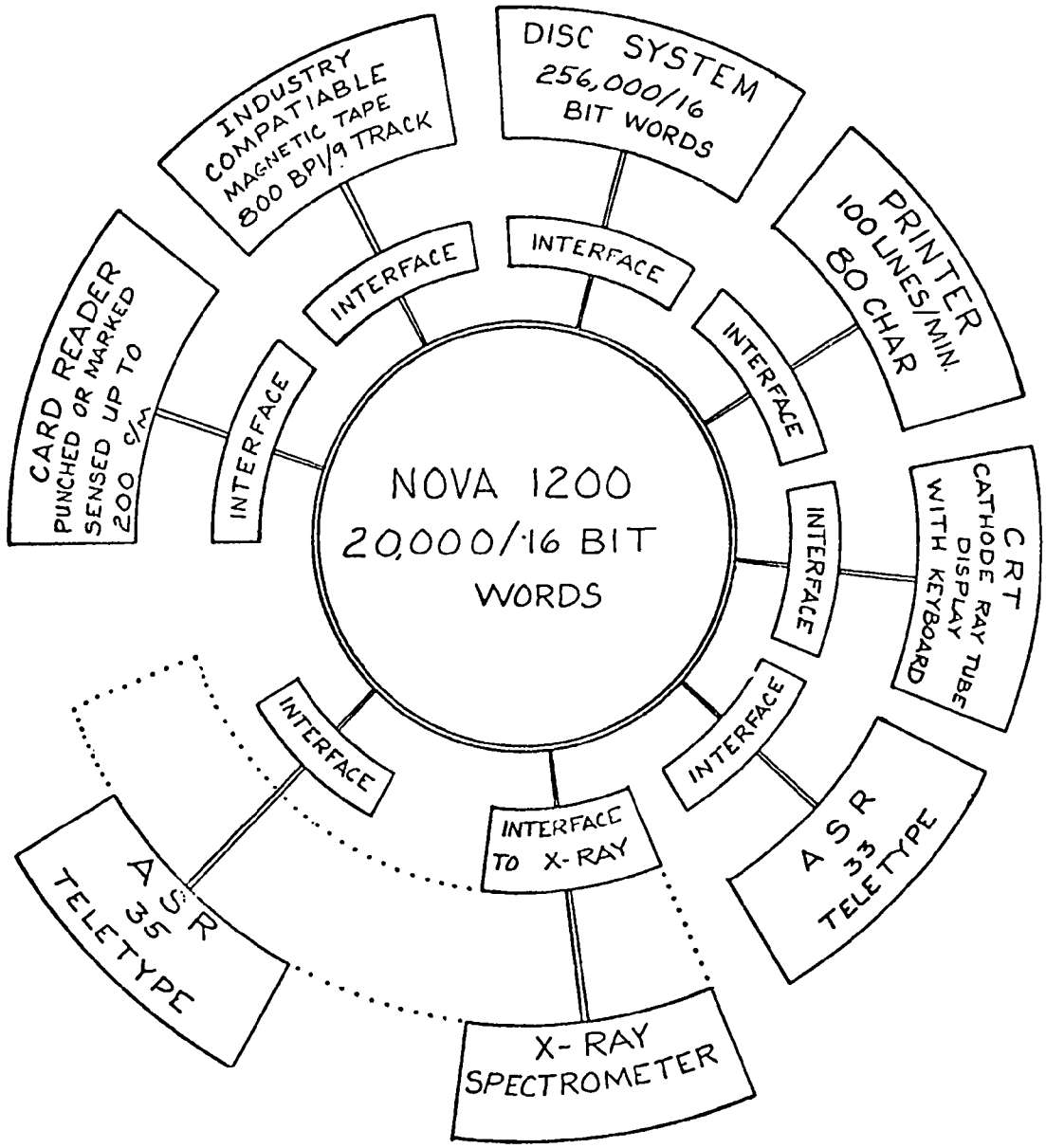

FIGURE 9-1 - LABORATORY DATA ANALYSIS SYSTEM USED AT SHAWNEE

9.1 Laboratory Data Analysis Hardware

In addition to the X-ray fluorescence spectrometer, the hardware system consists of the following major components:

Nova 1200 (20 K)/Jumbo Chassis

Fixed Head Disk (256 K)

Magnetic Tape Transport (9 track/800 BPI/10½" reels/24 IPS)

