METHODOLOGY FOR INVESTIGATION OF INTERNAL COATING IN WATER MAINS

Thesis for the Degree of M. S. MICHIGAN STATE UNIVERSITY JOHN C. O'MALIA 1972







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ABSTRACT

METHODOLOGY FOR INVESTIGATION OF INTERNAL COATING IN WATER MAINS

By

John C. O'Malia

The purpose of this thesis is to develop a methodology in which to review any type of internal coating in a water main. It brings together an overview of the various scattered data and techniques into focus on several specific samples and conditions.

A review of the literature reveals that various identification techniques have been used in identifying various internal coatings (protective and non-protective).

The thrust of the methodology is to coordinate a multi-investigation as regards the identification of coatings or compounds. This investigation involved the use of chemical testing, X-ray diffraction and use of the petrographic microscope.

The coatings for testing were for both the Calcite (Calcium ion bearing) or iron bearing compounds.

The use of the three methods on the two coating systems did reveal that the combined tri-effort can be very informative, accurate and reinforcing. That is, that the strong feature of any one method compensates for any drawback that another method may have.

The method that allows the quickest and most accurate identification of any coating or compound is the use of X-ray diffraction. The initial use of the X-ray method then allows effective and efficient use of the chemical and petrographic microscope methods.

The visual aids to illustrate the laboratory techniques as regards each methodology will be most helpful in refining the physical parameters that are involved in the protective coating mechanism on the internal surface of a water main.

METHODOLOGY FOR INVESTIGATION OF INTERNAL

COATING IN WATER MAINS

By

John C. O'Malia

A THESIS

Submitted to Michigan State University in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

Department of Civil and Sanitary Engineering



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DEDICATION

This thesis is dedicated to my family.

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/ TABLE OF CONTENTS

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																Page
DEDICAT	ION	•	•	•	•	•	•	•	•	•	•	•	•	•	•	ii
ACKNOWLE	EDGME	NTS	•	•	•	•	•	•	•	•	•	•	•	•	•	iii
LIST OF	FIGU	RES	•	•	•	•	•	•	•	•	•	•	•	•	•	vi
Chapter																
I.	INTF	RODU	CTI	ON	•	•	•	•	•	•	•	•	•	•	•	1
II.	LITE	RAT	URE	RE	VIE	W	•	•	•	•	•	•	•	•	•	3
		The	Th	eor	ус	of C	lorr	osi	.on	•	•	•	•	•	•	4
		Par mbo	tec	tiv	re C	alc	i in cium		irbo	nat	.ng :e (a r Coat	ing	- J•	•	5
		The	Coa	tin	ugs	• Vol	'gen	• •		• Dro		.ve	•	•	•	7
		The	coa	re tin	OI	vei	.001	су	TU	Pro	tec		e	_	_	9
		Pro	tec	tiv	ve C	oat	ing	Us	ing	PC	lyr	ohos	pha	ites	•	10
		The	Coa	tin	igs	•	•	•	•	•	•	•	•	•	•	12
III.	THEC	RET	ICA	гc	ONS	SIDE	RAT	ION	IS	•	•	•	•	•	•	20
		Int	rod	uct	ion	1.	•	•	•	•	•	•	•	•	•	20
		Two	TY	pic	al	Cor	ros	10n	i Ce	118		•	•	•	•	21
		FOI	mat	10n Dif			.str	Y	• •	•	• £	• T=+	•	•	•	22
		V-T	ay Coa	DII tin	IId	in	.on Wat		Mai	nci ng	⊥у	TUC	.ern	lar		29
		Opt	ica	1 C	rvs	stal	.log	rap	hv		•	•	•	•	•	34
					- 4		J	-		-	-	-	-	-	-	
IV.	EXPE	RIM	ENT	AL	TES	ST A	PPA	RAT	US	ANE) MA	TER	IAL	•	•	52
		Che	mic	al	Tes	tin	ıg	•	•	•	•	•	•	•	•	52
		X-r	ay	Dif	fra	cti	.on	•	•	•	•	•	•	•	•	52
		Pet	rog	rap	hic	: Mi	.cro	sco	pe	•	•	•	•	•	•	53
		Tes	t S	pec	ime	ns	•	•	•	•	•	•	•	•	•	54

