

## INFORMATION TO USERS

This reproduction was made from a copy of a document sent to us for microfilming. While the most advanced technology has been used to photograph and reproduce this document, the quality of the reproduction is heavily dependent upon the quality of the material submitted.

The following explanation of techniques is provided to help clarify markings or notations which may appear on this reproduction.

1. The sign or "target" for pages apparently lacking from the document photographed is "Missing Page(s)". If it was possible to obtain the missing page(s) or section, they are spliced into the film along with adjacent pages. This may have necessitated cutting through an image and duplicating adjacent pages to assure complete continuity.
2. When an image on the film is obliterated with a round black mark, it is an indication of either blurred copy because of movement during exposure, duplicate copy, or copyrighted materials that should not have been filmed. For blurred pages, a good image of the page can be found in the adjacent frame. If copyrighted materials were deleted, a target note will appear listing the pages in the adjacent frame.
3. When a map, drawing or chart, etc., is part of the material being photographed, a definite method of "sectioning" the material has been followed. It is customary to begin filming at the upper left hand corner of a large sheet and to continue from left to right in equal sections with small overlaps. If necessary, sectioning is continued again—beginning below the first row and continuing on until complete.
4. For illustrations that cannot be satisfactorily reproduced by xerographic means, photographic prints can be purchased at additional cost and inserted into your xerographic copy. These prints are available upon request from the Dissertations Customer Services Department.
5. Some pages in any document may have indistinct print. In all cases the best available copy has been filmed.

**University  
Microfilms  
International**

300 N. Zeeb Road  
Ann Arbor, MI 48106



**Order Number 1333261**

**Tailings pond seepage and sulfate equilibrium in the Pima  
Mining District, Pima County, Arizona**

**Scovill, Georgia Lynn, M.S.**

**The University of Arizona, 1988**

**U·M·I**

**300 N. Zeeb Rd.  
Ann Arbor, MI 48106**



**PLEASE NOTE:**

In all cases this material has been filmed in the best possible way from the available copy. Problems encountered with this document have been identified here with a check mark .

1. Glossy photographs or pages \_\_\_\_\_
2. Colored illustrations, paper or print \_\_\_\_\_
3. Photographs with dark background \_\_\_\_\_
4. Illustrations are poor copy \_\_\_\_\_
5. Pages with black marks, not original copy \_\_\_\_\_
6. Print shows through as there is text on both sides of page \_\_\_\_\_
7. Indistinct, broken or small print on several pages
8. Print exceeds margin requirements \_\_\_\_\_
9. Tightly bound copy with print lost in spine \_\_\_\_\_
10. Computer printout pages with indistinct print \_\_\_\_\_
11. Page(s) \_\_\_\_\_ lacking when material received, and not available from school or author.
12. Page(s) \_\_\_\_\_ seem to be missing in numbering only as text follows.
13. Two pages numbered \_\_\_\_\_. Text follows.
14. Curling and wrinkled pages \_\_\_\_\_
15. Dissertation contains pages with print at a slant, filmed as received \_\_\_\_\_
16. Other \_\_\_\_\_  
\_\_\_\_\_  
\_\_\_\_\_





TAILINGS POND SEEPAGE AND SULFATE EQUILIBRIUM  
IN THE PIMA MINING DISTRICT, PIMA COUNTY, ARIZONA

by

Georgia Lynn Scovill

---

A Thesis Submitted to the Faculty of the  
DEPARTMENT OF HYDROLOGY AND WATER RESOURCES  
In Partial Fulfillment of the Requirements  
For the Degree of

MASTER OF SCIENCE  
WITH A MAJOR IN HYDROLOGY

In the Graduate College

UNIVERSITY OF ARIZONA

1 9 8 8

## STATEMENT BY AUTHOR

This thesis has been submitted in partial fulfillment of requirements for an advanced degree at The University of Arizona and is deposited in the University Library to be made available to borrowers under rules of the Library.

Brief quotations from this thesis are allowable without special permission, provided that accurate acknowledgment of source is made. Requests for permission for extended quotation from or reproduction of this manuscript in whole or in part may be granted by the head of the major department or the Dean of the Graduate College when in his or her judgement the proposed use of the material is in the interests of scholarship. In all other instances, however, permission must be obtained from the author.

SIGNED: Georgia Lynn Scovill

## APPROVAL BY THESIS DIRECTORS

This thesis has been approved on the date shown below:

R. L. Bassett  
R. L. Bassett  
Associate Professor  
Hydrology and Water Resources

4/22/88  
Date

J. F. Arttola  
J. F. Arttola  
Assistant Research Scientist  
Soil and Water Sciences

4/22/88  
Date



## ACKNOWLEDGMENTS

I would like to express my sincere gratitude to the individuals who generously gave of their time and talent to help make this thesis work reality. First I wish to thank Dr. M.M. Minnich who envisioned the initial research, and employed me as her research assistant. Second, I want to thank Dr. J.F. Artiola, Dick Ackley, and Dr. D.M. Hendricks for their assistance in performing numerous laboratory analyses, and Dr. R.L. Bassett for his assistance with the computer modeling.

In addition, special appreciation is extended to the members of my thesis committee: Drs. R.L. Bassett, J.F. Artiola, and S.N. Davis for their helpful suggestions in writing this manuscript. I thank the entire Department of Soil and Water Science for funding my research assistantship, secretaries Reva Falk and Jan Raffler for their endless expertise and instruction in word processing, and Priscilla Sheets for drafting the maps.

Finally, I wish to thank my instructors at the University of Arizona, my friends, and my family for helping me achieve a higher education.

## TABLE OF CONTENTS

	Page
LIST OF ILLUSTRATIONS . . . . .	6
LIST OF TABLES . . . . .	7
ABSTRACT . . . . .	8
1. INTRODUCTION . . . . .	9
Purpose and Scope of Study . . . . .	9
Location, Physiography, Climate . . . . .	10
Mining Development . . . . .	11
Ore Processing . . . . .	15
2. GEOHYDROLOGY OF THE PIMA MINING DISTRICT . . . . .	17
Geologic Setting . . . . .	17
Geology of the Mountains . . . . .	17
Sedimentary Units in the Basin . . . . .	19
Hydrologic Conditions . . . . .	21
Flow Patterns of the Surface and Ground Water . . . . .	21
Ground Water Quality . . . . .	23
3. ANAEROBIC CHAMBER EXPERIMENT . . . . .	25
Introduction . . . . .	25
Impact of Mining Activity . . . . .	25
Water Movement in Tailings Ponds . . . . .	26
Aquatic Chemistry of Tailings Impoundments . . . . .	27
Research Goals . . . . .	29
Methods . . . . .	31
Collection of Field Samples . . . . .	31
Experimental Set-Up . . . . .	31

TABLE OF CONTENTS--Continued

	Page
Chemical Analysis . . . . .	33
Results and Discussion . . . . .	36
4. EQUILIBRIUM MODELING OF SELECT WATER CHEMISTRIES . . . . .	44
Purpose and Goals . . . . .	44
Methods . . . . .	45
Results and Discussion . . . . .	48
5. SUMMARY AND CONCLUSIONS . . . . .	54
APPENDIX A: WELL NUMBERING SYSTEM . . . . .	58
APPENDIX B: WATER QUALITY DATA - UPPER SANTA CRUZ GROUND WATER BASIN . . . . .	61
APPENDIX C: WATER QUALITY DATA - TAILINGS PONDS IN THE PIMA MINING DISTRICT . . . . .	73
LITERATURE CITED . . . . .	75

## LIST OF ILLUSTRATIONS

Figure	Page
1. Location of the Pima mining district . . . . .	12
2. Geologic map of part of the Pima mining district . . . . .	14
3. Plate 1 - Water Level Elevation . . . . .	in pocket
4. Plate 2 - Anhydrite Saturation Indecies . . . . .	in pocket
5. Plate 3 - Calcite Saturation Indecies . . . . .	in pocket
6. Plate 4 - Fluorite Saturation Indecies . . . . .	in pocket
7. Plate 5 - Gypsum Saturation Indecies . . . . .	in pocket

## LIST OF TABLES

Table	Page
1. Temperature, redox, pH, and electrical conductivity of water from a tailings pond in the Pima mining district . . .	32
2. Identification of water and treatments in anaerobic chamber . . . . .	34
3. Temperature, redox, pH, and electrical conductivity of liquid samples in the anaerobic chamber . . . . .	38
4. Chemical composition of water samples from the anaerobic chamber experiment . . . . .	41
5. Chemical composition of water collected from tailings ponds in the Pima mining district . . . . .	42
6. Elemental composition of tailings solids . . . . .	43
7. Mineral saturation indecies ( $\log(IAP/KT)$ ) generated by PHREEQE for select water chemistries in the Pima mining district . . . . .	49

## ABSTRACT

Mining activity in the Pima mining district has been suspected of contributing sulfate and total dissolved solids to ground water downgradient of the mines. High concentrations of various ions in tailings impoundments suggest that tailings-pond recharge may be a source of the contamination.

Tailings slurry was used in an experiment which indicated that significant quantities of sulfate are not produced in the tailings ponds due to inorganic oxidation of sulfide minerals by aqueous Fe(III) and/or Mn(IV). Water quality of the tailings ponds was compared with historical water quality analyses in the Pima district. The U.S. Geological Survey computer program PHREEQE was then used to model mineral saturation indices for anhydrite, calcite, fluorite, and gypsum in water chemistries throughout the study area. Patterns showing water in wells downgradient of the mines to be progressively less saturated, or more undersaturated, than water in the tailings ponds with respect to these four minerals rule out the claim that tailings pond recharge is acquiring salts as it percolates to the aquifer. The evidence supports the opposing argument that tailings pond seepage is contributing to the sulfate and total dissolved solids content in ground water downgradient of the ponds.

## CHAPTER 1

### INTRODUCTION

#### Purpose and Scope of Study

Tailings pond water from the Pima mining district was first monitored in an investigation in the early 1970's which revealed elevated TDS (total dissolved solids), sulfates, calcium, molybdenum and in some cases, high cyanides (Engineers Testing Laboratories, 1973). Subsequent analyses by Thurnblad (1982) and this study confirmed the presence of high levels of TDS, sulfate, and calcium in tailings water.

Ground water quality data collected in the early 1970's by the U.S. Geological Survey showed increased concentrations of sulfate and TDS downgradient of the tailings ponds. Two other studies by W.A. Wahler and Associates (1973), and Hail (1974) found ground water which exceeded suggested Arizona State sulfate and TDS drinking water limits in three out of four monitor wells drilled at the bases of four different tailings ponds. The high sulfate and TDS levels in the tailings ponds suggests that they may be a source of the degraded water found in the downgradient wells.

The purpose of this study is to investigate the impact of tailings pond seepage on the quality of ground water downgradient of the mines in the Pima mining district. The primary focus is upon the dissolved sulfate content of the tailings pond water which is suspected of contributing to sulfate contamination in ground water downgradient of

the mines. A laboratory experiment was performed (Chapter 3) to test whether pyrite oxidation may occur without microbial catalysis in water-saturated tailings and if hematite and birnessite are sufficiently soluble under slightly acidic conditions to furnish Fe(III) and Mn(IV) ions as oxidants for reduced sulfur minerals in carbonate-buffered tailings impoundments in the Pima mining district. Geochemical modeling of mineral saturation indices using the U.S. Geological Survey computer program PHREEQE was performed (Chapter 4) to determine the importance of anhydrite, calcite, fluorite, and gypsum in controlling the water chemistry of the study area.

Research into the oxidation of sulfide minerals in massive-sulfide mining districts and the geochemical equilibrium of sulfate in the local environment can help identify the source(s) of sulfate contamination associated with mining activity and thereby facilitate implementation of effective control measures to prevent further ground water degradation.

#### Location, Physiography, Climate

The area of interest for this study lies within a six quadrangle block delineated by townships 16, 17, and 18 south, and ranges 12 and 13 east. Centered in this area and approximately 24 to 48 km south of Tucson, Arizona, is the Pima mining district, one of the world's premier porphyry copper deposits (Fig. 1).

The study area lies within the southern portion of the Tucson basin. The Tucson basin is a broad northwest trending alluvial valley



in the Basin and Range physiographic province. The Sierrita Mountains, Black Mountain, and the Tucson Mountains bound the basin to the west. The Santa Rita, Empire, Rincon, and Tanque Verde Mountains form the eastern boundary. The Tucson basin encompasses 2590 square kilometers of the Upper Santa Cruz River drainage area, is about 80 km long, and 24 to 32 km wide in the southern and central parts (Davidson, 1973).

The climate in the study area is typical of the semiarid Sonoran Desert. The mean annual temperature in Tucson is 19.6 degrees Celsius (67.3 °F) with the highest mean monthly temperature occurring in July (30.1 °C), and the lowest in January (10.0 °C). Potential pan evaporation is greater than 203 centimeters per year or nearly seven times the annual precipitation of about 30.5 cm per year in the Tucson area. Rainfall occurs as either high intensity thunderstorms from July to September or long duration frontal storms from December to March (Laney, 1972). The major streams are ephemeral and dry during more than 300 days each year. Flows due to rainfall generally last three days or less, whereas flows generated by snowmelt from the surrounding mountains may last somewhat longer.

#### Mining Development

The Pima mining district may be one of the oldest known mineral-bearing regions in the United States with a history that dates back to the first visit by the Jesuits near the turn of the 17th century (Titley, 1981). By 1872, the first mining claim, the San Xavier, was filed in Arizona territory (Langlois, 1978). Five years later the district was

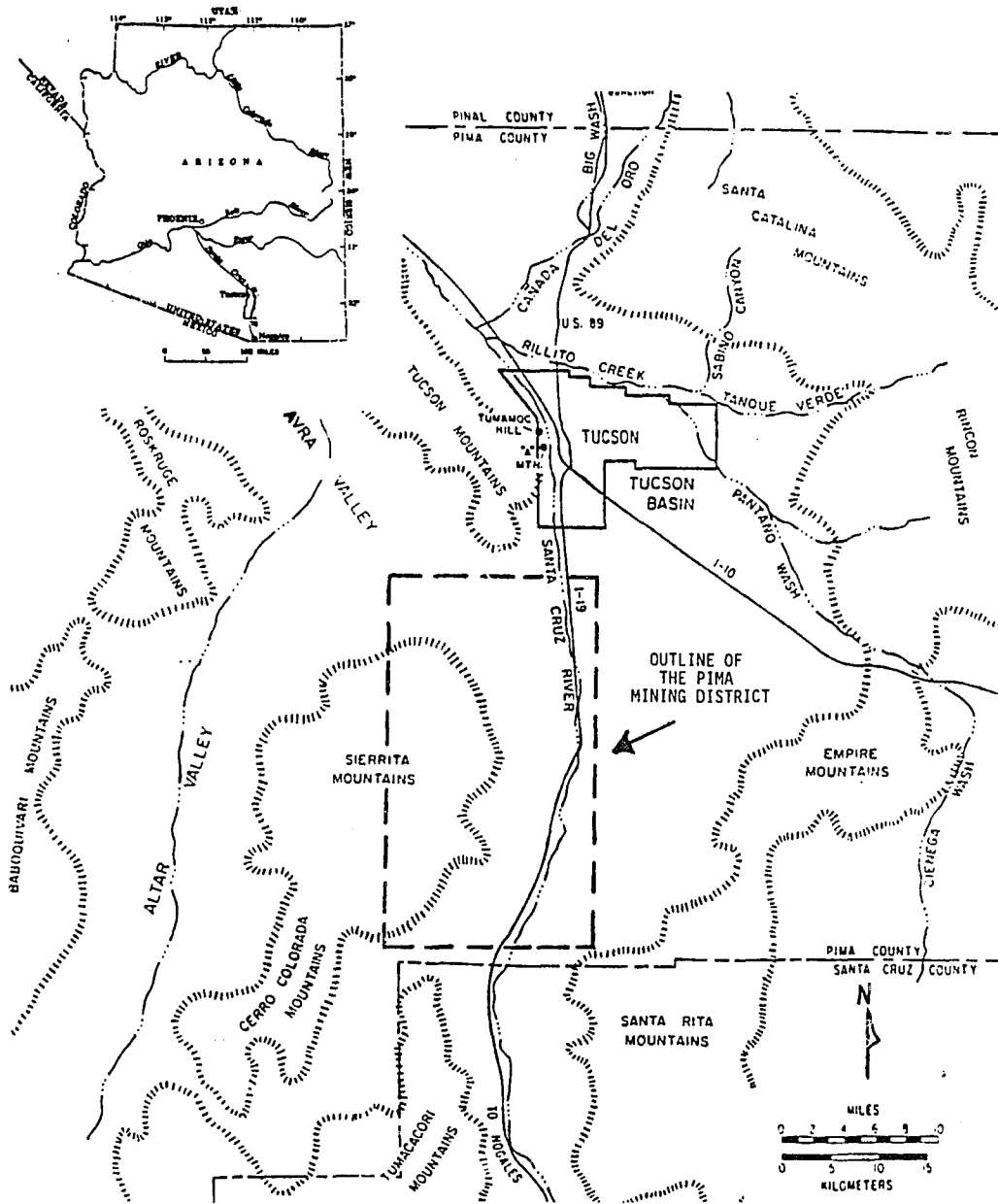


Fig. 1. Location of the Pima mining district (modified from the Arizona Geological Society and the University of Arizona 1986 Symposium (March 22, 1986), and Davidson (1973)).

formally established and underground mining of enriched lead-silver ores began on a broadened scale (Titley, 1981). During the early years of production, ores containing lead, silver, copper, zinc, molybdenum, and gold mined from small underground operations generated millions of dollars in revenue.

An era of "modern mining" began in 1950 when the Pima copper deposit was discovered by R.E. Thurmond and W.E. Heinrichs, Jr. of the United Geophysical Company. Electromagnetic anomalies warranted further exploration of the ore body by shaft sinking and underground work. The drilling results indicated a large quantity of fairly low-grade ore instead of a smaller quantity of high-grade ore, thus in 1955 the decision was made to develop the deposit as an open-pit mine (Thurmond, 1958). Following the development of the Pima deposit, discoveries of additional bodies of disseminated copper led to the development of the Mission, Sierrita-Esperanza, and Twin Buttes open-pit mines (Fig. 2).