Automata Marked Sense, Punched Card Reader

ASR 33 Teletype

KSR 35 Teletype

Beehive CRT Terminal

Data Products Line Printer (80 column, 1100 LPM)

The fixed disk is used for storage of all data in data handling programs. The Beehive CRT terminal is used as the basic input/output device for the user of the data analysis system. The ASR 33 Teletype is used as a backup to the CRT and to supply the capability of the paper tape reader/punch. The KSR 35 (without paper tape feature) is included for the basic control of the X-ray equipment. As mentioned previously, the system input is basically card oriented using marked sense cards. The magnetic tape transport provides the capability of storing data on magnetic tapes for transfer to other sites as well as storage of the basic data handling system, the disk operating system with FORTRAN compiler, and diagnostic routines for the major hardware components. The line printer provides a permanent hard copy of all data.

9.2 Laboratory Data Analysis Software

The software system can be divided logically into three parts: (1) executive system, (2) application routines, and (3) diagnostic routines.

9.2.1 Executive System

The executive system for the laboratory data handling system is an extension of the vendor supplied disk operating system. The system provides comprehensive file handling capabilities and protection. The executive system allows the execution of the laboratory data system as well as program generation and development software including a FORTRAN compiler, editor, debugger, etc. The executive system retrieves appropriate files from disk storage as commanded from the user operating input device.

The executive system provides the user a variety of commands to perform the laboratory data handling. These include data input, report generation, generation of magnetic tape files, and automatic operation of the X-ray fluorescence spectrometer. Upon receiving a data input command, the system reads the data, retrieves the appropriate application programs, performs necessary calibrations and computations, and stores the raw data as well as the resultant computed values. The executive system also performs bookkeeping functions such as scheduling samples to be taken and scheduling the analysis of these samples.

9.2.2 Application Routines

The laboratory application routines actually perform the function as instructed by the executive system. The application routines are initiated under user control; however, the user is not required to insure that appropriate disk files are input into the computer memory. Most application routines are written in FORTRAN which allows easy modification if laboratory computations are changed or if new procedures are implemented in the laboratory.

9.2.3 Diagnostic Routines

This software package operates independently of the previously mentioned packages. The primary function is for trouble-shooting hardware failures to localize the equipment that is malfunctioning, and for performing preventative maintenance. These routines guide the user through series of tests on each peripheral device to check all phases of operation. The test routines may be input from any of three input devices: (1) the teletype paper tape reader, (2) the card reader, and (3) the magnetic tape unit. This allows for diagnostic testing even if one of the input units becomes inoperative. The printout for a typical set of analyses is given in Figure 9-2.

RESULTS OF SAMPLE ANALYSES

SAMPLE ID	S231	RUN NUMBER 4093-1	
SAMPLE POINT	3816	DATE 10-17-72 TIME	600

	FIELD	LABORATORY
TEMPERATURE(C)	0.0	28.0
CONDUCTIVITY	.0000E 0	.3700E 4
PH	.0000E 0	.5900E 1

SPECIES SOUGHT	METHOD	CONCENTRATION (MOLES/LITER)
LIQUIDS		
CATIONS		
CALCIUM(CA)	X-RAY	0.214501E -1
MAGNESIUM(MG)	ATOMIC ABSORPTION	0.141391E -2
SODIUM(NA2O)	ATOMIC ABSORPTION	0.543719E -3
POTASSIUM(K2O)	X-RAY	0.000000E 0
ANIONS		
SULFITES(SO2)	AMPEROMETRIC DEAD-STOP	0.476762E -3
SULFATES(SO3)	X-RAY	0.177543E -1
TOTAL SULFUR(AS SO3)	X-RAY	0.182310E -1
CARBON DIOXIDE(CO2)	NON-DISPERSIVE IR	0.213625E -2
CHLORIDES(CL)	X-RAY	0.160921E -1
SOLIDS		WT % SOLIDS
CATIONS		
CALCIUM(CAO)	X-RAY	0.314831E 2
MAGNESIUM(MGO)	ATOMIC ABSORPTION	0.101349E 1
ANIONS		
SULFITES(SO2)	AMPEROMETRIC DEAD-STOP	0.105390E 2
SULFATES(SO3)	X-RAY	0.340664E 2
TOTAL SULFUR(AS SO3)	X-RAY	0.189169E 2
CARBON DIOXIDE(CO2)	SOLID CARBON DIOXIDE	0.134229E 2
WT % SOLIDS IN SLURRY		0.686516E 1

FIGURE 9-2 - TYPICAL PRINT-OUT OF ANALYTICAL DATA

10.0 SUMMARY

The chemical analysis of the key species in lime/limestone based sulfur dioxide removal processes is the basis for the engineering evaluation of the system performance. The problem area encompasses five individual steps.