Chapter

V.	EXPERIMENTAL	PROC	EDURE	Ξ.	•	•	•	•	•	•	•	60
	Introduc	tion			_							60
	Visual T	nsnec	Fion	•	•	•	•	•	•	•	•	60
	Fuelueti	on of		-inc	•	or.	~	•	•	•	•	00
	Evaluati		igal	T A	13 77+	; ; ;		ipou	ius			62
	USING Erroluoti		Cal	Tue	2110	T T T	Cal	.101	•	•	•	02
	Evaluati	on or	Coat	ind	js		Con	ipoui	nas			<u> </u>
	Using	x-ra	γιαε	ent:	LII	cat	100	•	•	٠	٠	65
	Evaluati	on of	Coat	ing	JS	or	Con	pour	nds			
	Using	the	Petro	ogra	aph	1C	Mic	rose	cop	е		_
	for I	denti	ficat	ior	n .	•	٠	•	•	•	٠	70
VI.	DATA	• •	•	•	•	•	•	•	•	•	•	82
	Remarks	on Da	ta Fo	orma	at	and	Nc	tat	ion	•	•	82
	Protecti	ve Coa	atind	ıs	•			•				84
	Tron Com	nound	s and	$\hat{\mathbf{A}}$	hat	ina	s.	•		•		92
	11011 001	pound	b unc		540	- y		•	•	•	•	
NTT	DISCUSSION C	ה סבכו	יוד יייכ									164
VII.	DIDCODDION C		0110	•	•	•	•	•	•	•	•	104
	Conoral											164
	General	• •		•	•	٠	•	•	•	•	•	104
	Protecti	ve Coa	ating	JS	•	•	٠	•	٠	•	•	164
	Iron Com	pound	s and	d Co	bat	ing	s.	•	•	•	•	171
VIII.	CONCLUSIONS	• •	•	•	•	•	•	•		•	•	191
IX.	RECOMMENDATI	ONS .	•	•	•	•		•			•	196
BTBLTOG	RAPHY.			•				-			•	200
0101100		• •	•	•	•	•	•	•	•	•	•	
ADDENDT	CFC											204
AFF ENDI		• •	•	•	•	•	•	•	•	•	•	204
7	Data for Non		. Mi	~~~	1	~						206
Α.	Data for Non	-opaqi		.nei	ar	5.	٠	•	•	•	•	200
-		. .	-	1-		~ .				•		
в.	Calcium (Ca)	and .	Iron	(Fe	e)	Per	cen	tage	28	ın		
	Various Comp	ounds	•	•	•	•	•	•	•	•	•	207
с.	X-ray Diffra	ction	Data	1.	•	•	•	•	•	•	•	208
D.	Some Calcula	tions	of "	'd"	Sp	aci	ng	for	Ca	lci	te	
	(CaCO ₂ or Ca	0 • CO2) Usi	nq	Br	aqq	's	Equa	ati	on		211
	. j		–	2		22		•				
E.	Data on Mine	rals t	for T	Ise	of	Pe	tro	arar	bi	с		
	Microscope		v					 		-		214
		• •	•	•	•	-	•	•	•	•	-	
F	Crystal Grou	n Dati	-									221
£. •	Crystar Grou	P Dale		٠	•	•	٠	•	•	•	٠	لل متد متد