Presently, two mining companies are operating mines in the Pima mining district: ASARCO at the San Xavier and Palo Verde-Mission-Pima complexes in the northern part of the district, and Cyprus Sierrita (formerly Duval Sierrita) at the Sierrita-Esperanza deposit in the southern part of the district. At the time of this writing, the Twin Buttes deposit is no longer being mined. For a twenty year period spanning the years 1962 to 1982, concerted open-pit mining in the district flourished establishing the district as one of the largest copper-molybdenum ventures in Arizona (Titley, 1986). However, a sustained slump in copper prices from about 1982 to 1987 necessitated cutbacks in

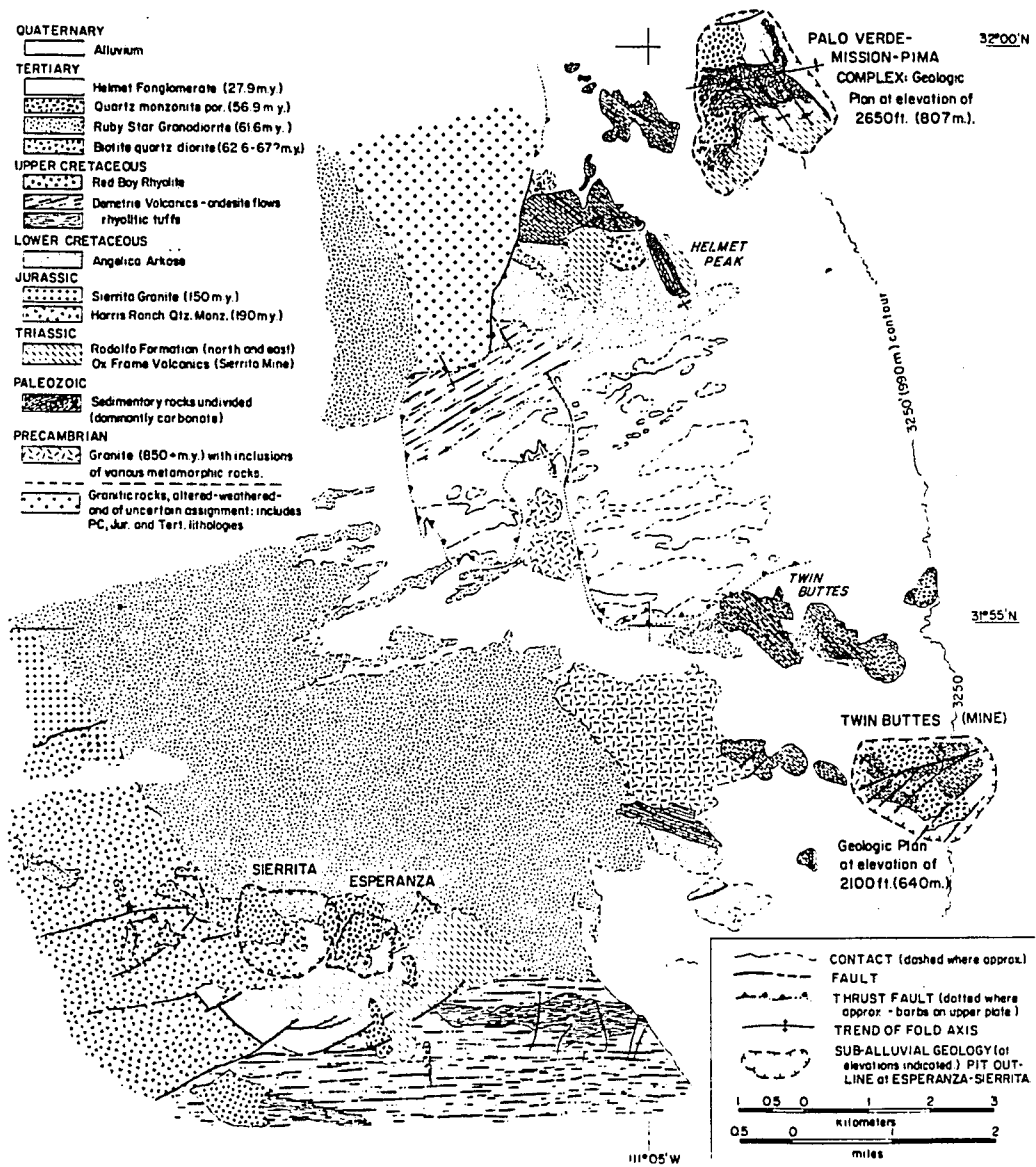


Fig. 2. Geologic map of part of the Pima mining district. The map does not show the North San Xavier Orebody, which lies several km north of the area shown (from Titley, 1982).

operations at all of the mines, and cessation of operations in the Twin Buttes deposit. Rising copper prices and recovery of higher-grade ores has prompted renewed production in the district in 1988.

### Ore Processing

Ores produced in the Pima mining district vary in composition from location to location; however, the main economic minerals typically mined in the district are chalcopyrite and molybdenite which occur as low-grade ores in a quartz-monzonite porphyry to quartz-diorite host rock (Janes and Johnson, 1976). The low-grade ores typically contain 0.3% to 1.0% copper, but small amounts of high-grade ores such as chalcocite, bornite, cuprite, chrysocolla, and native copper are also mined.

Copper and molybdenum in the low-grade ores are concentrated to marketable 25% to 30% concentrates by a physicochemical method of froth floatation. In the floatation process reagents classified as collectors, frothers, and modifiers are added to a slurry of finely-pulverized rock. The collector creates a hydrophobic surface on the copper or molybdenum minerals which enables them to attach onto a rising current of air bubbles. Frothers impart a temporary toughness to the mineral-laden bubbles thereby minimizing breakage before the froth can be skimmed from the pulp. Modifiers perform four basic functions: 1) prevent floatation of unwanted minerals (depressants), 2) increase the efficiency of collectors (activators), 3) control pH, or 4) disperse gangue slimes (dispersants). Ultimately, a mineral-laden froth forms on the surface

of the ore pulp. This froth is recovered as concentrate, and the remaining gangue is sent to the tails (Engineering Fundamental Series, 1982a).

## CHAPTER 2

## GEOHYDROLOGY OF THE PIMA MINING DISTRICT

Geologic Setting

## Geology of the Mountains

The Sierrita, Santa Rita, and Empire Mountains are composed mainly of low to moderately permeable sedimentary, metamorphic, and intrusive igneous rocks. Large masses of Mesozoic to middle Tertiary volcanic rocks with minor amounts of interbedded conglomerate and sandstone form the Tucson Mountains, Black Mountain, and much of the Sierrita Mountains (Davidson, 1973). Somewhat younger, more vesicular and fractured volcanics, middle to late Tertiary in age, crop out on Black Mountain and on the eastern slopes of the Tucson Mountains. Sedimentary rocks of low water-yielding capacity crop out in large areas of the Sierrita and Santa Rita Mountains. They are Paleozoic to Mesozoic in age, and include primarily sand-, silt-, and claystones, conglomerate, volcanic flows and tuff, and agglomerate. Although some of these units have moderate to high porosity and permeability, the rocks of the mountains bounding the Tucson basin generally act as impermeable barriers to ground water flow (Davidson, 1973).

The Sierrita Mountains were formed when a large body of granodiorite intruded the igneous, sedimentary, and volcanic rocks of the study area approximately 60 million years ago. Cooper (1973) named this massive intrusive unit the Ruby Star Granodiorite (Fig. 2). The batholith forms the core of the Sierrita Mountains. Three other early

Tertiary intrusive rocks became mineralized locally in the Pima mining district: a diorite, andesite, and quartz monzonite porphyry. The porphyry is associated with and presumed to be genetically related to all the major copper deposits in the district (Himes, 1972).

Intrusion of the granodiorite batholith caused folding, faulting, and alteration of the original Paleozoic and Mesozoic rocks. The alteration-mineralization process responsible for formation of the primary mineral assemblages is believed to be contemporaneous with and related to emplacement of the early Tertiary quartz monzonite porphyry (Langlois, 1978). Specific mineralization depends upon the type of host rock which the porphyry contacted. Faults and fractures acted as either conduits or barriers to movement of the altering fluids. Paleozoic dolomites and impure limestones were altered to skarns containing calc silicate minerals such as garnet, diopside, actinolite-tremolite, and epidote. Pure limestones and sandstones were altered to marble and quartzite (Himes, 1972). Where the quartz monzonite porphyry intruded host rocks of felsic igneous mineralogy, alteration formed potassic and propylitic mineral assemblages (Titley, 1981) such as sericite, clay, metasomatic quartz and orthoclase (Kinneson, 1966).

Following the skarn alteration of carbonate rocks, sulfide minerals, primarily chalcopyrite, and magnetite replaced the calcium, magnesium, and iron silicate skarn minerals. At the same time, hydrothermal alteration and sulfide deposition also occurred in the overlying clastic metasediments and in the quartz monzonite porphyry (Himes, 1972).



The economically valuable ores in the Pima mining district are typically epithermal, mineralogically complex, and consist primarily of quartz-pyrite gangue with accessory base and precious metal sulfides and sulfosalts (Titley, 1982). Chalcopyrite ( $\text{CuFeS}_2$ ) occurring in veinlets, disseminations, and small massive replacements of skarn is the principle copper-bearing mineral throughout the district. Accessory molybdenite ( $\text{MoS}_2$ ) which occurs primarily in quartz veinlets and as coatings on fracture surfaces is the major source of molybdenum. Galena ( $\text{PbS}$ ), sphalerite ( $\text{ZnS}$ ), and tennantite-tetrahedrite ( $\text{Cu}_{12}(\text{As,Sb})_4\text{S}_{13}$ ) are important sources of lead, zinc, and copper. Minor amounts of silver are also produced (Himes, 1972; Aiken and West, 1978; Langlois, 1978; King, 1978).

The Pima mining district is divided into northern and southern parts. Cooper (1960) postulated that the orebodies of the northern part lie within an allochthonous block which moved 10.5 km  $\text{N}10^\circ\text{-}20^\circ\text{W}$  along the San Xavier thrust fault from its place of origin in the southern part of the district. The ores of the southern half of the district are presumed to be the autochthonous roots of the northern half.

#### Sedimentary Units in the Basin

The Tucson basin aquifer consists of four distinct sedimentary units: the Pantano Formation and Tinaja beds of Tertiary age, and the Quaternary Fort Lowell Formation and surface deposits that underlie the flood plains and major stream channels. Collectively, these four units comprise a single water-bearing unit that is as much as 610 meters

thick and composed of loosely consolidated to moderately cemented silty sand to silty gravel (Davidson, 1973).

The Pantano Formation is the oldest unit, Oligocene in age (Laney, 1972), and is typically a reddish-brown silty sandstone to gravel that is weakly to strongly cemented by calcium carbonate. It contains a few interbedded volcanic flows, tuffs, and mudstone beds which contain gypsum in places. Subsurface cores of the Pantano Formation are lighter in color and less tightly cemented than exposures along the margin of the basin (Davidson, 1973). The porosity of the sandstone and gravel in the Pantano Formation ranges from 20% to 27% with hydraulic conductivity ranging from very low to about 4.08 m/d (meters per day).

The Helmet Fanglomerate, a correlative of the Pantano Formation, is exposed near the center of the Pima mining district (Fig. 2). According to Cooper (1960), the fanglomerate is about 3,200 meters thick in the Sierrita Mountain area and is predominantly a coarse, ill-sorted conglomerate characterized by angular pebbles and boulders in a silty matrix. It most likely formed as fan deposits near the base of a tectonically active mountain mass. Today the Pantano Formation and its correlative Helmet Fanglomerate form most of the aquifer west of the Santa Cruz Fault and south of the Tucson Mountains (Davidson, 1973).

The Tinaja rocks unconformably overlies the Pantano Formation and are a major part of the aquifer in the Tucson basin. The dominant lithology at the basin margins is a coarse-grained sandy gravel which grades into a gypsiferous clayey silt and mudstone towards the center of the basin. Tinaja beds of Miocene to Pliocene age crop out in the

southern part of the Sierrita Mountains with tuffaceous gravel deposits overlying felsic flows, tuff, and interbedded conglomerate and gravel (Davidson, 1973). The porosity ranges from 24% to 35% and the hydraulic conductivity varies from 0.408 to 16.3 m/d.

The Ft. Lowell Formation is the thickest highly permeable and most productive unit in the basin (Laney, 1972). It unconformably overlies the Tinaja beds and older deposits and is probably early to middle Pleistocene in age. The Ft. Lowell grades from a silty gravel near the basin margins into a silty sand and clayey silt in the central part (Davidson, 1973). Volcanic rock fragments are especially abundant in a montmorillonitic silty clay matrix near the Sierrita and Tucson Mountains where weathered detritus has accumulated in alluvial fans. The porosity ranges from 26% to 34% with hydraulic conductivities ranging from approximately 6.1 to 28.5 m/d.

The surficial deposits include alluvial fan, sheetflow, and stream channel deposits (Davidson, 1973). They overlie all older sedimentary units ranging from a thin veneer to a cover several meters thick. The surficial deposits are unsaturated most of the time since they generally lie above the water table. However, deposits along streams transmit large amounts of streamflow to the underlying units.

### Hydrologic Conditions

#### Flow Patterns of the Surface and Ground Water

Aside from irrigation return flows from local golf courses and agriculture, and discharge of sewage effluent, water in the Santa Cruz River drainage basin originates as precipitation, most of which

evaporates or is transpired by plants. Some of the precipitation becomes direct runoff and streamflow, most of which infiltrates to the ground water reservoir (Davidson, 1973). In a recent study by Cluff et al. (1987), historic records of average daily streamflow on the Santa Cruz River near Tucson between the years 1918 to 1981 showed an average annual measured runoff of  $0.019 \text{ km}^3$  (15,263 acre-feet). However, as was mentioned previously, the major streams in the Tucson basin, including the Santa Cruz River, remain dry during more than 300 days each year.

Surface water runoff in the Pima mining district generally flows down the east slope of the Sierrita Mountains in natural washes and arroyos. Where possible, runoff from areas upgradient of mining operations is diverted around tailings impoundments and other mine-related structures and back into washes downgradient (PEDCo. Environmental, 1983). Owing to high evapotranspiration losses, very little of this surface water runoff contributes to ground-water recharge. Near mining operations in the Pima district, most recharge to local ground water is from tailings pond percolation (PAG, 1983a).

The general direction of ground-water movement along the Santa Cruz River is northerly. Mountain-front recharge from the Santa Rita and Empire Mountains flows to the northwest whereas recharge from the Sierrita Mountains flows east-northeasterly (Plate 1). Local movement is complex owing to variations in transmissivity and specific pumping patterns. Two quite significant localized cones of depression occur in the Pima mining district to interrupt the general ground water flow pattern (Plate 1). One is located near the ASARCO well fields D(16-13)

25, 26, 35, and 36; the other occurs near the Twin Buttes mine (formerly Anamax) and has been attributed to pit dewatering (PAG, 1979). Ground water west of the mines is typically present in fractured hardrock with low permeabilities. Thus, the mining companies draw the bulk of their water used in mineral processing from well fields near the Santa Cruz River.

#### Ground Water Quality

The overall quality of ground water in the Tucson basin is generally good. Ground water less than 213 meters below the land surface contains under 500 mg/l of dissolved solids, is a calcium-sodium-bicarbonate type, is hard to moderately hard, and contains less than 1.0 mg/l fluoride. Deeper water is a sodium-bicarbonate type, soft, and of excellent quality (Laney, 1972). However, water drawn from wells penetrating formations deeper than 305 meters may contain high concentrations of fluoride. In addition, anomalously high concentrations of fluoride, sodium, sulfate and chloride occur in ground water drawn along the Santa Cruz River where major faulting has taken place. Laney (1972) attributes the unusually high concentration of these ions to upward leakage of deep water that has reacted with gypsiferous mudstone in the center of the basin and moved along the faults to the near-surface deposits.

Available data on water quality and ground-water movement in the Pima mining district (PAG, 1979, 1983a, 1983b; PEDCo. Environmental, 1983) have provided evidence that seepage from the tailings ponds has recharged the aquifer. In a tailings pond

monitoring study, PEDCo. Environmental (1983) found all water downgradient of a tailings pond (formerly Cyprus-Pima) in the northern half of the district to be of a calcium-sulfate type, with mean total dissolved solids (TDS) concentrations ranging from 709-920 mg/l, calcium (107-148 mg/l), magnesium (26-34 mg/l), sodium (51-56 mg/l), sulfate (297-405 mg/l), and chloride (47-92 mg/l). Secondary Drinking Water Standards limits for sulfate (250 mg/l) and TDS (500 mg/l) were exceeded in all wells downgradient of the tailings pond in this study.

North of the Cyprus-Pima ponds, TDS contents in wells near the ASARCO ponds were found to exceed 1000 mg/l, and sulfate concentrations exceeded 500 mg/l. However, levels of TDS and sulfate were found to be regionally highest in the southern portion of the Pima mining district near the Cyprus-Sierrita pond. Here TDS levels in monitor wells exceeded 2,000 mg/l and sulfate concentrations greater than 1,400 mg/l were found (PAG, 1983a, 1983b). Hardness has been attributed primarily to calcium, and ranged from over 1,400 mg/l  $\text{CaCO}_3$  near the Cyprus-Sierrita ponds and 800 mg/l  $\text{CaCO}_3$  near the ASARCO ponds.

## CHAPTER 3

## ANAEROBIC CHAMBER EXPERIMENT

Introduction

## Impact of Mining Activity

Large-scale open-pit mining of the low-grade copper and molybdenum ores in the Pima mining district has significantly altered conditions of the local surface morphology. Up to 60 meters of alluvial overburden has been stripped from areas atop the orebodies and transported to nearby disposal piles. Removal of the ore has created enormous pits, some of which are over 305 meters deep and over 2 km<sup>2</sup> in size. In addition, numerous tailings ponds, some covering more than 2.6 km<sup>2</sup>, store waste materials from the copper milling process. PAG (1983b) reported findings from a 1981 land use survey of the mining district which revealed 9.7 km<sup>2</sup> of open-pits, 25.1 km<sup>2</sup> of tailings ponds, and 54.7 km<sup>2</sup> of land which were used for disposal of overburden and activities related to ore crushing, milling, and processing.

Mining activity in the Pima district has also impacted the hydrologic environment in several important ways. Increased reliance on open-pit mining and onsite initial ore processing has increased the demand for water such that extensive ground water pumpage has created a local cone of depression (Plate 1). On the other hand, tailings pond seepage has recharged the aquifer and is suspected of degrading the quality of ground water in wells downgradient of the mines (PAG, 1983a, 1983b).

Tailings impoundments in the Pima mining district receive slurries of approximately 50% water and 50% finely-crushed waste rock which are sent to the tails after copper and molybdenum have been extracted from the ore in the froth floatation process (PAG, 1983b). The slurry is initially alkaline ( $\text{pH} \geq 10$ ) since mills which treat sulfide mineral ores, such as the chalcopyrite and molybdenite mined in the Pima district, operate with an alkaline pulp to produce optimum metallurgical results and prevent equipment corrosion (Engineering Fundamental Series, 1983a). Solids sent to the tails consist primarily of quartz-pyrite gangue rich in sulfur-bearing minerals which formed the bulk of the low-grade ores (Engineering Fundamental Series, 1982b; Ramsey, 1976; Janes and Johnson, 1976).

#### Water Movement in Tailings Ponds

Given a preponderance of very fine rock fragments in tailings ponds, it is likely that water movement through the tails is slow. Wahlers and Associates (1973) estimated infiltration rates of 0.0061 mm/s (millimeters per second) to 0.00021 mm/s on tailings material compacted over a range of field densities. The total amount of water escaping from a tailings structure is influenced by the geology of the site, surface evaporation losses, and the degree of compaction and sliming at the bottom of the ponds. Where materials underlying the tailings pond are relatively impermeable, the total amount of seepage will be less than if the underlying materials are permeable. In which case, seepage will generally flow vertically downward, and the total volume of seepage may be great (Swaisgood and Toland, 1972).



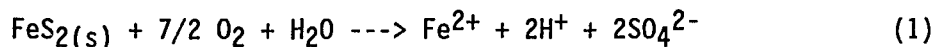
In the Pima mining district, tailings impoundments are located on permeable to moderately permeable natural soils or formations 76.2 to 134 meters above the water table (PAG, 1983b). Infiltration on alluvial soils near tailings ponds has been found to be approximately 0.0091 mm/s (PAG, 1983a). Seepage through the unsaturated foundation materials beneath a tailings impoundment has been described by McWhorter and Nelson (1980) as taking place in three distinct stages. During Stage I, a wetting front advances downward through the vadose material. The foundation material above the wetting front may or may not be saturated. Stage II occurs after the wetting front has contacted an impervious stratum or the phreatic surface of an aquifer creating a rising ground water mound. In stage III, saturated seepage occurs after the ground water mound has risen to the height of the impoundment.

#### Aquatic Chemistry of Tailings Impoundments

Chemical analyses of the water in tailings ponds of the Pima mining district have revealed unquestionably high concentrations of sulfate. Much of this sulfate results from the dissolution of soluble sulfate minerals contained in the waste rock. Sulfate also originates from products and the breakdown-products of reagents added to the finely-crushed mineral slurry during ore processing. Whether or not significant quantities of sulfate are being produced due to oxidation of sulfide minerals in tailings ponds of the Pima district is an issue which had not been investigated prior to this research.