1) Sampling

2) Sample Handling

3) Sample Analysis

4) Data Processing

5) Data Evaluation

Figure 10-1 shows the methods selected to accomplish the individual tasks.

The pH and the temperature of the slurry are measured *in situ*. A positive pressure filtration system separates the liquid from the solids. The solids content of the slurry is calculated from the solid to liquid ratio.

The liquid is thermodynamically unstable and must be quenched by appropriate techniques. An aliquot is diluted in an aqueous hydrogen peroxide solution. Sulfite is oxidized and sulfate precipitation is avoided by the dilution involved. Total sulfur, calcium, chloride, potassium, sodium, magnesium, and catalytically active trace constituents such as manganese, cobalt, copper, iron, and nickel are determined in this sample using the procedures as indicated by Figure 10-1.

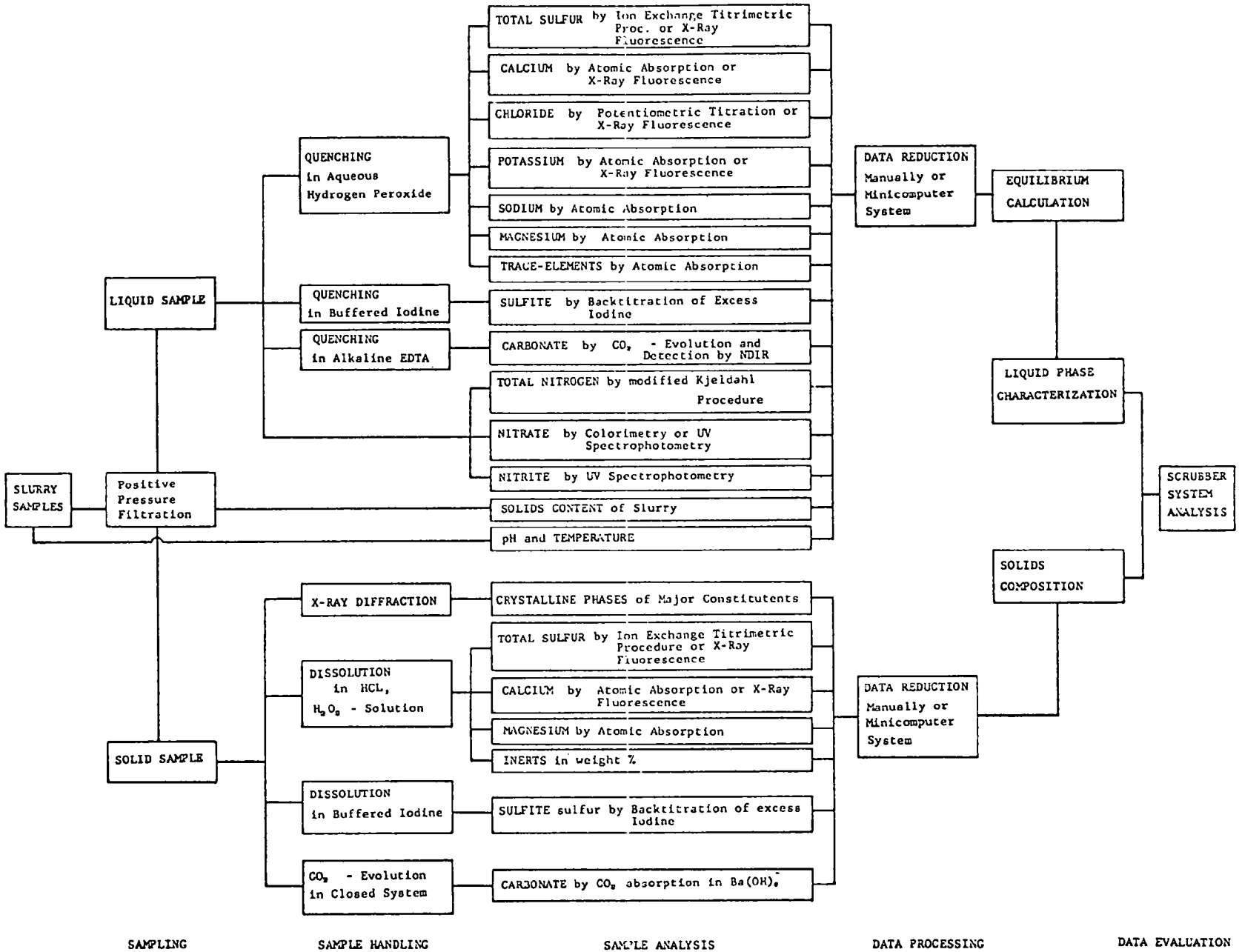

FIGURE 10-1: SCRUBBER SLURRY ANALYSIS SCHEME

A second aliquot is quenched directly in a buffered iodine solution thus avoiding any sulfite losses. Excess iodine is back-titrated using standard arsenite and a dead stop procedure for end point detection.

A sample to determine carbonate is quenched in an alkaline EDTA solution. The EDTA prevents calcium carbonate precipitation. The alkaline environment lowers the CO_2 partial pressure of the sample. The CO_2 determination involves evolution from an acidified sample and determination by a nondispersive infrared analyzer.

Total nitrogen, nitrate, and nitrite are determined by a modified Kjeldahl procedure and by ultraviolet spectroscopy. A colorimetric procedure based on the interaction of nitrate with chromotropic acid is specific for nitrate.

The X-ray fluorescence unit was interfaced with a minicomputer for rapid field measurements and data reduction. Data not measured by X-ray fluorescence are entered into the system through a card reader, a CRT or a teletype. The system stores all the data on a magnetic tape. In this fashion they can be read directly in a larger computer for chemical equilibrium calculation. A hard copy of the data is provided by the printer.

The solid sample obtained in the filtration step is processed in a similar fashion. Part of the crystals are finely powdered. Subsequent X-ray diffraction determines the crystalline phases of the major constituents.

The solid sample is dissolved prior to chemical analysis. Dilute hydrochloric acid containing hydrogen peroxide is used to dissolve approximately 1 g solids. Total sulfur, calcium,