Page

v

LIST OF FIGURES

Figure					Page
1.	Tuberculation	•	•	•	21
2.	Calcite Coating	•	•	•	22
3.	Special Types of Planar Nets	•	•	•	30
4.	Lattice Plane	•	•	•	31
5.	Diffraction of X-Rays	•	•	•	33
6.	Petrographic Microscope	•	•	•	36
7.	Plane-polarized Electromagnetic Wave.	•	•	•	37
8.	Plane-polarized Electromagnetic Wave.	•	•	•	38
9.	Passage of Light through a Microscope Containing Polarizing Filters	•	•	•	39
10.	Upper & Lower Filter	•	•	•	41
11.	Becke Line Method	•	•	•	47
12.	Half or Oblique Illumination	•	•	•	49
13.	Half or Oblique Illumination in Plan.	•	•	•	50
14.	l" Cast Iron Water Pipe Nipple with Con Blister (M = 4x)	rrc •	sion •	n •	58
15.	Chemical Testing Equipment	•	•	•	64
16.	Petrographic Microslope	•	•	•	72
17.	Data Sheet	•	•	•	81
18.	Calcite: 1-A	•	•	•	86
19.	Protective Coating: 1-B	•	•	•	88
20.	Cast Iron: 1-C	•	•	•	90
21.	Calcite 1-A-I		•	•	93

22.	Calcite 1-A-II	•	•	95
23.	Calcite 1-A-III	•	•	97
24.	Calcite 1-A-IV	•	•	99
25.	Calcite 1-A-V	•	•	101
26.	Protective Coating 1-B-I	•	•	103
27.	Protective Coating 1-B-II	•	•	105
28.	Fe_2^{0} (Pure)	•	•	109
29.	Fe ₂ 0 ₃ (Pure) @ 1 Hr 500°C	•	•	111
30.	Fe_2^{0} (Pure) plus nH_2^{0}	•	•	113
31.	$Fe_2^{0}_3$ (Pure) plus nH_2^{0} @ 1 Hr 500°C.	•	•	115
32.	Fe0. Fe_2^{0} or Fe_3^{0} or \cdots	•	•	118
33.	Fe0. $Fe_2^{0}_3$ or Fe 0 @ 1 Hr 500°C.	•	•	120
34.	No "d" Spacing as the Material Tested wa Amorphous (without crystal structure)	s.	•	122
35.	No "d" Spacing as the Material Tested wa Amorphous (without crystal structure)	.s •	•	124
36.	No "d" Spacing as the Material Tested wa Amorphous (without crystal structure)	s •	•	126
37.	FeCO ₃ @ 1 Hr 500°C	•	•	128
38.	FeCO ₃ @ 1 Hr 500°C	•	•	130
39.	FeCO ₃ @ 1 Hr 500°C	•	•	132
40.	Corrosion Sample - Top	•	•	134
41.	Corrosion Sample - Bottom	•	•	136
42.	Corrosion Sample - Top 1 Hr 500°C	•	•	138
43.	Corrosion Sample - Bottom 1 Hr 500°C.	•	•	140
44.	Hematite - Fe_{20} , Reagent Grade, Index O 2.00, M - 240x	il -	•	144
45.	Magnetite - FeO. Fe ₂ 0 ₃	•	•	146

Figure

46.	Siderite - FeCO 2.00, M - 240	(Forma)	tion)	Index	Oil	-	•	•	148
47.	Siderite - FeCO Index Oil - 2	(Forma .0, M -	tion) 240x	Becke	Line •	e •	•	•	150
48.	Siderite - FeCO		• •	• •	•	•	•	•	152
49.	Siderite - FeCO		• •	• •	•	•	•	•	154
50.	Corrosion Sample	e - Pipe	Nipp	le Tak	en fi	rom	тор	ο.	156
51.	Corrosion Sample Bottom	e - Pipe	Nipp]	le Tako	en fi	rom •	•	•	158
52.	Corrosion Sample	e - Pipe	Nipp	le Tak	en fi	com	Тор	ο.	160
53.	Corrosion Sample Bottom	e - Pipe	Nipp]	le Tako	en fi •	rom •	•	•	162
54.	Calcite	•••	• •	•••	•	•	•	•	225
55.	Aragonite	• •	• •	• •	•	•	•	•	225
56.	Apatite	• •	• •	• •	•	•	•	•	226
57.	Vivianite	•••	• •	• •	•	•	•	•	226
58.	Ankerite	•••	• •	•••	•	•	•	•	227
59.	Hematite	•••	• •	•••	•	•	•	•	227
60.	Magnetite	•••	• •	•••	•	•	•	•	228
61.	Siderite	• •	• •	• •	•	•	•	•	228
62.	Goethite	•••	• •	• •	•	•	•	•	229
63.	Lepidocrocite .	• • •	• •	• •	•	•	•	•	320