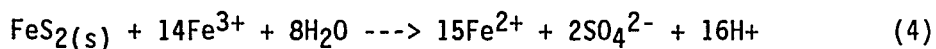
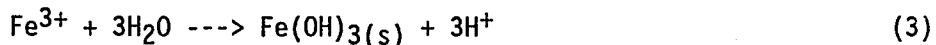
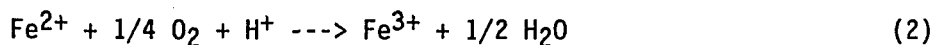
Nordstrom (1982) and Toran (1987) are two scientists who have recently published reports on the oxidation of sulfide minerals. The

oxidation of pyrite typically begins when bacteria belonging to the genera Metallogenium or Thiobacillus catalize the following reaction:



The acidity produced by this reaction in surface water has long been referred to as acid mine drainage.

According to studies on aqueous pyrite oxidation (Nordstrom, 1982), continued oxidation of ferrous iron generates even more acidity (Eqns. 2 and 3), and if the pH were to drop low enough ( $\text{pH} \leq 3$ ), ferric iron may become soluble and oxidize pyrite even more rapidly than oxygen (Eqn. 4):



In environments characterized by an absence of oxygen and low pH, ( $\text{pH} \leq 3$ ), Nordstrom (1982) argued that pyrite may be oxidized rapidly by aqueous ferric iron as described above by equation (4). However, the dramatic drop in pH due to the acidity produced in equations (1), (3), and (4) does not occur in the surface waters of tailings ponds of the Pima mining district, although it is a common problem in many coal and sulfide mining areas. The reason for this is that the tailings impoundments contain abundant carbonates and lime which occur naturally in the ore rock or were added as floatation reagents to the pulp during ore processing. The abundance of carbonates and lime in the impoundments buffers the pond surface water to near neutral pH.

Although the near-surface conditions of a tailings pond can be monitored relatively easily, the specific conditions existing at the base of a tailings impoundment are inaccessible. Assuming that the environment at the base of a tailings pond is a water-saturated system, sulfide oxidation is unlikely to be extensive because oxygen diffusion through water is slow. Furthermore, it is not known if sulfur- or iron-oxidizing bacteria inhabit the basal environment of a tailings pond to biologically catalyze the oxidation of pyrite.

#### Research Goals

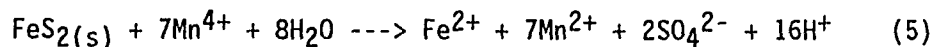
In light of these uncertainties, the primary goal of the experiment described below was to provide concrete evidence indicating whether or not significant quantities of sulfate may be produced due to in-situ oxidation of sulfide minerals in tailings ponds of the Pima mining district. The experiment was designed specifically to see if: 1) the dissolved oxygen content of tailings pond water is sufficient to start pyrite oxidation without bacterial catalysis, and 2) if the acidity produced by the oxidation reaction would be sufficient to solubilize ferric iron and/or tetravalent manganese which may then oxidize sulfide minerals in the tails under anoxic conditions. No attempt was made to include the possible effects of microbial activity on these processes.

When the details of this experiment were first formulated, information regarding the identity of specific minerals which form the bulk of tailings solids in the Pima district was limited to broad generalizations. For example, we knew that the tails contained abundant quartz, feldspar, and various quantities of iron-, sulfur-, and carbonate-

bearing minerals. The specific types, quantities, and distribution of minerals were said to be highly variable depending upon the mineralogy/petrology of the ore being processed during any particular day. Because the Pima mining district is situated in an area of massive sulfide mineralization, we believed that sulfide minerals could form a significant proportion of the tailings solids.

To simulate the natural environmental conditions which we believed could exist at the base of a tailings impoundment, hematite and birnessite were added as treatments to tailings solution in our experiment. Although the solubility of hematite is extremely low ( $K_{sp} < 10^{-36}$ ), it was added to provide a natural source of ferric iron for numerous reasons. Foremost was that hematite is widely distributed in rocks of all ages and occurs in contact metamorphic deposits or as an accessory mineral in feldspathic igneous rocks such as those which host the ores of the Pima mining district. Moreover, hematite was readily available in reagent-grade form for laboratory use.

Because manganese is commonly present in most crystalline rocks, we believed that it may also be present in the tails. Tetravalent manganese, if soluble under slightly acid conditions, may serve as an electron acceptor similar to Fe(III) in the inorganic oxidation of pyrite (Eqn. 5):



Manganous-manganite in the form of birnessite was selected as a source of Mn(IV) ions in our experiment because it is naturally occurring and one of the most common forms of mineralized manganese in soils.

Furthermore, birnessite could be easily synthesized in the laboratory free from foreign ions (McKenzie, 1971).

### Methods

#### Collection of Field Samples

Fresh tailings slurry was collected in buckets from a spigot which was discharging into a tailings pond (confidential source) in the Pima mining district. Tailings water was collected at the decant tower near the center of the same pond. Temperature and pH were recorded on site (Table 1).

#### Experimental Set-Up

The tailings water was filtered in the laboratory through Whatman #2 filter paper to remove particulates. Sixteen dark grey plastic bottles were then filled with 2000 ml of the filtered tailings water. Four identical bottles were filled with distilled deionized water (DDW) that was deoxygenated by boiling it and bubbling it with nitrogen gas.

The tailings slurry was thoroughly mixed in a plastic container, and then 10.0 grams (wet weight) were added to each of the bottles containing tailings water. Seven pre-weighed aluminum pans were filled with 10.0 grams of slurry and oven-dried for several days to determine the average dry weight of tailings solids added to the grey bottles. Ferric iron in the form of reagent grade hematite ( $\text{Fe}_2\text{O}_3$ , 99.8% purity) and Mn(IV) in the form of birnessite ( $\delta\text{-MnO}_2$ ) which was synthesized according to methods by McKenzie (1971), were added as treatments in quadruple replicates as follows: 1)  $\text{Fe}_2\text{O}_3$ , 0.2% suspension, 2)  $\delta\text{-MnO}_2$ , 0.2% suspension, 3)  $\text{Fe}_2\text{O}_3 + \delta\text{-MnO}_2$ , 0.1% suspensions, and 4) no treatment.

Table 1. Temperature, redox, pH, and electrical conductivity of water from a tailings pond in the Pima mining district

	S A M P L E S					
	Fresh Tailings Slurry (spigot)	Tailings Water (decant tower)		Filtered	Tailings	Water
Date	9/9/87	9/9/87	9/10/87	11/9/87	11/16/87	11/17/87
Temp. (°C)	32	23	26	27	28	28
pH (pH units)	10.8	8.6	7.6	6.8	ND*	ND
Eh (mV)	ND	ND	98	ND	177	ND
EC (micro- mhos/cm)	ND	ND	ND	ND	ND	3200

\*No Data.

The bottles containing DDW were treated with the same proportions of  $\text{Fe}_2\text{O}_3$ ,  $\delta\text{-MnO}_2$ , and  $\text{Fe}_2\text{O}_3 + \delta\text{-MnO}_2$ , and served as controls (Table 2). The percentage of solids in suspension was kept low to facilitate mixing, monitoring of conditions with electrodes, and homogeneous sampling.

#### Chemical Analysis

The bottles were housed in an XPL-855-AC anaerobic chamber (PLAS-LABS) and incubated under nitrogen gas at a constant temperature of  $28^\circ\text{C} - 32^\circ\text{C}$ . A Markson Ag/AgCl combination electrode was used to monitor pH, and a conductivity dip cell (Amber Science, Inc.) was used to measure Electrical Conductivity (EC). A Cole-Parmer combination platinum electrode was used to measure oxidation-reduction (redox) values after standardizing in pH 4 and pH 7 buffer solutions saturated with quinhydrone (Jones, 1966; Allinger et al., 1971). Redox values were recorded after equilibrating the electrode in each bottle for one minute while stirring with a magnetic stirrer.

Liquid samples were taken periodically from the bottles for analysis using 5 ml disposable syringes. All samples were filtered using Magna nylon 66 membrane filters in 25 mm easy pressure syringe filter holders (Gelman Sciences) to remove suspended solids ( $<0.5$  microns). Samples analyzed for soluble Fe(II) were filtered directly into 125 ml plastic separatory funnels containing weak hydrochloric acid or potassium dihydrogen phosphate buffer solution (pH 6.5) and analyzed immediately. Samples drawn for measurement of major anions were filtered directly into a DIONEX 2320i ion chromatograph. Samples designated for metal analyses were filtered into plastic storage vials,

Table 2. Identification of water and treatments in anaerobic chamber

BOTTLE NO.	VOLUME TAILINGS LIQUID (ml)	VOLUME DDW (ml)	OXIDE TREATMENTS			TAILINGS SOLIDS		
			TYPE	WEIGHT (g)	PERCENT SUSPENSION (%)	WET WEIGHT (g)	DRY WEIGHT (g)	SUS-PEN-SION (%)
1-A	2000	0	Fe <sub>2</sub> O <sub>3</sub>	4.00	0.2	9.96	6.80	0.34
1-B	2000	0	Fe <sub>2</sub> O <sub>3</sub>	4.00	0.2	10.09	±0.41	±0.02
1-C	2000	0	Fe <sub>2</sub> O <sub>3</sub>	4.00	0.2	10.04	"	"
1-D	2000	0	Fe <sub>2</sub> O <sub>3</sub>	4.00	0.2	10.03	"	"
2-A	2000	0	MnO <sub>2</sub>	4.00	0.2	9.96	"	"
2-B	2000	0	MnO <sub>2</sub>	4.00	0.2	10.03	"	"
2-C	2000	0	MnO <sub>2</sub>	4.00	0.2	10.02	"	"
2-D	2000	0	MnO <sub>2</sub>	4.00	0.2	10.02	"	"
3-A	2000	0	Fe <sub>2</sub> O <sub>3</sub>	2.00	0.1	10.04	"	"
			MnO <sub>2</sub>	2.00	0.1			
3-B	2000	0	Fe <sub>2</sub> O <sub>3</sub>	2.00	0.1	10.00	"	"
			MnO <sub>2</sub>	2.00	0.1			
3-C	2000	0	Fe <sub>2</sub> O <sub>3</sub>	2.00	0.1	10.02	"	"
			MnO <sub>2</sub>	2.00	0.1			
3-D	2000	0	Fe <sub>2</sub> O <sub>3</sub>	2.00	0.1	9.99	"	"
			MnO <sub>2</sub>	2.00	0.1			
4-A	2000	0	none	0	0	9.97	"	"
4-B	2000	0	none	0	0	9.97	"	"
4-C	2000	0	none	0	0	10.04	"	"
4-D	2000	0	none	0	0	9.98	"	"
5	0	2000	Fe <sub>2</sub> O <sub>3</sub>	4.00	0.2	0	0	0
6	0	2000	MnO <sub>2</sub>	4.00	0.2	0	0	0
7	0	2000	Fe <sub>2</sub> O <sub>3</sub>	2.00	0.1	0	0	0
			MnO <sub>2</sub>	2.00	0.1			
8	0	2000	none	0	0	0	0	0



acidified with 0.15% nitric acid, and refrigerated at 4°C until analyses were made using an IL951 AA/EA spectrophotometer (flame mode). Dissolved carbon content was determined on filtered samples with a Beckman 915A total carbon analyzer and Beckman 865 infrared detector.

Dried tailings solids were analyzed in two separate digests: a HCl/HNO<sub>3</sub> acid digest and an alkaline oxidative digest (Tabatabai, 1982). The acid digests were analyzed for the major cations by atomic absorption spectrophotometry. The alkaline digests were analyzed by ion chromatography for total sulfur. Carbon content of the solids was measured by wet combustion.

All of the forementioned water quality and solids analyses were performed at the University of Arizona's Soil, Water, Plant Testing Laboratory (SWPTL) under the direct supervision of Drs. M.M. Minnich and J.F. Artiola. Methodology, operating procedures, and quality control were performed according to guidelines established for the SWPTL by Artiola (1988).

To detect the presence of dissolved Fe(II) in the experimental solutions, a colorimetric procedure based on bathophenanthroline (4,7-diphenyl-1,10-phenanthroline) was used. Lee and Stumm (1960) recommended this procedure to detect trace quantities of ferrous iron in the presence of ferric iron. Shapiro (1966), Ghosh et al. (1967), and McMahon (1967, 1969) worked to refine the technique and eliminate errors due to factors such as time, acidity, light, and loss of precipitate. Details of the specific method used in this study were described by Macalady et al. (1982).

Mineralogic analysis of the tailings powder was performed by x-ray diffraction using a Phillips XRG 3000 diffractometer equipped with a vertical goniometer. Cu-K $\alpha$  radiation was used with a single crystal (graphite) monochromator and pulse height selection to remove Cu-K $\beta$  and reduce background radiation. Scans were made at 2° 2 $\theta$  per minute. Dr. D.M. Hendricks from the Department of Soil and Water Science at the University of Arizona, supervised the process and interpretation of results.

### Results and Discussion

Temperature, redox (Eh), pH, and Electrical Conductivity (EC) of the experimental solutions housed in the anaerobic chamber were monitored periodically over a period of 68 days. During the first 17 days, the pH of samples containing tailings water remained between 7.0 to 7.5 and did not vary due to treatment. Throughout the same time period the pH of the distilled deionized water (DDW) controls also did not vary, although the different oxide treatments had a dramatic affect on pH (Table 3). For example, treatment of DDW with hematite (sample 5) raised the pH from pH 5.0 to pH 5.6, and addition of birnessite raised the pH of DDW as high as pH 9.9 (sample 6).

Soluble ferrous iron was not detected, and redox values remained positive in both the tailings water solutions and the solutions prepared in a DDW base during the first 2½ weeks, which suggested that conditions were the same as at the start of the experiment. Because no change in either redox or pH had occurred after 2½ weeks, we decided to flush the chamber with a mixture of 90% nitrogen (N $_2$ ) and 10% hydrogen (H $_2$ ) gases

as had been done in the initial purging procedure. Water vapor (fog) was produced which indicated that oxygen had been present in the chamber, perhaps due to degassing of the tailings water. The water vapor was then removed by circulating the internal chamber atmosphere through dessicant canisters in the system.

Probe measurements were repeated one week after flushing the chamber with the  $N_2/H_2$  gas mixture, and for the first time redox values were negative (Table 3, 10/9/87) indicating oxygen deficiency and the onset of reducing conditions in the solutions. However, on 11/9/87, one month later, aqueous Fe(II) was still absent, and the pH of tailings water solutions remained at near neutral values. Only in samples (6) and (7), the DDW controls containing birnessite, did the pH drop significantly from an initial pH 9.9 - 9.7 to pH 7.8 - 7.4. When redox conditions were checked one week later on 11/16/87, the Eh values were once again positive indicating that the internal chamber atmosphere had reverted to an oxidizing climate.

The sudden reversal of negative redox values to positive values most likely reflects oxygen contamination which could be attributed to human error while transferring equipment through the portals and/or leakage in the chamber's valves or seals. When we were unable to detect either a drop in pH or aqueous Fe(II) in samples containing tailings solution after a period of two months, it became apparent that pyrite oxidation was not occurring to a significant degree as described by equation (1). And because the pH remained above pH 7.0, we could not expect aqueous Fe(III) or Mn(IV) to be available as possible oxidants of pyrite or any other sulfide minerals in the tailings solids.

Table 3. Temperature, redox, pH, and electrical conductivity of liquid samples in the anaerobic chamber<sup>1</sup>

		S A M P L E S							
Date	Measurement	1	2	3	4	5	6	7	8
9/11/87	Temp. (°C)	27.5	27.5	27.5	27.5	27.5	27.5	27.5	27.5
	pH (pH units)	7.2	7.0	7.0	7.2	5.9	9.9	9.7	5.0
	Eh (mV)	133	213	229	175	223	57	67	312
	EC (micro-mohs/cm)	3100	3150	3100	3000	5.2	75	54	2.0
9/14/87	Temp.	32	32	32	32	32	32	32	32
	pH	7.2	7.2	7.2	7.2	5.6	9.9	9.5	5.0
	Eh	155	223	220	156	330	112	118	367
	EC	3050	ND*	ND	3025	5.7	81	50	2.4
9/28/87	Temp.	31	31	31	31	31	31	31	31
	pH	7.5	7.4	7.4	7.3	5.6	9.5	9.2	5.0
	Eh	167	215	209	194	232	65	86	246
	EC	3050	3200	3100	3100	6.1	100	66	3.2
10/9/87	Temp.	32	32	32	32	32	32	32	32
	pH	7.9	7.9	7.9	8.0	6.1	8.9	8.4	5.3
	Eh	-158	-170	-140	-160	-370	-212	-208	-420
	EC	3000	3200	3150	3100	6.4	115	74	2.6
10/19/87	Temp.	30	30	30	30	30	30	30	30
	Eh	-85	-275	-190	-352	-280	-200	-190	-330
	EC	3200	3300	3200	3200	7.1	120	82	3.2
11/9/87	Temp.	27	27	27	27	27	27	27	27
	pH	7.4	7.5	7.5	7.5	5.8	7.8	7.4	5.0
11/16/87	Temp.	28	28	28	28	28	28	28	28
	Eh	155	195	194	127	159	143	142	185
11/17/87	Temp.	28	28	28	28	28	28	28	28
	EC	3150	3300	3200	3200	7.3	140	96	3.7

<sup>1</sup>pH, Eh, and EC measurements were made after equilibrating electrodes in the samples for one minute while stirring with magnetic stir bars.

\*No Data.

Analysis of the chemical composition of the tailings pond water used in the chamber experiment (Table 4) showed that the tailings pond water in samples 1 through 4 contained substantial amounts of sodium, fluoride, chloride, bromide, and especially sulfate. These same samples contained approximately four times more bicarbonate than tailings water which was not housed in the anaerobic chamber (Table 5). The increase in bicarbonate was attributed to dissolution of soluble carbonates present in the tailings solids (Table 6) which were added to samples 1 through 4. Unexpected high levels of total organic carbon (TOC) in samples pulled from the chamber were probably due to contamination.

An elemental analysis of the tailings solids (Table 6) showed calcium, iron, sulfur, and carbonate to be major components. The major minerals which were found in a mineralogic analysis of the powdered tailings solids are the following (in approximate order of decreasing abundance): quartz, mica (muscovite), anhydrite, feldspar, and pyrite. In addition, lesser amounts of nahcolite, olivine, ankerite, apatite, and goetite were detected.

Although the X-ray diffraction analysis of the tailings solids was only qualitative, reduced sulfur minerals were not found to be significant. Limited availability of sulfides in the tails was unexpected, but would certainly explain why we did not detect evidence of sulfide oxidation in our experiment, especially since solid tailings material comprised only  $0.34 \pm 0.02$  percent of the total volume in each solution. Even if reduced sulfur minerals had formed a significant proportion of the tailings solids, their oxidation would be unlikely in

our experiment without the presence of bacteria that thrive under neutral pH to catalyze the reaction.

Because the design of the experiment was based upon a false assumption that sulfide minerals were significant components of the tailings solids, the specific goals of our research regarding oxidation of sulfide minerals by aqueous Fe(III) and Mn(IV) in carbonate-buffered tailings impoundments obviously could not be achieved. In order to salvage some of the information we had collected, we opted to use the data on chemical compositions of the tailings water and solids to address another important issue regarding recharge of tailings pond water and sulfate equilibrium in the Pima mining district. Details of this study are presented in the following chapter.

Table 4. Chemical composition of water samples from the anaerobic chamber experiment<sup>1</sup>

CONSTITUENT (mg/l)	S A M P L E							
	1	2	3	4	5	6	7	8
Calcium	ND*	ND	ND	ND	ND	ND	ND	ND
Magnesium	ND	ND	ND	ND	ND	ND	ND	ND
Sodium	119	120	122	120	0.27	0.31	0.30	0.11
Potassium	50	146	108	62	1.0	47	30	0.80
Iron	BDL**	BDL	BDL	0.38	BDL	BDL	BDL	BDL
Manganese	0.17	3.6	5.0	0.13	0.06	BDL	BDL	BDL
Copper	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Zinc	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Lead	0.10	0.05	BDL	BDL	BDL	BDL	BDL	BDL
Chromium	BDL	BDL	BDL	0.06	BDL	BDL	BDL	BDL
Fluoride	1.60	1.73	1.68	1.69	BDL	0.13	0.15	BDL
Chloride	73.7	73.5	63.5	63.7	8.7	7.5	5.5	13.6
Bromide	0.37	0.34	0.36	0.37	BDL	BDL	BDL	BDL
Nitrite	0.52	0.44	0.40	0.30	0.07	0.08	0.08	0.11
Nitrate	0.30	0.27	0.29	0.18	0.32	0.37	0.50	0.36
Sulfate	1,546	1,733	1,672	1,665	2.8	1.1	1.6	0.83
Bicarbonate	43.8	49.9	50.9	50.1	0.4	58.6	38.1	BDL
Total Organic Carbon	4.6	3.6	3.2	4.6	3.6	5.6	6.9	3.7

<sup>1</sup>Metals analyzed Dec. 2-4, 1987. Anions analyzed Nov. 10, 1987.