magnesium and weight percent inerts are determined in this sample. The analytical methods are the same as those chosen for liquid sample analysis.

Sulfite is determined on a solid sample dissolved in a buffered iodine solution. Excess iodine is back-titrated with arsenite solution and a dead stop technique for end point detection.

The carbonate analysis is performed by dissolving a solid sample in sulfuric acid in a closed system. The evolved CO_2 is absorbed in barium hydroxide solution. Excess barium hydroxide is back-titrated to the phenolphthalein end point. The data processing in the field is done by the minicomputer and the peripheral devices.

The analysis scheme was checked and developed by sampling and analysis of several pilot plants. They included the OAP in-house test facility and pilot plants at the Tidd Plant, Key West, Colbert Steam Plant, and at Shawnee.

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TECHNICAL REPORT DATA
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16. ABSTRACT The report gives results of a study to develop appropriate sampling and analytical methods to be used at EPA's test facility at Shawnee. Three problem areas developed in analyzing the thermodynamically unstable slurry streams encountered in lime/limestone-based SO2 wet scrubbing processes: sampling, sample handling, and chemical analysis. Positive-pressure filtration was found to lower the mass transfer phenomena during the filtration step to an acceptable level. Quenching of the filtered liquid was chosen to avoid changing sample composition. Two sets of analytical methods were selected for application at Shawnee: the back-up methods are based on atomic absorption and wet chemical procedures; and the rapid field methods are based on X-ray fluorescence, atomic absorption, and wet chemical analysis. The X-ray fluorescence spectrometer was automated by interfacing it with a NOVA 1200 minicomputer. Additional peripheral devices have the function of processing all raw data. The raw data are input to the system with a card reader, a teletype, or a CRT. The final results are stored on a magnetic tape. A hard copy is provided by a printer.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS		b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Air Pollution	Sulfur Oxides	Air Pollution Control	13B
Sampling	Desulfurization	Stationary Sources	14B
Analyzing	Scrubbers	Atomic Absorption	7B
Slurries	X-Ray Fluorescence		20F
Calcium Oxides	Automation		7A
Limestone	Spectrometers		8G

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