CHAPTER I

INTRODUCTION

It was reliably estimated a little over 13 years ago that the replacement cost of all water distributions systems in the United States was ten billion dollars (1). In addition, it was estimated that 60% of all water works capital is in the water distribution system. The internal area of a water distribution system for a population of 25,000 has been estimated to be 17 acres or 740,000 square feet (2). These staggering statistics point to a need to maintain a water distribution system in near perfect shape.

Technology will surely lead to development of corrosion resistant pipe. However, we are presently installing pipe that can corrode and deteriorate and must maintain thousands of miles of installed pipe that is deteriorating.

In partial answer to reducing or eliminating corrosion in the water distribution system several "protective coatings" have evolved and experienced much laboratory refinement. Calcium carbonate (calcite) is one protective coating that has proved beneficial over many

years. In the past fourteen years, the refinement of the calcite protective coating--through water chemistry--has evolved to a workable anti-corrosion mechanism that has field application.

Refinements of the coating process have, however, related to the mechanism of deposition and not to the coating formation and/or composition.

It has been the object of this thesis to develop a methodology for investigating the corrosion products, calcite protective coating and iron compounds that are a result of the protective coating mechanism or are caused by corrosion before, during or after the coating process.

To accomplish the investigation reported here, water chemistry, X-ray defraction and optical crystallography were used on various Calcite and iron compound formations or coatings. The development of an orderly investigation or methodology to correlate the unknown to the known has advantages not only for identifying coating composition and structure, but for refinement of the coating process.

CHAPTER II

LITERATURE REVIEW

In 1903, M. Whitney (3) first stated the electrochemical theory of corrosion. In the ensuing years his thesis has been used, refined and reused to predict this natural phenomena. Many techniques for water main corrosion control, some successful and others with limited success, have been tried over the years and include; (a) pH adjustment, (b) deareation for removing oxygen and carbon dioxide, (c) silicate feed, (d) poly and glassy phosphates, (e) mechanically applied inert internal pipe coatings, (f) biological growth control using chlorination, and (g) a balanced control of pH-alkalinitycalcium carbonate.

The presence of calcium carbonate in most domestic water supplies makes this compound a logical choice as a corrosion inhibitor. Calcium carbonate appears in nature in three forms. The one most common and stable at standard temperature and pressure is Calcite. The other two (Aragonite and Vaterite) are either unstable at standard temperature and pressure or readily alter to Calcite.

The Theory of Corrosion

The corrosion process can be quite complex. Corrosion is an electrochemical balance between the anode and cathode areas and generally is described with the following reaction:

anode: Fe[°] (metal)
$$\rightarrow$$
 Fe⁺⁺ + 2e⁻ (1)

cathode:
$$2H + 2e \rightarrow 2H^+$$
 (2)

Secondary reactions that occur in the aqueous

$$2H + 1/20_2 \rightarrow H_20$$
 (3)

$$Fe^{++} + 2OH^{-} \rightarrow Fe(OH)_{2} \tag{4}$$

$$4Fe (OH)_{2} + O_{2} \rightarrow 4H_{2}O \ 2Fe_{2}O_{3}$$
(5)

The corrosion cell is an electrolytic cell in which metal is removed from the anode (negative) during the passage of a direct current between the cathodic (positive) area and the anodic area. The cathode area is usually adjacent to, and larger than, the anodic area.