\*No Data.

\*\*Below the Detection Limit of 0.05 mg/l for the IL951 AA/AE flame spectrophotometer used to analyze metals.

Table 5. Chemical composition of water collected from tailings ponds in the Pima mining district

Constituent (mg/l)	This Study	ASARCO TAILINGS PONDS <sup>1</sup>			
		Pond #1	Pond #2		
Calcium	662	530	552	615	760
Magnesium	3.2	<1	5	2	1
Sodium	119	190	163	166	240
Potassium	50	49	70	---	72
Carbonate	BDL**	35	0	0	0
Bicarbonate	12	0	39	41	18
Chloride	65	43	26	38	32
Sulfate	1,712	1,600	1,558	1,745	2,400
Nitrate	3.2	2	2	<1	2
Fluoride	1.62	2	3.7	0.6	2.3
Iron	BDL	<0.08	---	---	0.05
Manganese	<0.05	<0.04	---	---	0.08
Arsenic	ND*	<0.005	---	---	<0.01
Chromium	<0.05	<0.04	---	---	<0.01
Selenium	ND	0.013	---	---	<0.01
Molybdenum	ND	1.9	5.5	16	2.0
Lead	<0.05	---	---	---	<0.01
Copper	<0.05	---	---	---	0.01
Zinc	<0.05	---	---	---	0.14
Cadmium	ND	---	---	---	<0.01
Boron	ND	---	0.4	---	0.13
Vanadium	ND	---	---	---	<0.1
Electrical Conductivity (micromhos/cm at 25°C)	3,200	2,993	---	---	3,351
Total Dissolved Solids	ND	3,500	---	2,629	3,333
Total Organic Carbon	2.1	7.8	---	---	6.7
Field pH (pH units)	8.6	---	---	---	5.5
Lab pH (pH units)	7.6	10.1	6.7	5.0	6.5
Date	9/9/87	5/4/81	2/17/71	10/18/71	8/20/81
Lab		U of A	ETL	ETL	BC Labs

<sup>1</sup>Pima Association of Governments, Ground-Water Monitoring in the Tucson Copper Mining District, September 1983, p. 51.

\*No Data.

\*\*Below Detection Limit.



Table 6. Elemental composition of tailings solids<sup>1</sup>

Element	C O N C E N T R A T I O N	
	g/Kg	Percent
Ca	20.2	2.02
Mg	4.2	0.42
Na	0.13	0.013
K	0.59	0.059
Fe	20.2	2.02
Mn	0.34	0.034
Cu	0.66	0.066
Zn	0.34	0.034
Pb	0.12	0.012
Cr	0.012	0.001
SO <sub>4</sub> -S	17.2	1.72
CO <sub>3</sub>	14.2	1.42
TOC*	1.19	0.12

<sup>1</sup>Metal analyses performed Dec. 2-4, 1987, sulfur analysis Dec. 15, 1987, and carbon analysis Dec. 11, 1987.

\*Total Organic Carbon.

## CHAPTER 4

## EQUILIBRIUM MODELING OF SELECT WATER CHEMISTRIES

Purpose and Goals

The sulfate anion is the most prevalent form of sulfur in oxidizing environments. In addition, sulfate is considered to be highly mobile and stable in the vadose zone since few natural mechanisms impede its mobility. Open-pit mining in the Pima district exposes enormous quantities of pyrite and other sulfide minerals to the atmosphere. The tailings ponds are the ultimate receptical of finely-crushed, sulfate-rich gangue. Degradation of ground water quality due to influx of sulfate is a common problem encountered in sulfide-mining districts, including the Pima area.

The discovery of increased concentrations of sulfate in ground water of the Pima mining district has spurred significant controversy. The very high levels of sulfate present in the tailings ponds (Table 5) suggest that the ponds are a source of the degraded water found in downgradient wells (PAG, 1983a). However, at least four sources may contribute to the elevated concentrations of sulfate found in the wells downgradient of the mines: 1) migration of sulfate with tailings pond seepage, 2) dissolution of gypsum and anhydrite minerals in the vadose zone and/or aquifer materials, 3) increased pumpage of poorer quality deep ground water, and 4) dissolution of soluble sulfates and oxidation of sulfides in the mineralized ore bodies and surrounding rocks. The latter two possibilities are considered unlikely. This is because most of the wells in which elevated sulfate and TDS are found have not been

deepened, and because pit dewatering has created substantial cones of depression near each pit (Plate 1) causing ground water to move toward the pits rather than away from them. Furthermore, ground water flow in the bedrock is believed to be much less than that in the alluvial sediments which form the aquifer (PAG, 1983a).

More evidence was needed to determine whether the increased concentration of sulfate in wells downgradient of the mines was perhaps due to migration of sulfate with tailings pond seepage, or if water from the tailings ponds was acquiring additional sulfate from dissolution of gypsum and anhydrite in the vadose zone and/or aquifer materials. Geochemical models are useful tools to identify the geochemical processes which regulate the concentration of dissolved constituents in a water source, and to quantify the effects of temperature, speciation, sorption, and solubility on the concentrations of dissolved constituents. Geochemical modeling of the minerals and phases which control the present water chemistry in the Pima mining district was performed to confirm whether tailings pond recharge may contribute to the observed sulfate contamination in downgradient wells, or if tailings water is acquiring sulfate and other selected salts from the dissolution of minerals in the vadose zone and/or aquifer.

#### Methods

The U.S. Geological Survey computer program PHREEQE (Parkhurst et al., 1980) was used in this study for purposes of chemical equilibrium modeling. PHREEQE is a Fortran IV computer program designed to perform speciation and mass transfer calculations to find

the distribution of aqueous complexes and the saturation states of mineral phases which may be present in a given water source.

Water quality data (1981-1982) for 53 wells and two pit waters in the Upper Santa Cruz Ground Water Basin were obtained from PAG (1983b) and are included in Appendix B. Water quality analyses (1971-1981) of three tailings ponds: #1 ASARCO, #2 Anamax, and Cyprus Sierrita (formerly Duval Sierrita) were obtained from PAG (1983a) and are included in Appendix C along with the water quality data of a confidential tailings pond which were obtained by the author in this study. The forementioned information totalling 58 water chemistries was entered into the PHREEQE computer program which modeled saturation indices of suggested mineral phases which were likely to be involved in chemical reactions occurring in ground water of the Pima mining district.

Mineral saturation indices,  $SI = \text{Log}(IAP/KT)$ , were computed where IAP is the ion activity product, K is the equilibrium constant for a given mineral, and T is the water temperature ( $^{\circ}\text{C}$ ). A saturation index of zero suggests the water chemistry is at equilibrium with the corresponding mineral phase. Negative SI values suggest undersaturation, and positive SI values indicate supersaturation.

The mineral saturation indices are reported as logarithmic values, that is, a saturation index of +1.0 means that water is ten times supersaturated with the mineral of interest. A saturation index of -2.0 implies that the water chemistry is 100 times undersaturated with a particular mineral phase. If a certain water chemistry is undersaturated with respect to a mineral phase, it is possible for the

solution to dissolve that mineral, if present, until equilibrium is established. Conversely, if a water chemistry is supersaturated with respect to a particular mineral phase, that mineral may either precipitate out of solution, or as water chemistries mix, a water more highly saturated with respect to a mineral may augment the concentration of its dissolved components in water less saturated with the same mineral.

To compute the saturation state of a water chemistry with respect to specified mineral phases, the solution temperature, pH, and redox potential (Eh) are first entered into the PHREEQE program from reliable analytic data. PHREEQE then calculates the ionic strength of the solution and thermodynamic activity of all species and complexes in solution. The ion activity product (IAP) for a mineral is then computed as the product of the thermodynamic activities of the ions and complexes which make up that mineral. For example, the IAP of calcite ( $\text{CaCO}_3$ ) is equal to the activity of calcium times the activity of carbonate. Finally, PHREEQE computes the saturation state of a mineral by dividing its IAP by the product of its equilibrium constant (K) and the solution temperature (T). If the saturation index (IAP/KT) equals 1.0, ie., the  $\log(\text{IAP}/\text{KT})$  is zero, then that mineral of interest is at equilibrium with the specified water chemistry.

Error in the above calculations is a factor of the completeness of the analysis. Although the concentrations of most trace metals were either missing or below detection limits, their concentrations were too low to effect the ionic strengths of the solutions, and hence too low to have significant effect upon the activities of remaining species.

The reliability of water quality data we used in the model was good as indicated by the cation-anion balances. With only a few exceptions, the cation-anion balances were less than three percent, an acceptable tolerance limit for purposes of our study.

### Results and Discussion

The saturation indices of four select mineral phases modeled by PHREEQE for the water chemistries listed in Appendices (B) and (C) have been tabulated in Table 7. Anhydrite ( $\text{CaSO}_4$ ), calcite ( $\text{CaCO}_3$ ), fluorite ( $\text{CaF}_2$ ), and gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) were selected as the most probable mineral phases which may have a geochemical impact on the observed water quality in the Pima mining district. Maps have been prepared to show the mineral saturation indices for anhydrite (Plate 2), calcite (Plate 3), fluorite (Plate 4), and gypsum (Plate 5). A discussion of the information of these maps is presented in the following paragraphs.

All but two of the water chemistries were found to be undersaturated with respect to anhydrite (Plate 2). Anhydrite supersaturation occurred only in water from the Cyprus Sierrita (formerly Duval Sierrita) tailings pond and the confidential tailings pond. The mineral saturation indices suggest that the ground water becomes progressively more and more undersaturated with anhydrite as it moves towards the Santa Cruz River. Thus, tailings seepage could augment the background concentrations of calcium and sulfate in the local ground water. That is, it cannot acquire additional sulfate or calcium by dissolution of minerals in either the vadose zone or aquifer.

Table 7. Mineral saturation indices (Log(IAP/KT)) generated by PHREEQE for select water chemistries in the Pima mining district

LOCATION AND DATE OF WATER SAMPLE	M I N E R A L P H A S E			
	Anhydrite	Calcite	Fluorite	Gypsum
D(19-12) 36dca 7/28/82	-1.17	-0.02	-1.20	-1.95
D(19-13) 29cab 7/22/82	-1.32	-0.23	-0.68	-2.08
D(19-13) 21baa 7/22/82	-1.24	-0.36	-1.21	-2.00
D(19-13) 7ddd 7/20/82	-3.60	-0.98	-2.87	-4.38
D(19-13) 6aad 7/28/82	-2.90	-0.19	-1.55	-3.71
D(19-13) 5dba 7/20/82	-2.74	-0.47	-1.93	-2.68
D(19-13) 3acc 7/22/82	-1.48	-0.34	-1.11	-2.25
D(18-13) 29dcd 10/20/82	-0.92	-0.13	NP*	-1.70
D(18-13) 27acc 11/2/82	-2.48	-0.08	-1.41	-3.28
D(18-13) 26abb 8/31/82	-1.40	-0.15	-1.09	-2.16
D(18-13) 21bcc 9/30/82	-0.11	+0.46	NP	-0.89
D(18-13) 21aaa 9/30/82	-0.20	+0.41	NP	-0.98
D(18-13) 16bbb 9/30/82	-1.07	-0.29	NP	-1.86
D(18-13) 14bdb 11/1/82	-2.01	-0.25	-1.43	-2.81
D(18-13) 10dcd 7/22/82	-2.64	-0.66	-1.78	-3.43
D(18-13) 12cdb 4/21/82	-1.63	-0.42	-0.87	-2.40
D(18-11) 2cbd 10/1/82	-1.36	+0.08	-1.21	-2.10
D(18-11) 2aad 9/14/82	-1.60	-0.59	-0.97	-1.44

\*Not Present.

LOCATION AND DATE OF WATER SAMPLE	M I N E R A L P H A S E			
	Anhydrite	Calcite	Fluorite	Gypsum
D(18-13) 4bdc 9/15/81	-1.54	+0.53	-1.47	-2.36
D(18-13) 1cbc 9/15/81	-2.13	+0.39	-1.03	-2.95
D(17-12) 36cdb 10/1/82	-2.12	+0.01	-0.71	-2.03
D(17-13) 34bad 6/15/82	-0.68	+0.23	-1.40	-1.46
D(17-13) 36cbc 4/20/82	-1.19	-0.11	-1.26	-1.94
D(17-13) 27dbb 6/14/82	-2.50	+0.61	-1.63	-3.28
D(17-13) 26bcc 6/14/82	-1.71	+0.93	-1.69	-2.49
D(17-13) 26cad 6/14/82	-2.53	+0.72	-1.42	-3.31
D(17-13) 25bab 4/9/82	-2.10	-0.21	-0.73	-2.92
D(17-13) 25dcd 4/19/82	-1.59	-0.08	-1.04	-2.36
D(17-13) 22acc 7/15/82	-1.81	-0.40	-1.38	-2.66
D(17-13) 24acc 4/9/82	-2.07	-0.63	-0.85	-2.91
D(17-12) 13ddb 7/14/82	-1.76	-0.28	-1.43	-1.66
D(17-13) 17aba 7/13/82	-2.38	-0.83	-1.53	-3.20
D(17-13) 11dcd 7/15/82	-2.00	-0.63	-1.16	-2.80
D(17-13) 12dbc 7/15/82	-1.45	-0.57	-1.26	-2.24
D(17-14) 7ddd 7/6/82	-1.47	-0.01	-1.42	-2.26
D(17-14) 6aab 4/16/82	-1.24	+0.07	-1.53	-2.00
D(16-12) 33ddd 1/14/82	-1.51	-0.03	+0.09	-2.22
D(16-12) 35bca 9/18/81	-2.37	+0.15	+0.03	-2.31
D(16-12) 36bda 9/13/82	-0.17	+1.09	-0.20	-0.91
D(16-13) 35aaa 9/16/82	-2.08	-0.39	-0.77	-2.93
D(16-13) 35bbb 9/16/82	-0.83	-0.13	-1.13	-1.68



LOCATION AND DATE OF WATER SAMPLE	M I N E R A L   P H A S E			
	Anhydrite	Calcite	Fluorite	Gypsum
D(16-13) 35bdd 9/15/82	-1.79	-0.36	-0.95	-2.66
D(16-13) 28add 9/30/82	-0.72	+0.32	-1.37	-1.54
D(16-13) 26aaa 9/14/82	-2.41	-0.43	-0.45	-3.13
D(16-13) 26caa 9/15/82	-1.35	-0.15	-0.81	-2.22
D(16-14) 30cdc 9/13/82	-1.29	+0.05	-1.68	-2.04
D(16-14) 29aaa 9/13/82	-1.16	+0.14	-1.33	-1.93
D(16-12) 23aa 9/20/82	-1.45	-2.16	-0.74	-1.41
D(16-13) 21dad 9/30/82	-0.58	+0.48	-1.29	-1.38
D(16-14) 20bbb 1/20/82	-1.44	-0.02	-1.75	-2.21
D(16-14) 21ddc 7/30/82	-2.02	-0.82	-1.55	-2.83
D(16-14) 7dcb 3/31/82	-1.13	+0.10	-1.33	-1.89
D(16-14) 6bba 7/8/82	-1.59	-0.35	-0.18	-2.36
D(15-13) 34dad 7/16/82	-1.88	-0.58	-0.95	-2.66
D(15-14) 31bcb 7/8/82	-1.87	-0.42	-1.73	-2.65
Cyprus Sierrita Tailings Pond 11/23/81	+0.08	+1.27	NP	-0.70
Anamax Tailings Pond #2 9/10/71	-0.71	+0.33	-0.88	-1.49
ASARCO Tailings Pond #1 5/4/81	-0.01	+1.88	+0.43	-0.79
Tailings Pond (Confidential) in the Pima Mining District 9/9/87	+0.09	-0.36	+0.34	-0.69

Mineral saturation indices for calcite (Plate 3) show the ground water in the study area to be supersaturated in three different zones. One zone occurs in the southern half of the Pima mining district near the Cyprus Sierrita and Twin Buttes (formerly Anamax) tailings ponds. Another occurs in the northern half of the district and is centered around ASARCO's Mission pit and tailings ponds. A third localized zone of ground water supersaturated with calcite lies east-northeast of the ASARCO mining area and east of the Santa Cruz River.

It appears that the presence of carbonate/bicarbonate and calcium in ground water in the vicinity of the mines is associated with mining activity since two of the zones supersaturated with calcite include large tracts of mining property, and calcium is a major component of the total dissolved solids in the tailings ponds. According to Laney (1972), the zone of calcite supersaturation east of the Santa Cruz River is most likely attributable to a combination of one or more of the following factors: 1) upwelling along the Santa Cruz Fault of deep water that has reacted with gypsiferous mudstone in the center of the Tucson basin, 2) solution of relic salts, and/or 3) irrigation return flows from land under agriculture.

The pattern of mineral saturation indices for fluorite (Plate 4) is somewhat less clear than those for anhydrite and calcite. A lack of information on the fluoride content of water near the Cyprus Sierrita mines resulted in output from PHREEQE which indicated that fluorite is not present in that area. However, the mineral saturation indices for the remaining water chemistries show the water in the #1

ASARCO tailings pond and the confidential tailings pond (Table 7) to be supersaturated with fluorite, and the water in the #2 Anamax tailings pond to be moderately undersaturated with fluorite. Ground water downgradient of both the ASARCO and Anamax tailings impoundments is more highly undersaturated with fluorite than water in the ponds, and thus could acquire inputs of fluoride from tailings pond recharge.

In the case of gypsum (Plate 5), all of the water chemistries were found to be undersaturated. However, it is clear that the ground water becomes increasingly undersaturated with respect to gypsum towards the Santa Cruz River. Seepage from tailings ponds in the Pima mining district therefore, cannot acquire additional sulfate or calcium as it percolates through the vadose zone or aquifer materials. Tailings pond seepage can however, contribute to the concentration of these ions in wells situated hydrologically downgradient as it recharges the ground water reservoir.

## CHAPTER 5

## SUMMARY AND CONCLUSIONS

Increased concentrations of sulfate and total dissolved solids occur in ground water downgradient of the mines in the Pima mining district. These constituents threaten the quality of water available to the Continental, Green Valley, and Sahuarita communities which lie east of the Pima mining district. Indeed, the impact of ground water degradation in the Pima mining district is of concern to all communities in the entire Tucson basin. Controversy over speculated sources of the sulfate and total dissolved solids contamination are unnecessary and unproductive. Identification of the source(s) of contamination should not be for punitive purposes, but rather to prevent the spread of such contamination.

Extensive monitoring of the tailings pond water and ground water in the mining district began in the early 1970's. Seepage of water from the tailings ponds was shown to have recharged the aquifer at least nine years prior to the time of this writing (PAG, 1979). Whether or not, and to what degree tailings pond recharge may be contributing to the presence of sulfate and total dissolved solids in the ground water continues to invoke debate. The research conducted in this project was performed with the intent of providing new and conclusive evidence to help resolve this debate.

Samples of solids and water were obtained from the tails of a mining company (confidential) in the Pima mining district for use in a laboratory experiment designed to test whether in-situ oxidation of

sulfide minerals may be contributing to the high concentrations of sulfate found in tailings ponds of the Pima district. Specific experimental goals were to see if oxidation of sulfide minerals could occur in water-saturated tailings solids without bacterial catalysis, and if hematite and/or birnessite were sufficiently soluble under slightly acid, anoxic conditions to provide Fe(III) and Mn(IV) ions as inorganic oxidants of reduced sulfur minerals.

The specific goals of the experiment were unable to be achieved due to the unexpected finding that reduced sulfur minerals represent a relatively low proportion of the tailings solids. However, this revelation alone suggests that oxidation of sulfide minerals in the tails does not contribute significant quantities of sulfate to tailings pond water in the Pima mining district primarily because the availability of pyrite and other sulfide minerals is limited.

The high concentrations of sulfate found in tailings water can be primarily attributed then to the dissolution of sulfate-bearing minerals in the gangue during ore processing, and the presence of sulfur compounds, and their breakdown products, which are added to slurries of finely-crushed ore during the froth floatation of copper and molybdenum. Any sulfate produced by in-situ oxidation of sulfide minerals in the tails would be incidental to the high concentrations of sulfate originally present in the tailings slurry as a result of ore processing.

Water quality data gathered in this experiment were compared with historical water quality records to confirm the presence of sulfate, calcium, and fluoride in tailings pond water at concentrations

much higher than compared to typical ground water in the Tucson basin. The U.S. Geological Survey computer program PHREEQE was subsequently employed to model mineral saturation states for anhydrite, calcite, fluorite, and gypsum. These four mineral phases were selected because they most likely control the chemical equilibrium of sulfate, calcium, and fluoride found in wells downgradient of the tailings impoundments.

Ground water in wells downgradient of the mines was found to be less saturated, or more undersaturated, with respect to anhydrite, calcite, fluorite, and gypsum than water from the tailings ponds and/or mine pits. Furthermore, the degree to which each mineral becomes less saturated, or more undersaturated, increased with distance away from the mined areas. This evidence suggests that seepage of tailings pond water, which has been shown to have recharged the aquifer, can only augment the background concentrations of dissolved sulfate, calcium, and fluoride in ground water downgradient of the mines. The evidence does not support the suggestion that tailings pond recharge is picking up additional salts from dissolution of gypsum, anhydrite, or fluorite as it percolates through the vadose and/or aquifer materials.

The research in this study has provided new evidence which indicates that leakage of water from tailings ponds in the Pima mining district can only contribute to the concentrations of sulfate, calcium, and fluoride in wells downgradient of the mines. The presence of these ions in ground water threatens to degrade the quality of water, and thus the quality of life, for residents of the local communities. State governmental agencies such as the Department of Environmental Quality and the Department of Mines and Mineral Resources should work

with the individual mining companies to implement more effective control measures to minimize seepage of water from existing tailings impoundments. Any new ponds should be constructed with the best available demonstrated control technology to prevent leakage and the subsequent degradation of ground water quality in the Pima mining district.

APPENDIX A  
WELL NUMBERING SYSTEM



WELL NUMBERING SYSTEM<sup>1</sup>

The well numbers used by the Geological Survey in Arizona are in accordance with the Bureau of Land Management's system of land subdivision (Fig. A1). The land survey in Arizona is based on the Gila and Salt River meridian and base line, which divide the State into four quadrants. These quadrants are designated counterclockwise by the capital letters A, B, C, and D. All land north and east of the point of origin is in A quadrant, that north and west in B quadrant, that south and west in C quadrant, and that south and east in D quadrant. The first digit of a well number indicates the township, the second the range, and the third the section in which the well is situated. The lower case letters a, b, c, and d after the section number indicate the well location within the section. The first letter denotes a particular 160-acre tract, the second the 40-acre tract, and the third the 10-acre tract. These letters also are assigned in a counterclockwise direction, beginning in the northeast quarter. If the location is known within the 10-acre tract, three lowercase letters are shown in the well number. In the example shown (Fig. A1), well number (D-4-5)19caa designates the well as being in the NE $\frac{1}{4}$ NE $\frac{1}{4}$ SW $\frac{1}{4}$  sec. 19, T. 4S., R. 5E. Where there is more than one well within a 10-acre tract, consecutive numbers beginning with 1 are added as suffixes.

---

<sup>1</sup>R.L. Laney, Chemical Quality of the Water in the Tucson Basin, Arizona, Washington, D.C., U.S. Government Printing Office, 1972, pages D6-D8.

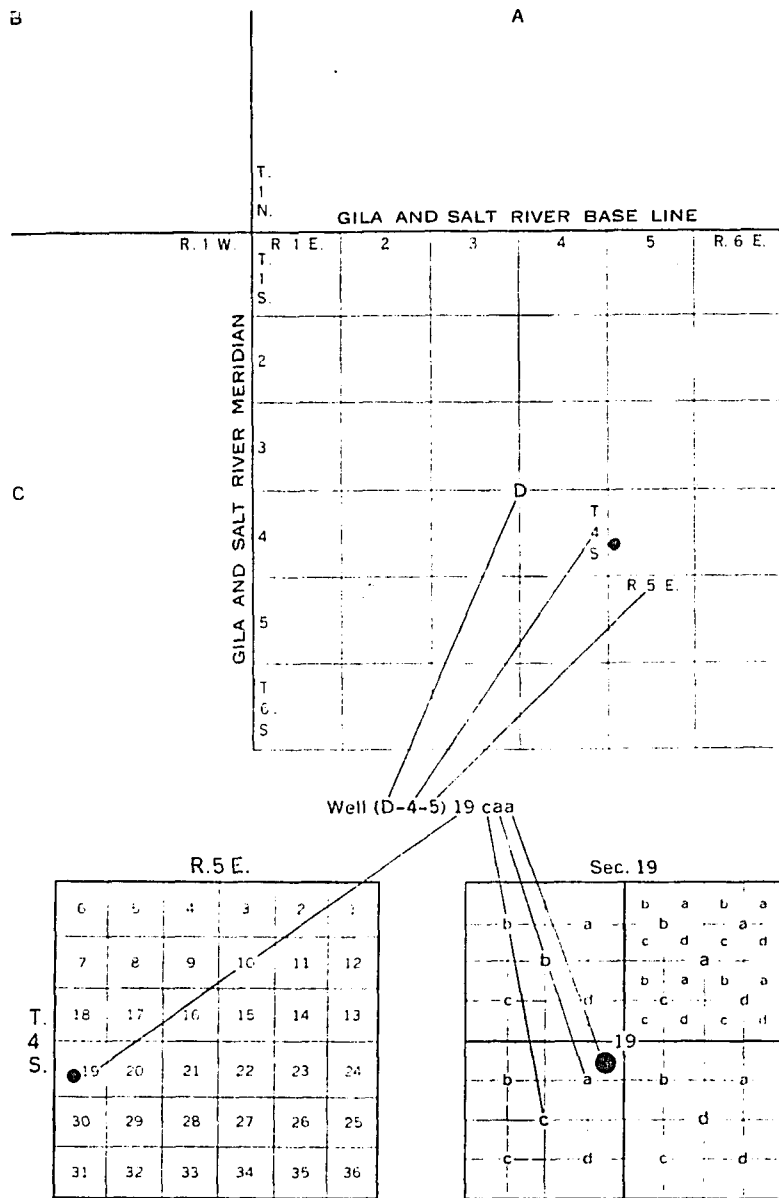


Fig. A1. Well-numbering system in Arizona (from Laney, 1972).

## APPENDIX B

## WATER QUALITY DATA:

UPPER SANTA CRUZ GROUND WATER BASIN<sup>1,2,3,4</sup>

---

<sup>1</sup>Pima Association of Governments, Region Wide Groundwater Quality in the Upper Santa Cruz Basin Mines Task Force Area, September 1983, Appendix D.

<sup>2</sup>All values in mg/l unless otherwise noted.

<sup>3</sup>Values of carbonate, if present, were converted to bicarbonate and added to the HCO<sub>3</sub> value.

<sup>4</sup>Temperature values of 25°C were assumed for analyses in which a particular water temperature was not specified.

WATER QUALITY DATA:  
UPPER SANTA CRUZ GROUND WATER BASIN

CON- STITUENT	WELL LOCATION AND DATE SAMPLED				
	D(19-12) 36dca 7/28/82	D(19-13) 29baa 7/22/82	D(19-13) 21baa 7/22/82	D(19-13) 7ddd 7/20/82	D(19-13) 6aad 7/28/82
Ca	124.	81.	102.	11.	37.
Mg	23.5	15.5	11.	47.	7.
Na	37.	61.	34.	24.	29.
K	4.5	3.4	4.	3.5	4.5
HCO <sub>3</sub>	277.	240.	175.	242.	207.8
Cl	34.0	12.	17.	7.1	8.1
NO <sub>3</sub>	32.3	12.4	28.4	3.5	5.8
SO <sub>4</sub>	180.	175.	166.	5.0	6.
F	0.45	0.95	0.45	0.2	0.47
Fe	ND*	ND	ND	ND	ND
Mn	ND	ND	ND	ND	ND
Cu	ND	ND	ND	ND	ND
Zn	ND	ND	ND	ND	ND
Br	ND	ND	ND	ND	ND
pH-Field	7.00	7.05	6.95	7.05	7.30
pH-Lab	NA**	NA	NA	NA	NA
Temp. (°C)	25.	23.	23.	25.	28.

\*No Data.

\*\*Not Applicable.

## WELL LOCATION AND DATE SAMPLED

CON- STITUENT	D(19-13) 5dba 7/20/82	D(19-13) 3acc 7/22/82	D(18-13) 29dcd 10/20/82	D(18-13) 27acc 11/2/82	D(18-13) 26abb 8/31/82
Ca	45.	69.	136.	37.5	79.5
Mg	10.	9.	31.	5.3	11.4
Na	24.	50.	55.	32.5	56.
K	3.3	4.	8.	3.2	5.3
HCO <sub>3</sub>	230.	197.	139.	199.	215.
Cl	6.4	14.9	72.	6.4	20.2
NO <sub>3</sub>	3.5	17.7	ND	3.1	27.0
SO <sub>4</sub>	8.	125.	331.	16.	140.
F	0.27	0.60	ND	0.54	0.59
Fe	ND	ND	ND	ND	ND
Mn	ND	ND	ND	ND	ND
Cu	0.02	ND	ND	ND	ND
Zn	ND	ND	ND	0.02	ND
Br	ND	ND	ND	ND	ND
pH-Field	6.95	7.05	ND	7.45	7.15
pH-Lab	NA	NA	7.2	NA	NA
Temp. (°C)	25.	24.	25.	27.	24.

## WELL LOCATION AND DATE SAMPLED

CON- STITUENT	D(18-13) 21bcc 9/30/82	D(18-13) 21aaa 9/30/82	D(18-13) 16bbb 9/30/82	D(18-14) 14bdb 11/1/82	D(18-13) 10dcd 7/22/82
Ca	428.	404.	108.	40.5	24.
Mg	60.	46.	14.	4.8	6.0
Na	263.	85.	50.	38.	29.
K	13.	14.	9.	3.4	3.0
HCO <sub>3</sub>	95.	95.	112.	183.	154.
Cl	76.	90.	38.	8.1	6.0
NO <sub>3</sub>	ND	ND	ND	2.7	3.1
SO <sub>4</sub>	1537.	1089.	245.	46.	16.
F	ND	ND	ND	0.52	0.43
Fe	ND	ND	ND	ND	ND
Mn	ND	ND	ND	ND	ND
Cu	ND	ND	ND	ND	ND
Zn	ND	ND	ND	ND	ND
Br	ND	ND	ND	ND	ND
pH-Field	ND	ND	ND	7.30	7.15
pH-Lab	7.7	7.6	7.2	NA	NA
Temp. (°C)	25.	25.	25.	27.	27.

## WELL LOCATION AND DATE SAMPLED

CON- STITUENT	D(18-13) 12cdb 4/21/82	D(18-11) 2cbd 10/1/82	D(18-11) 2aad 9/14/82	D(18-13) 4bdc 9/15/81	D(18-13) 1cbc 9/15/81
Ca	57.	78.	75.	60.	18.
Mg	8.2	46.	27.	13.8	0.8
Na	54.	40.	47.	48.	87.
K	4.0	1.2	1.3	6.7	4.8
HCO <sub>3</sub>	190.	289.	312.	204.	185.0
Cl	12.7	23.0	19.5	15.2	8.5
NO <sub>3</sub>	18.6	ND	8.4	9.3	4.4
SO <sub>4</sub>	100.	195.	104.	112.	78.
F	0.85	0.54	0.66	0.46	1.3
Fe	ND	ND	ND	ND	ND
Mn	ND	ND	ND	ND	ND
Cu	ND	ND	0.01	ND	ND
Zn	0.02	ND	ND	ND	ND
Br	0.3	ND	ND	ND	ND
pH-Field	7.05	7.35	6.65	ND	ND
pH-Lab	NA	NA	NA	7.9	8.3
Temp. (°C)	24.	21.	19.	29.	29.

## WELL LOCATION AND DATE SAMPLED

CON- STITUENT	D(17-12) 36cdb 10/1/82	D(17-13) 34bad 6/15/82	D(17-13) 36cbc 4/20/82	D(17-13) 27dbb 6/14/82	D(17-13) 26bcc 6/14/82
Ca	86.	179.	121.	31.5	55.
Mg	34.	37.	19.	7.8	6.9
Na	50.	56.	48.	33.	41.
K	8.2	7.	5.4	4.7	3.8
HCO <sub>3</sub>	453.	138.	226.	183.7	160.8
Cl	51.7	22.	52.8	9.9	23.7
NO <sub>3</sub>	1.8	7.6	44.3	5.3	4.4
SO <sub>4</sub>	26.	522.	182.	19.	82.
F	0.9	0.34	0.40	0.45	0.34
Fe	ND	ND	0.08	0.10	ND
Mn	ND	ND	ND	ND	ND
Cu	ND	ND	ND	ND	ND
Zn	ND	ND	0.13	0.07	ND
Br	ND	ND	0.7	ND	ND
pH-Field	6.95	ND	7.05	ND	ND
pH-Lab	NA	7.5	NA	8.3	8.5
Temp. (°C)	24.	25.	22.	25.	25.



## WELL LOCATION AND DATE SAMPLED

CON- STITUENT	D(17-13) 26cad 6/14/82	D(17-13) 25bab 4/9/82	D(17-13) 25dcd 4/19/82	D(17-13) 22acc 7/15/82	D(17-13) 24acc 4/9/82
Ca	32.5	25.	60.	37.5	20.5
Mg	5.0	1.5	8.5	10.8	1.2
Na	35.	64.	61.	49.	68.
K	3.4	2.7	3.5	5.0	2.1
HCO <sub>3</sub>	181.8	167.7	205.	178.	146.8
Cl	7.1	7.8	15.2	9.6	7.4
NO <sub>3</sub>	2.7	4.4	27.9	2.7	2.7
SO <sub>4</sub>	17.	55.	106.	79.	71.
F	0.56	1.5	0.69	0.64	1.5
Fe	ND	ND	0.05	ND	ND
Mn	ND	ND	ND	ND	ND
Cu	ND	ND	ND	ND	ND
Zn	ND	ND	ND	ND	0.01
Br	ND	0.3	0.05	ND	0.3
pH-Field	ND	7.55	7.35	7.15	7.25
pH-Lab	8.4	NA	NA	NA	NA
Temp. (°C)	25.	29.	24.	32.	31.

## WELL LOCATION AND DATE SAMPLED

CON- STITUENT	D(17-12) 13ddb 7/14/82	D(17-13) 17aba 7/13/82	D(17-13) 11dcd 7/15/82	D(17-13) 12dbc 7/15/82	D(17-14) 7ddd 7/6/82
Ca	90.	31.	33.	65.	73.5
Mg	26.	13.8	3.8	10.4	10.8
Na	23.	38.	51.	50.	44.
K	4.8	2.4	3.	3.3	4.
HCO <sub>3</sub>	359.	203.	165.	146.	185.
Cl	10.6	12.7	7.8	26.9	15.9
NO <sub>3</sub>	21.3	14.2	2.2	16.0	35.4
SO <sub>4</sub>	55.	25.	57.	136.	116.
F	0.37	0.55	0.79	0.54	0.42
Fe	ND	ND	ND	ND	ND
Mn	ND	ND	ND	ND	ND
Cu	ND	ND	0.06	ND	ND
Zn	ND	ND	ND	ND	ND
Br	ND	ND	ND	ND	ND
pH-Field	6.75	6.75	7.05	6.95	7.35
pH-Lab	NA	NA	NA	NA	NA
Temp. (°C)	23.	29.	27.	26.	26.

## WELL LOCATION AND DATE SAMPLED

CON- STITUENT	D(17-14) 6aab 4/16/82	D(16-12) 33ddd 1/14/82	D(16-12) 35bca 9/18/81	D(16-12) 36bda 9/13/82	D(16-13) 35aaa 9/16/82
Ca	116.	116.	34.	404.	22.
Mg	16.5	55.	27.	190.	2.1
Na	46.	145.	80.	142.	58.
K	4.8	6.6	3.5	10.2	3.7
HCO <sub>3</sub>	238.	446.	369.	234.	146.
Cl	32.6	210.	26.9	59.8	7.1
NO <sub>3</sub>	59.8	74.7	ND	35.4	1.8
SO <sub>4</sub>	158.	116.	29.	1700.	62.
F	0.3	2.0	3.4	1.2	1.6
Fe	ND	0.27	ND	ND	ND
Mn	ND	0.01	ND	ND	ND
Cu	ND	ND	0.03	0.10	ND
Zn	0.02	0.80	ND	ND	ND
Br	0.5	2.0	ND	ND	ND
pH-Field	7.20	6.95	7.50	8.05	7.45
pH-Lab	NA	NA	NA	NA	NA
Temp. (°C)	23.	18.	28.	21.	32.

## WELL LOCATION AND DATE SAMPLED

CON- STITUENT	D(16-13) 35bbb 9/16/82	D(16-13) 35bdd 9/15/82	D(16-13) 28add 9/30/82	D(16-13) 26aaa 9/14/82	D(16-13) 26caa 9/15/82
Ca	126.	36.	169.	7.5	60.
Mg	45.	10.2	107.	1.3	13.8
Na	63.	49.	102.	83.	86.
K	6.4	4.6	8.2	2.6	6.2
HCO <sub>3</sub>	128.	168.	388.	123.3	123.
Cl	64.4	9.6	101.	9.2	87.4
NO <sub>3</sub>	24.8	4.4	48.7	2.2	11.1
SO <sub>4</sub>	420.	82.	580.	85.	174.
F	0.60	1.1	0.44	4.1	1.1
Fe	ND	ND	ND	ND	ND
Mn	ND	ND	ND	ND	ND
Cu	0.01	ND	0.01	0.05	0.01
Zn	ND	ND	ND	ND	ND
Br	ND	ND	ND	ND	ND
pH-Field	7.20	7.20	7.15	7.95	7.39
pH-Lab	NA	NA	NA	NA	NA
Temp. (°C)	32.	34.	29.	33.	34.

## WELL LOCATION AND DATE SAMPLED

CON- STITUENT	D(16-14) 30cdc 9/13/82	D(16-14) 29aaa 9/13/82	D(16-12) 23aa 9/20/82	D(16-13) 21dad 9/30/82	D(16-14) 20bbb 1/20/82
Ca	116.	130.	38.5	205.	77.
Mg	19.6	29.	22.5	100.	12.4
Na	45.	44.	45.	186.	53.
K	4.9	4.2	44.	10.6	4.3
HCO <sub>3</sub>	236.	289.	57.2	430.	213.
Cl	38.6	36.5	12.0	102.	26.9
NO <sub>3</sub>	82.8	67.8	39.	21.7	29.0
SO <sub>4</sub>	146.	186.	237.	770.	130.
F	0.25	0.38	1.4	0.44	0.28
Fe	ND	ND	ND	ND	ND
Mn	ND	ND	ND	ND	ND
Cu	ND	ND	0.19	0.01	ND
Zn	0.13	0.05	ND	ND	0.06
Br	0.6	0.4	ND	ND	ND
pH-Field	7.20	7.15	6.0	7.25	7.30
pH-Lab	NA	NA	NA	NA	NA
Temp. (°C)	22.	24.	28.	27.	24.

## WELL LOCATION AND DATE SAMPLED

CON- STITUENT	D(16-14) 21ddc 7/30/82	D(16-14) 7dcb 3/31/82	D(16-14) 6bba 7/8/82	D(15-13) 34dad 7/16/82	D(15-14) 31bcb 7/8/82
Ca	24.	128.	56.	33.5	47.
Mg	1.7	28.	8.7	8.0	8.8
Na	39.	52.	50.	56.	35.
K	1.8	4.4	3.0	4.2	2.7
HCO <sub>3</sub>	86.6	280.	161.	165.	185.
Cl	6.4	38.6	16.3	10.3	9.9
NO <sub>3</sub>	3.5	56.3	17.3	2.7	6.7
SO <sub>4</sub>	67.	208.	110.	83.	62.
F	0.58	0.38	1.9	1.0	0.34
Fe	ND	0.10	ND	ND	ND
Mn	ND	0.01	ND	ND	ND
Cu	ND	ND	ND	ND	ND
Zn	ND	ND	ND	ND	ND
Br	ND	0.4	ND	ND	ND
pH-Field	7.25	7.15	7.20	7.15	7.10
pH-Lab	NA	NA	NA	NA	NA
Temp. (°C)	28.	23.	24.	25.	25.

APPENDIX C

WATER QUALITY DATA:

TAILINGS PONDS IN THE PIMA MINING DISTRICT

WATER QUALITY DATA:  
TAILINGS PONDS IN THE PIMA MINING DISTRICT<sup>1,2</sup>

T A I L I N G S   P O N D   L O C A T I O N

CONSTITUENT (mg/l)	#1 ASARCO <sup>3</sup>	#2 Anamax <sup>4</sup>	Cyprus Sierrita <sup>5</sup> formerly (Duval Sierrita)	Confidential Pond <sup>6</sup>
Ca	530.	137.	601.	662.
Mg	NA*	4.	7.	3.2
Na	190.	191.	267.	119.
K	49.	ND**	50.	50.
HCO <sub>3</sub>	71.2	49.	27.	12.
Cl	43.	42.	83.	65.
NO <sub>3</sub>	2.	1.	ND	3.2
SO <sub>4</sub>	1600.	615.	1948.	1712.
F	2.	0.7	ND	1.62
pH-Lab	10.1	8.20	9.3	7.6
Temp. (°C)	25.	25.	25.	25.
Date	5/4/81	9/10/71	11/23/81	9/9/87

<sup>1</sup>Values of carbonate, if present, were converted to bicarbonate and added to the HCO<sub>3</sub> value.

<sup>2</sup>Temperature values of 25°C were assumed for all analyses.

<sup>3</sup>Pima Association of Governments, Ground-Water Monitoring in the Tucson Copper Mining District, September 1983, p. 51.

<sup>4</sup>Ibid., p. 68.

<sup>5</sup>Ibid., p. 100.

<sup>6</sup>Selected values from Table 5, analysis 9/9/87.

\*Not Applicable.

\*\*No Data.



## LITERATURE CITED

- Aiken, D.M. and R.J. West. 1978. Some Geologic Aspects of the Sierrita-Esperanza Copper-Molybdenum Deposit, Pima County, Arizona. Arizona Geological Society Digest. 11:117-128.
- Allinger, N.L., M.P. Cava, D.C. DeJongh, C.R. Johnson, N.A. Lebel and C.L. Stevens. 1971. Organic Chemistry. Worth Publishers, Inc. p.381.
- Arizona Geological Society and the University of Arizona 1986 Symposium. Frontiers in Geology and Ore Deposits of Arizona and the Southwest. Field Trip Guidebook #12: Geologic Hazards of Tucson. March 22, 1986.
- Artiola, J.F. 1988. Manual of Operating Procedures for the Analysis of Selected Soil, Water, Plant Tissue, and Waste Chemical and Physical Parameters. (DRAFT). Soil, Water, Plant Testing Laboratory. Dept. of Soil and Water Science. University of Arizona.
- Cluff, C.B., L.T. Katz and G.L. Scovill. 1987. Effects of Channel Stabilization in Tucson Stream Reaches on Infiltration and Ground Water Recharge. Vol. II. Natural Streamflow Study. Final Report to Pima County Department of Transportation and Flood Control.
- Cooper, J.R. 1960. Some Geologic Features of the Pima Mining District, Pima County, Arizona. U.S. Geol. Survey Bul. 1112-C:63-103.
- Cooper, J.R. 1973. Geologic map of the Twin Buttes quadrangle, southwest of Tucson, Pima County, Arizona. U.S. Geol. Survey Misc. Geol. Inv. Map I-745.
- Davidson, E.S. 1973. Geohydrology and Water Resources of the Tucson Basin, Arizona. U.S. Geol. Survey Water Supply Paper 1939-E.
- Engineering Fundamental Series. 1982a. Selective Flootation: An Art as Well as a Science. Mining Eng. 34(3):275-279.
- Engineering Fundamental Series. 1982b. Sulfide and Nonsulfide Flootation Applications. Mining Eng. 34(4):377-381.
- Engineers Testing Laboratory. 1973. Materials Investigation, Farmers Investment Co. vs. Mines near Sahuarita, Arizona. Prepared by Coe and Van Loo. Phoenix, Arizona.

- Ghosh, M.M., J.T. O'Connor and R.S. Engelbrecht. 1967. Bathophenanthroline Method for the Determination of Ferrous Iron. *J. Amer. Water Works Assn.* 59:897-905.
- Hail, W.R. and W.A. Wahler and Associates. March 26, 1974. Letter to Gordon Davis, City of Tucson Planning and Research Engineer. Palo Alto, California. (Unpublished).
- Himes, M.D. 1972. Geology of the Pima Mine, Pima County, Arizona. (Masters Thesis). Dept. of Geosciences. University of Arizona.
- Janes, C.G. and L.M. Johnson. 1976. The Duval Sierrita Concentrator. In M.C. Fuerstenau (ed.) *Flotation Vol. 2*. American Institute of Mining, Metallurgical, and Petroleum Engineers, Inc. New York.
- Jones, R.H. 1966. Oxidation-Reduction Potential Measurement. *Instrumentation Soc. Amer. J.* 13(11):40-44.
- King, J.R. 1978. The Geology of the San Xavier North Porphyry Copper Deposit, Pima Mining District, Arizona. *Arizona Geological Society Digest.* 11:101-103.
- Kinneson, J.E. 1966. The Mission Copper Deposit. In S.R. Titley and C.L. Hicks (eds.) *Geology of the Porphyry Copper Deposits, Southwestern North America*. University of Arizona Press.
- Laney, R.L. 1972. Chemical Quality of the Water in the Tucson Basin, Arizona. U.S. Geol. Survey Water Supply Paper. 1939-D.
- Langlois, J.D. 1978. Geology of the Cyprus Pima Mine, Pima County, Arizona. *Arizona Geological Society Digest.* 11:103-113.
- Lee, G.F. and W. Stumm. 1960. Determination of Ferrous Iron in the Presence of Ferric Iron with Bathophenanthroline. *J. Amer. Water Works Assn.* 52:1567-1574.
- Macalady, D.L., C.P. Granlund, J.G. Granlund and S.L. Vervacke. 1982. On the Presence of Iron(II) in Oxygenated Surface Waters: Analytical Implications. *Water Res.* 16:1277-1283.
- McKenzie, R.M. 1971. The Synthesis of Birnessite, Cryptomelane, and Some Other Oxides and Hydroxides of Manganese. *Mineralogical Magazine.* 38:493-502.
- McMahon, J.W. 1967. The Influence of Light and Acid on the Measurement of Ferrous Iron in Lake Water. *Limnol. and Oceanog.* 12:437-442.

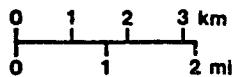
- McMahon, J.W. 1969. An Acid-Free Bathophenanthroline Method for Measuring Dissolved Ferrous Iron in Lake Water. *Water Res.* 3:743-748.
- McWhorter, D.B. and J.D. Nelson. 1980. Seepage in the Partially Saturated Zone Beneath Tailings Impoundments. *Mining Eng.* 32(4):432-439.
- Nordstrom, D.K. 1982. Aqueous Pyrite Oxidation and the Consequent Formation of Secondary Iron Minerals. *In* D.M. Kral and S. Hawkins (eds.) *Acid Sulfate Weathering: Proceedings of a Symposium.* Fort Collins, CO. 5-10 Aug. 1979. *Soil Sci. Soc. Am.* Madison, WI.
- PAG 1979. Upper Santa Cruz Groundwater Quality Baseline Report. Upper Santa Cruz Basin Mines Task Force. Vol. I. Pima Association of Governments.
- PAG 1983a. Ground-Water Monitoring in the Tucson Copper Mining District. Detailed Upper Santa Cruz Basin Mines Task Force Area Recommendations. Pima Association of Governments.
- PAG 1983b. Region Wide Groundwater Quality in the Upper Santa Cruz Basin Mines Task Force Area, Report and Detailed Recommendations. Pima Association of Governments.
- Parkhurst, D.L., D.C. Thorstenson and L.N. Plummer. 1980. PHREEQE - A Computer Program for Geochemical Calculations. *U.S. Geol. Surv., Water Resour. Invest.* 80-96.
- PEDCo. Environmental, Inc. 1983. Evaluation of Management Practices for Mine Solid Waste Storage, Disposal and Treatment. Vol. II-Environmental Analysis Summary. U.S. EPA Contract No. 68-03-2900.
- Ramsey, T. 1976. The Cyprus Pima Concentrator. *In* M.C. Fuerstenau (ed.) *Flotation Vol. 2.* American Institute of Mining, Metallurgical, and Petroleum Engineers, Inc. New York.
- Shapiro, J. 1966. On the Measurement of Ferrous Iron in Natural Waters. *Limnol. and Oceanog.* 11:293-298.
- Swaigood, J.R. and G.C. Toland. 1972. The Control of Water in Tailings Structures. *In* C.L. Aplin and G.O. Argall, Jr. (eds.) *Proceedings of the First International Tailing Symposium.* Tucson, AZ. Oct. 31, Nov. 1, 2, and 3, 1972.
- Tabatabai, M.A. 1982. Sulfur. *In* A.L. Page (ed.) *Methods of Soil Analysis. Part 2-Chemical and Microbiological Properties.* 2nd Edition. Amer. Soc of Agronomy, Inc. and Soil Sci. Soc. Amer., Inc. p. 513.

- Thurmond, R.E. and W.R. Storms. 1958. Discovery and Development of the Pima Copper Deposit. Pima Mining Co., Pima County, Arizona. U.S. Bureau of Mines Info. Cir. 7822:1-19.
- Thurnblad, T.W. 1982. Stable Isotopes and Chemistry of Water as Source Indicators of Aquifer Recharge and Contamination. (Masters Thesis). Dept. of Hydrology and Water Resources. University of Arizona.
- Titley, S.R. 1981. Twin Buttes-Sierrita Mines, Pima Mining District. In Frontiers in Geology and Ore Deposits of Arizona and the Southwest. Field Trip Guidebook #9: Geology and Ore Deposits of the Pima Mining District. Arizona Geological Society and the University of Arizona 1986 Symposium.
- Titley, S.R. 1982. Some Features of Tectonic History and Ore Genesis in the Pima Mining District, Pima County, Arizona. In S.R. Titley (ed.) Advances in Geology of the Porphyry Copper Deposits, Southwestern North America. University of Arizona Press.
- Titley, S.R. 1986. Pima Mining District, Pima County, Arizona. Arizona Geologic Society Digest. 16:390-391.
- Toran, L. 1987. Sulfate Contamination in Groundwater from a Carbonate-Hosted Mine. J. Contam. Hydrol. 2:1-29.
- Wahler, W.A. and Associates. 1973. Investigation of Tailings Ponds Seepage. Becker Exploration Data. DRAFT. Prepared for City of Tucson, Arizona. Palo Alto, California. (Unpublished).

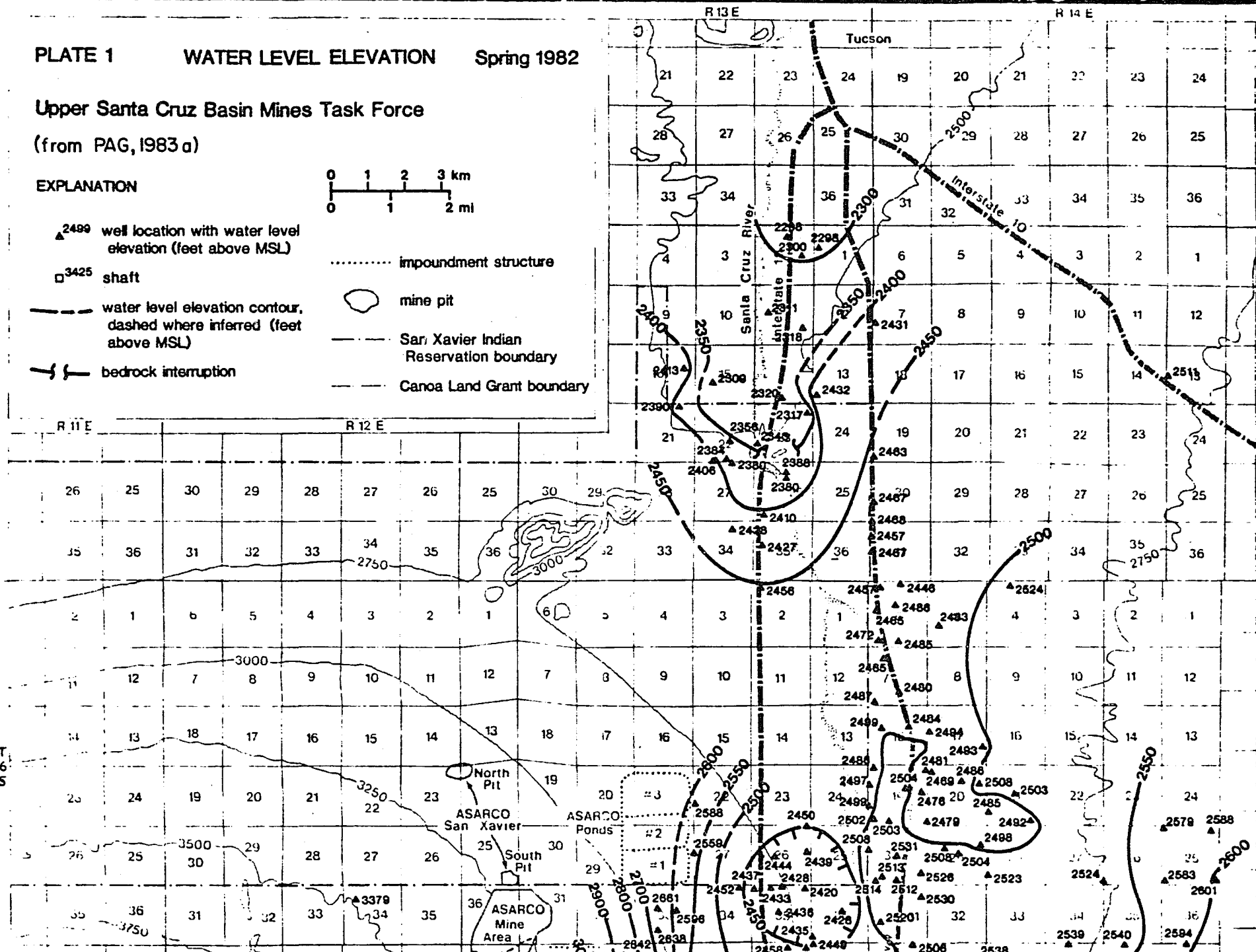
PLATE 1 WATER LEVEL ELEVATION Spring 1982

Upper Santa Cruz Basin Mines Task Force  
(from PAG, 1983 a)

EXPLANATION



- ▲ 2499 well location with water level elevation (feet above MSL)
- 3425 shaft
- water level elevation contour, dashed where inferred (feet above MSL)
- bedrock interruption
- ..... impoundment structure
- mine pit
- San Xavier Indian Reservation boundary
- Canoa Land Grant boundary



R 11 E

R 12 E

R 13 E

R 14 E

Tucson

Interstate 10

Santa Cruz River

ASARCO San Xavier

ASARCO Ponds

South Pit

ASARCO Mine Area

North Pit

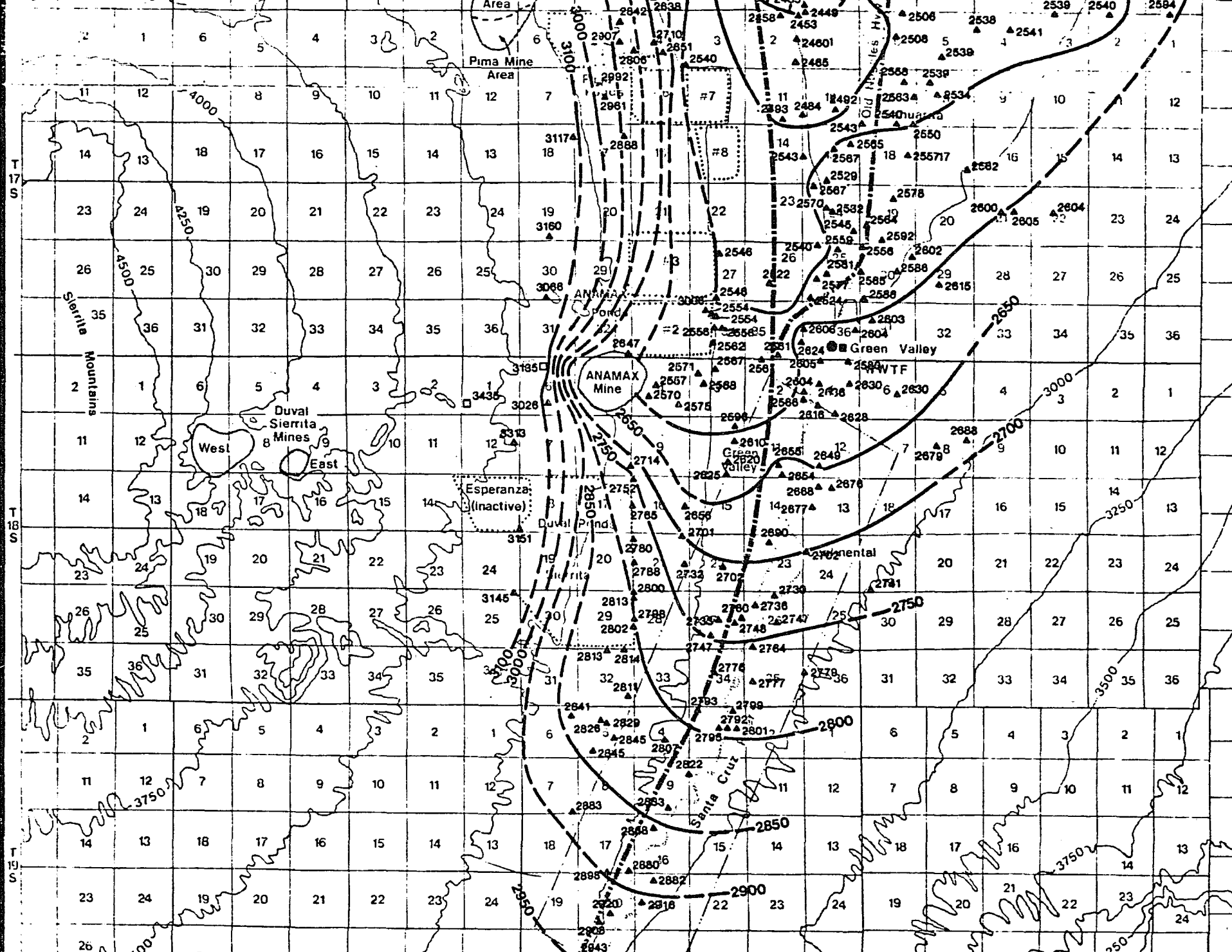
T 16 S

T 16 S

T 15 S

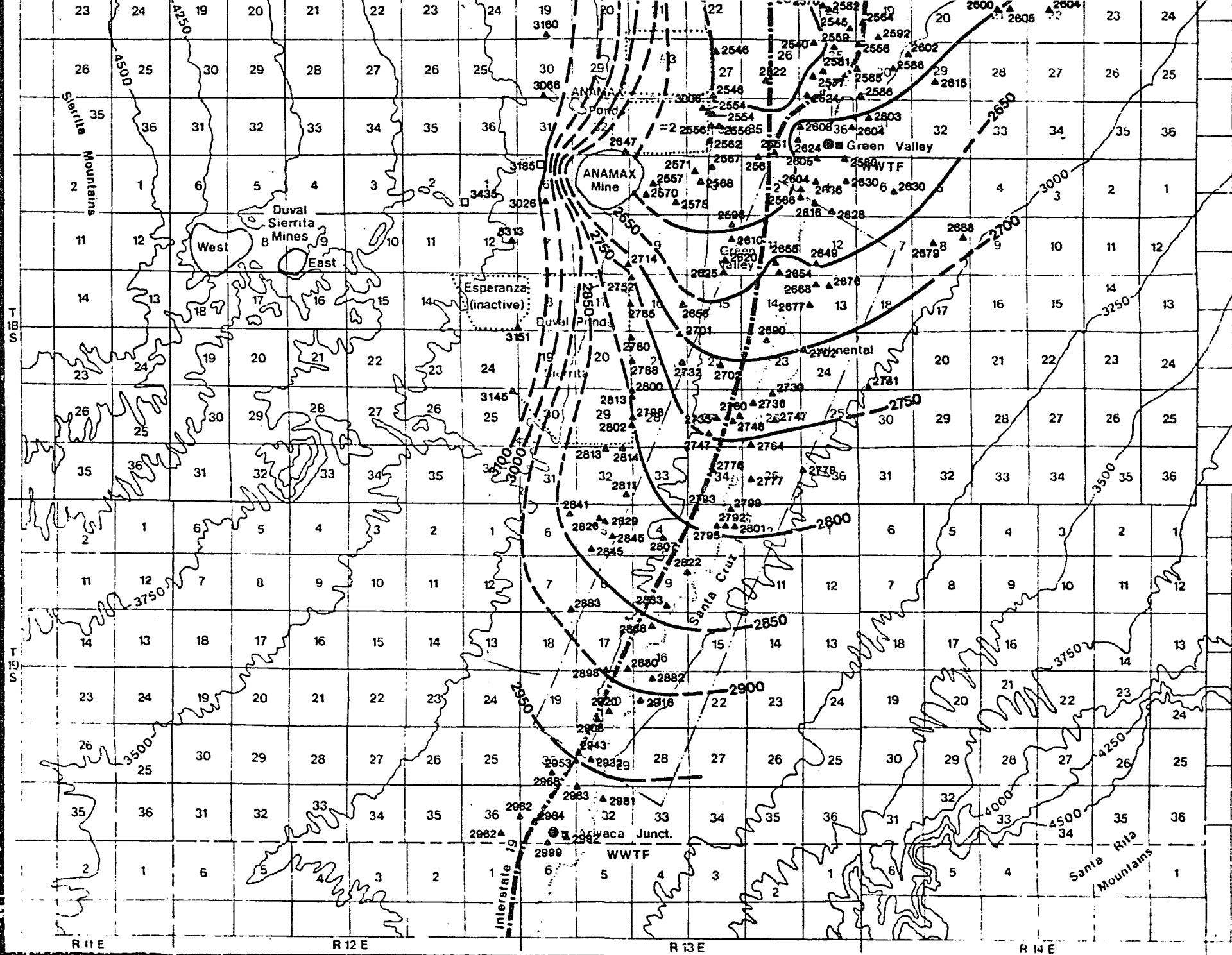
T 15 S













# Plate 2 - Anhydrite Saturation Indices

$$SI = \text{Log}(IAP/KT)$$

(adapted from PAG, 1983b)

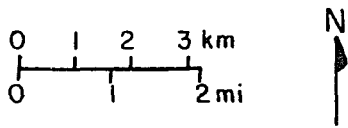
1971 - 1982

## EXPLANATION

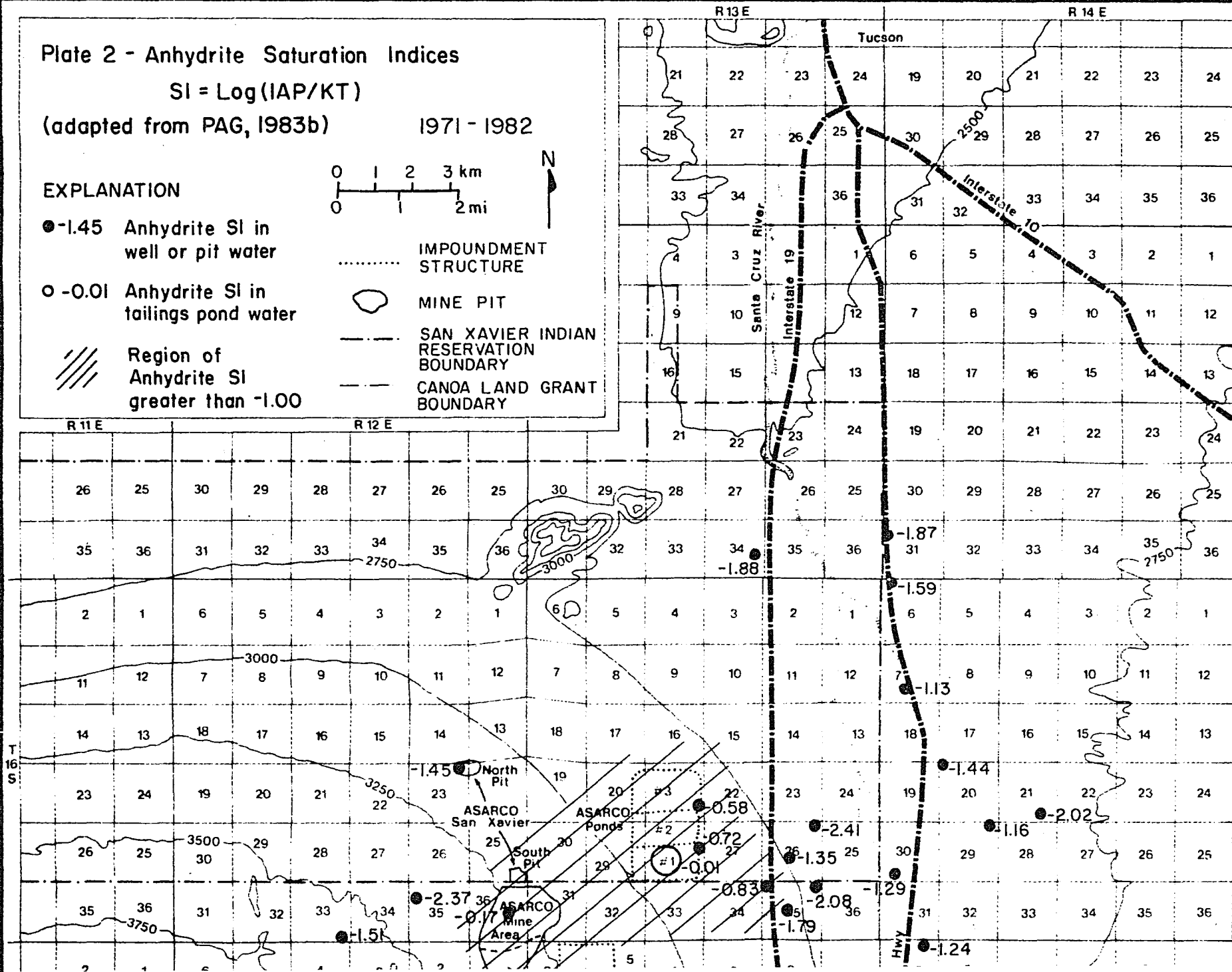
● -1.45 Anhydrite SI in well or pit water

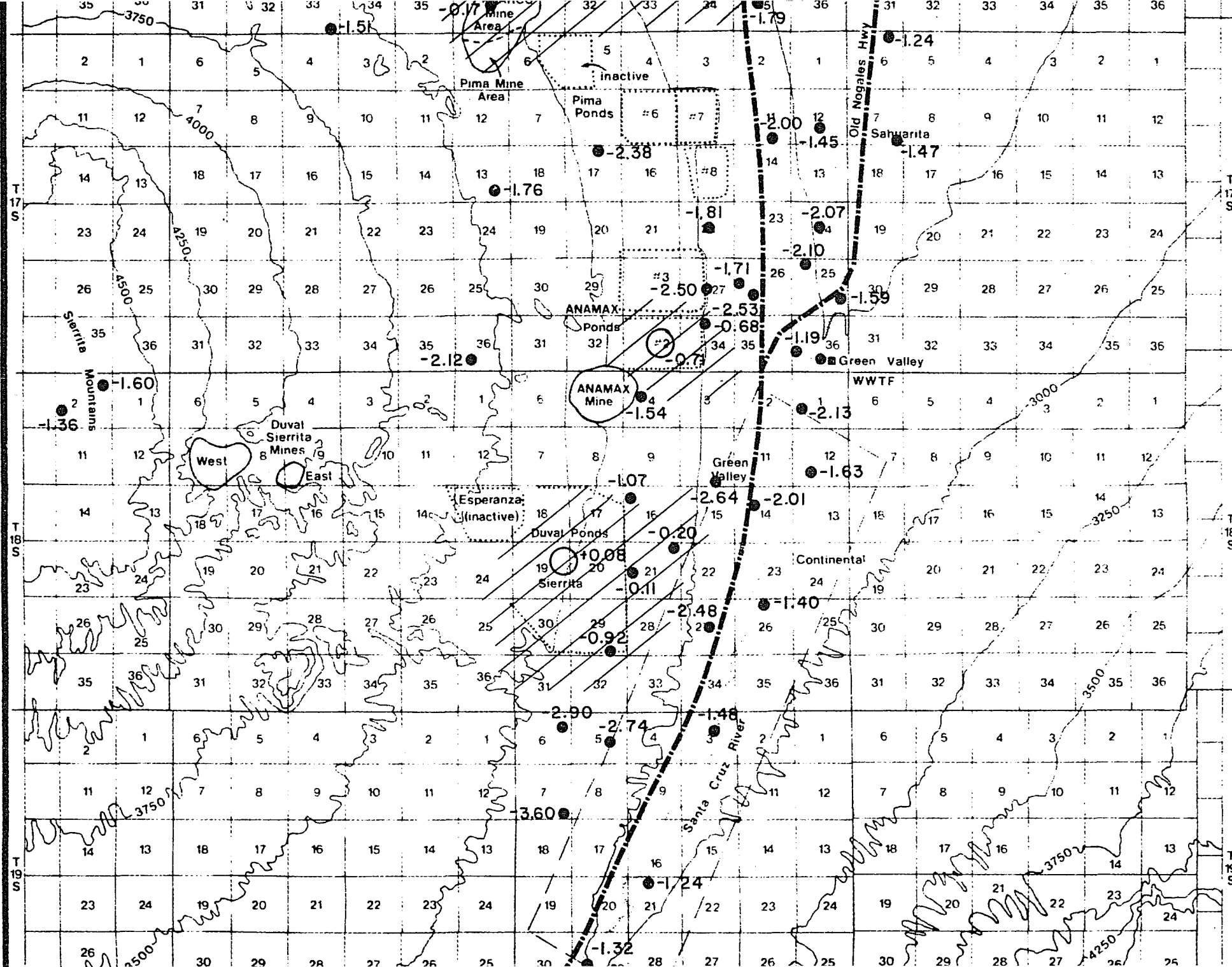
○ -0.01 Anhydrite SI in tailings pond water

Region of Anhydrite SI greater than -1.00



- ..... IMPOUNDMENT STRUCTURE
- MINE PIT
- - - SAN XAVIER INDIAN RESERVATION BOUNDARY
- - - CANOA LAND GRANT BOUNDARY





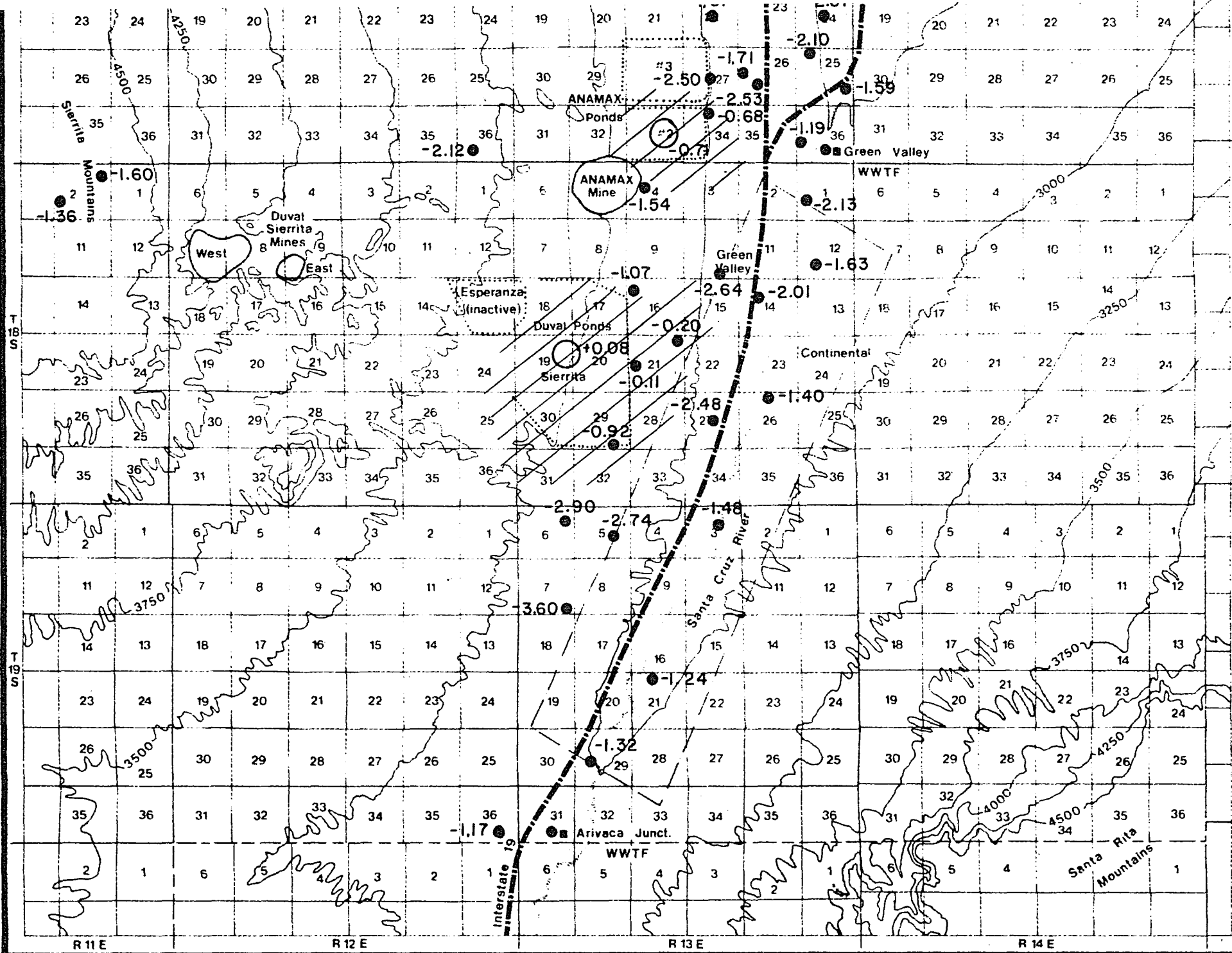


Plate 3 - Calcite Saturation Indices

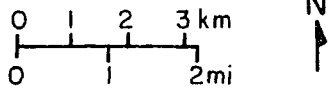
$$SI = \text{Log} (IAP/KT)$$

(adapted from PAG; 1983b)

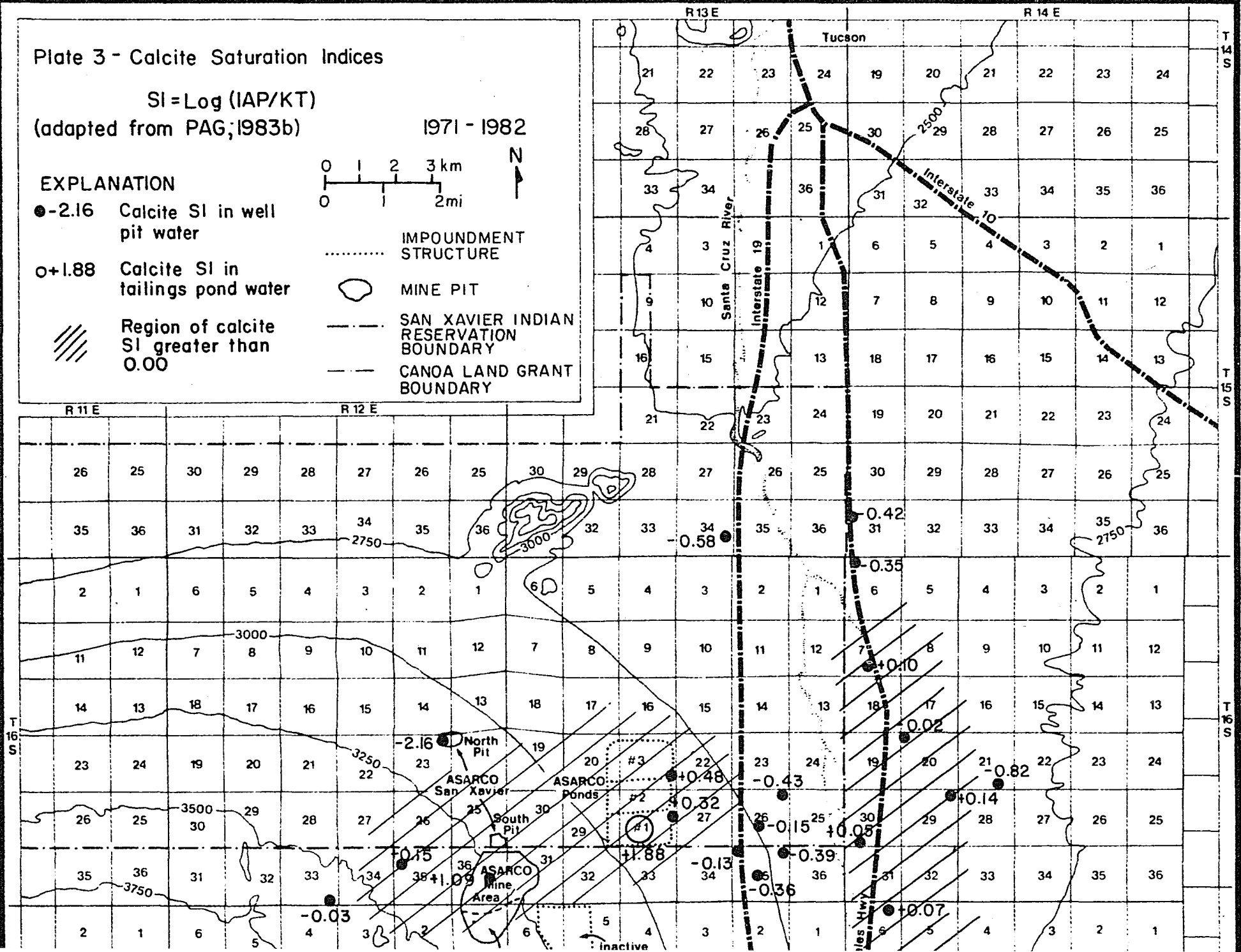
1971 - 1982

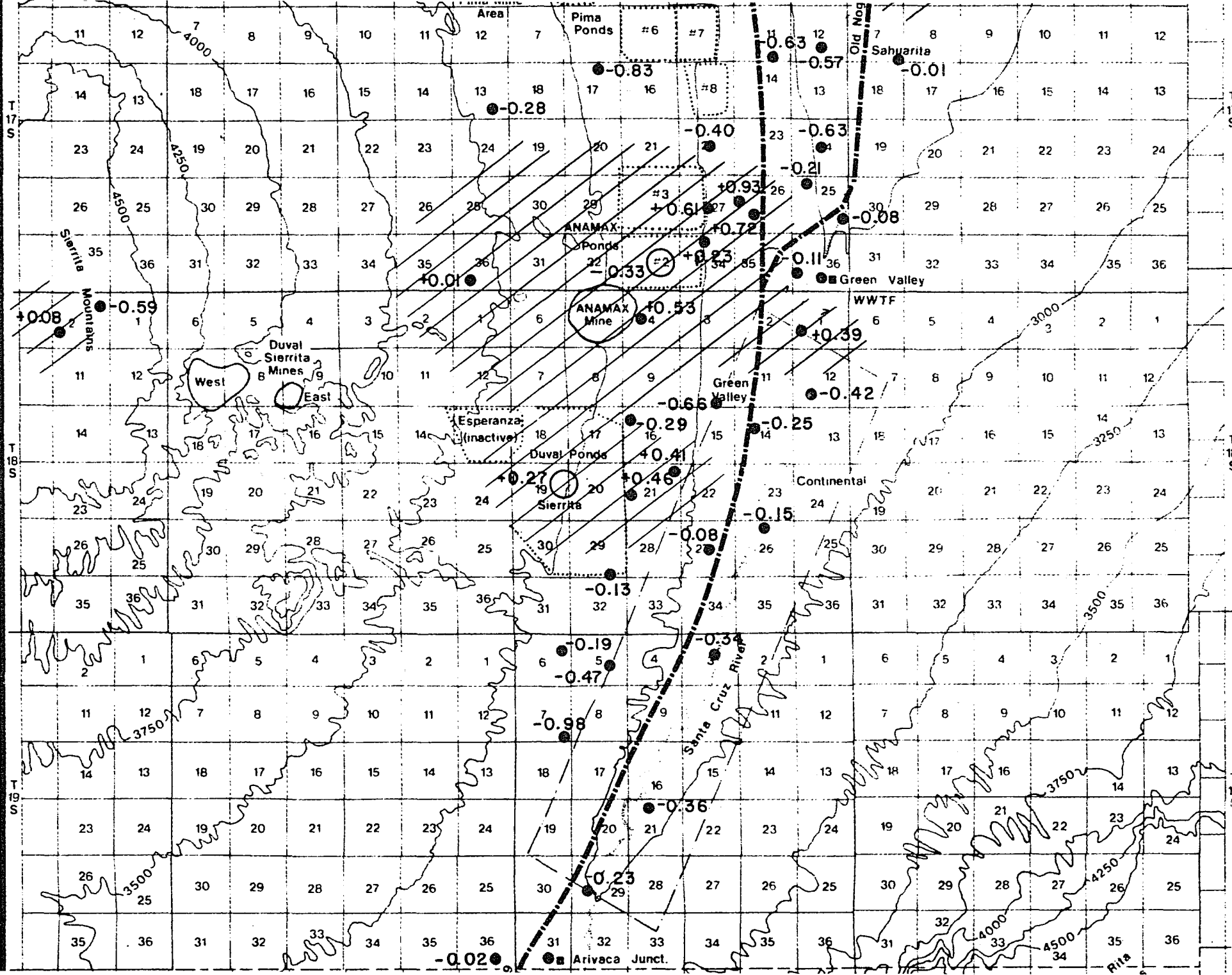
EXPLANATION

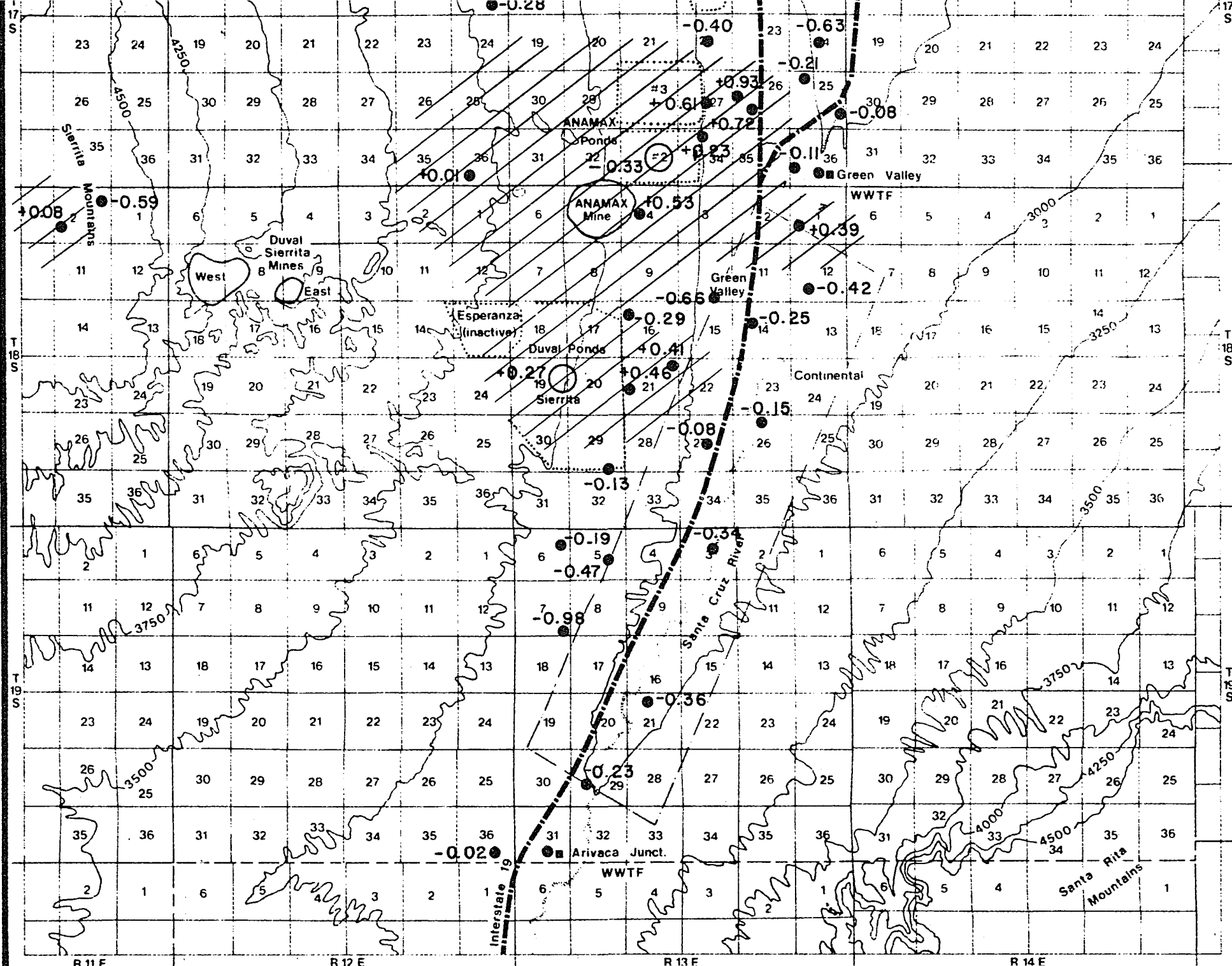
- -2.16 Calcite SI in well pit water
- +1.88 Calcite SI in tailings pond water
- Region of calcite SI greater than 0.00



- ..... IMPOUNDMENT STRUCTURE
- MINE PIT
- - - SAN XAVIER INDIAN RESERVATION BOUNDARY
- - - CANOA LAND GRANT BOUNDARY









# Plate 4 - Fluorite Saturation Indices

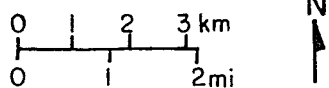
$$SI = \text{Log} (IAP/KT)$$

(adapted from PAG, 1983b)

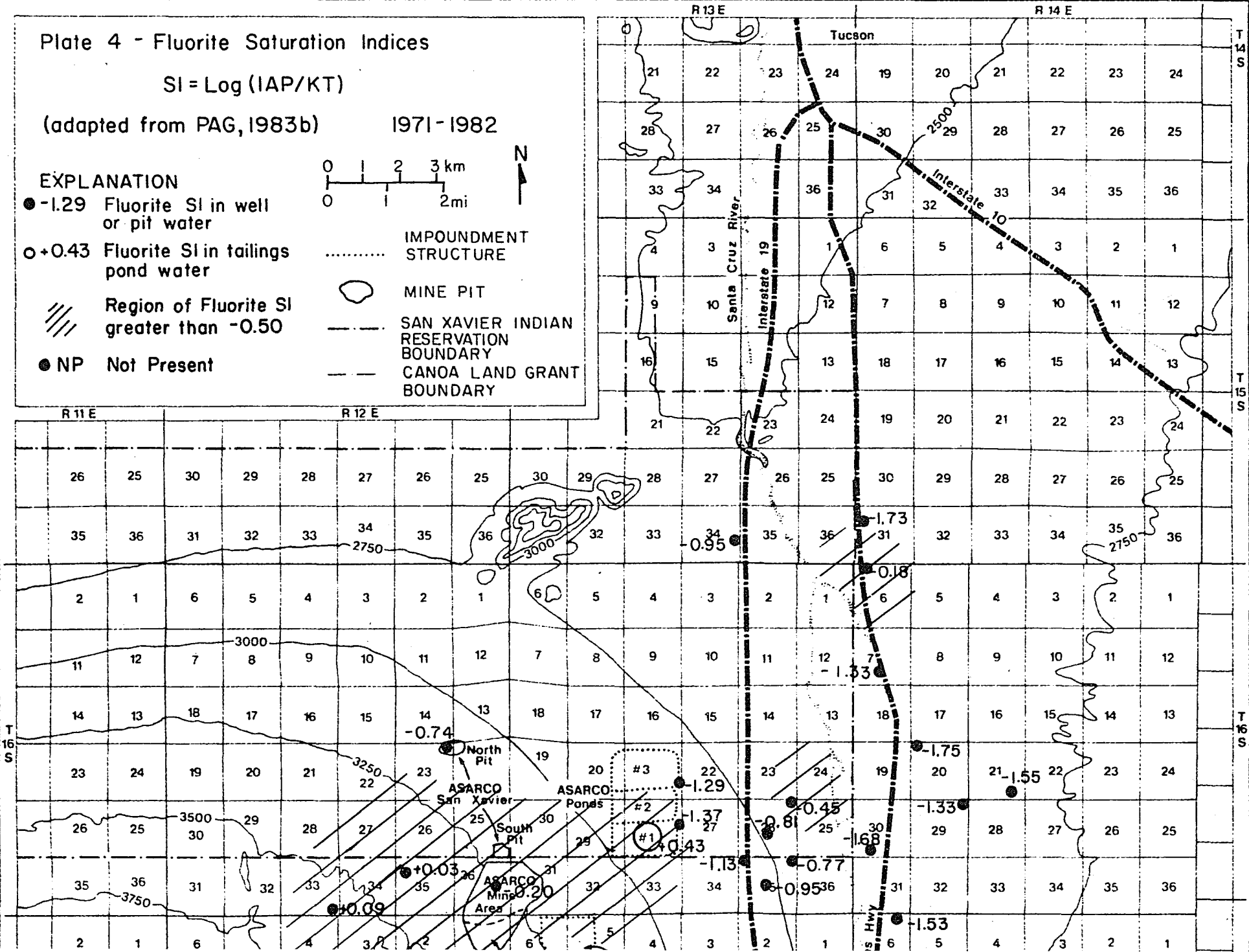
1971-1982

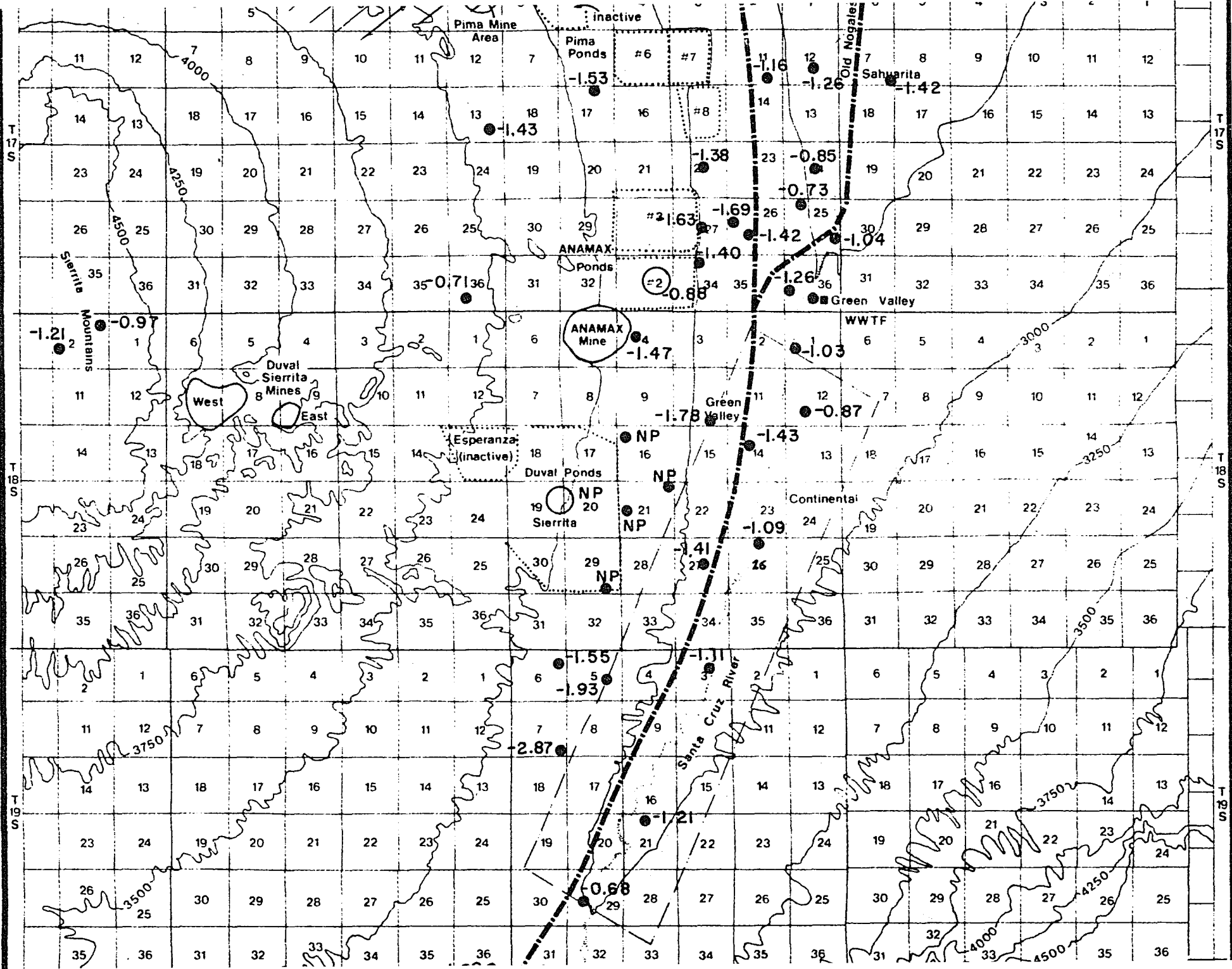
## EXPLANATION

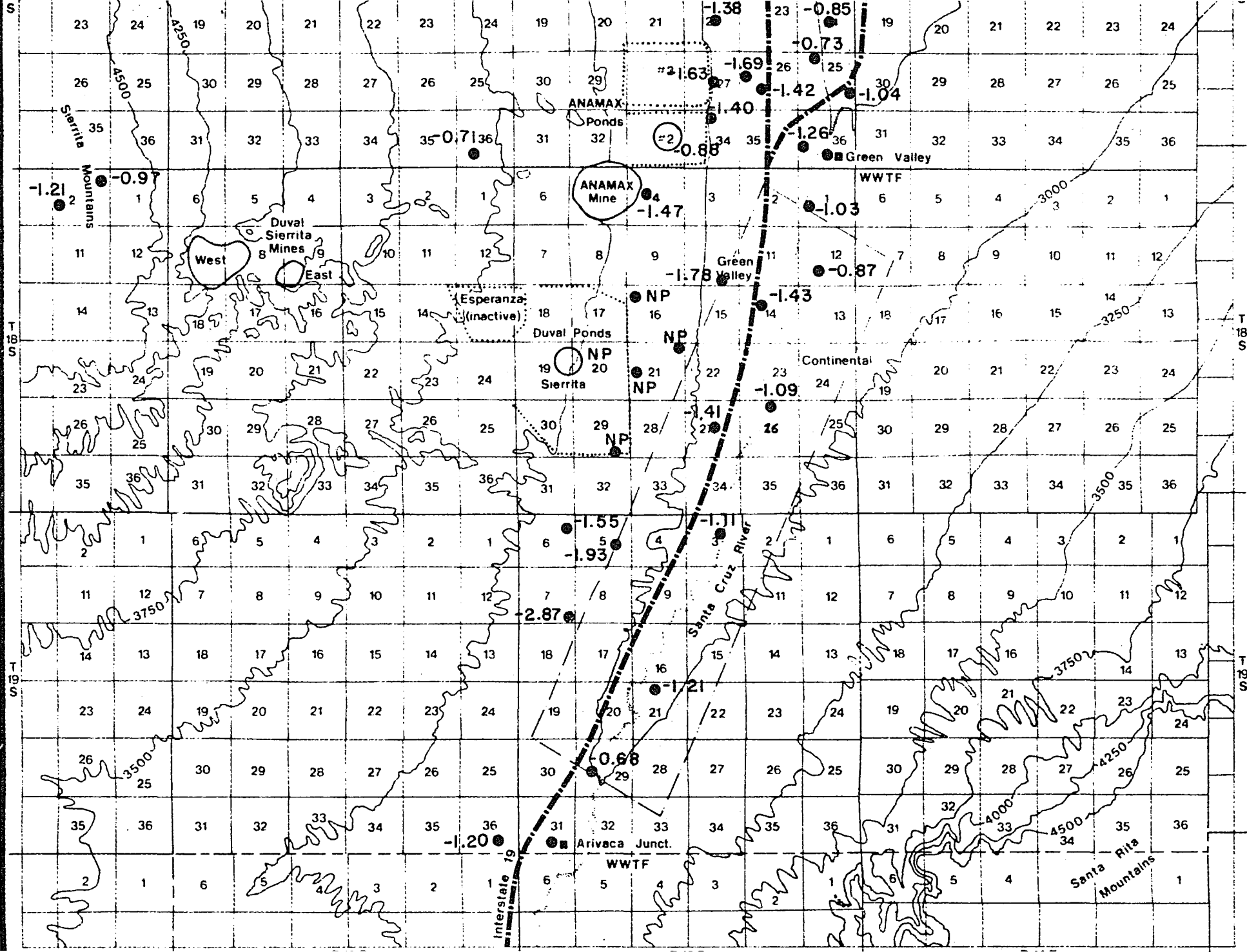
- -1.29 Fluorite SI in well or pit water
- +0.43 Fluorite SI in tailings pond water
- /// Region of Fluorite SI greater than -0.50
- NP Not Present



- ..... IMPOUNDMENT STRUCTURE
- MINE PIT
- SAN XAVIER INDIAN RESERVATION BOUNDARY
- CANOA LAND GRANT BOUNDARY







# Plate 5 - Gypsum Saturation Indices

$$SI = \text{Log} (IAP/KT)$$

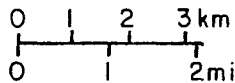
(adapted from PAG, 1983b) 1971-1982

## EXPLANATION

● -1.41 Gypsum SI in well or pit water

○ -0.79 Gypsum SI in tailings pond water

Region of Gypsum SI greater than -1.50



- ..... IMPOUNDMENT STRUCTURE
- MINE PIT
- SAN XAVIER INDIAN RESERVATION BOUNDARY
- CANOA LAND GRANT BOUNDARY