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A review of equations 2, 3 and 4 indicate that both oxygen and pH play important roles in the rate of corrosion. Many authors (14, 25, 31 and 34) have stated that dissolved oxygen is the most important mechanism of removing hydrogen from the cathode and increasing the rate of corrosion. Also, corrosion of iron in aqueous solutions has been found to be under cathodic control if the pH is less than 11. Therefore, some workers have postulated that if a metal is under cathodic control, the corrosion rate may be slowed by removing oxygen, by covering cathodic areas with protective coatings to reduce contact with oxygen or by altering the reactions of corrosion. Control of corrosion is a control of equation 2 and/or 3.

Parameters Used in Developing <u>a Protective Calcium</u> Carbonate Coating

The early recognition that calcium carbonate may form an internal protective coating for inhibiting corrosion were empirical. Baylis (15), as reported by Evans (14), in 1926 recommended that an aggressive water be treated with just sufficient alkali to cause it to develop calcium carbonate slowly on pipe interiors. Once the pipe had a continuous calcium carbonate layer, he recommended that alkali be added in such an amount that it would cease to deposit, but not dissolve the film.

In 1932, Tillman and others (5) developed a practical and useful test to determine the degree of water super- or under-saturation with calcium carbonate. This initial refinement or "marbel test" did provide control and predicted the tendency toward scale formation or

dissolution. Four years later, another more important test or index was developed--the "saturation index" by Langelier (6).

The "saturation index," based on physical chemistry principles, provided an indication of the duration of the chemical equilibrium driving force. A positive index indicated a tendency for the water to be scale forming and scale solution was association with a negative index. A discussion by Moore (7) described how a water might be adjusted by addition of lime and/or sodium carbonate to yield a positive scale forming indes.

The Langelier "saturation index" provided a new refinement (8, 9) by considering temperature effects on the pH of the water. Progress also resulted from the work of Larson and Buswell (10) who computed the effect of temperature and salinity on ionization constants. Ryznar (11) proposed an empirical "stability index" with the view of estimating the degree of scaling to be expected from a water with a specific alkalinity, calcium and hydrogen ion correlation.

Dye (12) suggested that the concentration of calcium carbonate in excess of the solubility product constant be called the "momentary excess" of calcium carbonate. The "momentary excess" is that concentration of calcium carbonate which under specific chemical and physical condition is available for precipitation. More

recently, McCauley (13) has proposed a new parameter to predict a tendency toward Calcite coating which he has termed "driving force index" and defined as the ratio of the product of the calcium and carbonate concentration over the solubility product of calcium carbonate (CaCO₃) all expressed as CaCO₃. The driving force index indicates the magnitude of the equilibrium force causing calcium carbonate (Calcite) deposition or coating.

The above parameters are indicative of the physical-chemical concepts that have evolved to predict calcium carbonate (Calcite) coating formation mechanism and the relationship between the physical conditions that effect the CaCO₃ equilibrium in water.

The Role of Oxygen in Protective Coatings

The role of oxygen in protective coating development poses one problem--does it or does it not enhance the protective coating? It has been an American water works practice to keep oxygen concentration to a minimum because oxygen appears as the primary factor controlling the corrosion rate. On the other hand, European workers, as reviewed by Evans (14), intentionally aerate a water to increase oxygen levels before it enters the pipeline. The European argument is that corrosion resulting from the oxygen content is desirable for promoting and

accelerating deposition of a calcium carbonate protective coating,

$$4e + O_2 + 2H_2O \rightarrow 4OH^-$$
 (6)

$$OH^{-} + Ca^{++} + HCO_{3}^{-} \rightarrow CaCO_{3}$$
 (Calcite) + $H_{2}O$ (7)

According to Schikorr (18) and others, an oxygen concentration of at least 6 mg. per liter is necessary to produce a protective coating. Many authors, including Evans (14), believe that a coating of calcium carbonate over a layer of iron (ferric oxide) rust will become more protective if oxygen is present in large amounts, largely because the rust will then be formed very close to the metal.

Evans (14) has reviewed the works of several authors (30) who conducted experiments with oxygen present or absent, to observe the electrical current. The data confirm that the aerated electrode becomes the cathode and show that dissolved oxygen causes a solution to become a better conductor of electrical currents, thus stimulating corrosion velocity.

Other authors have stated that if a metal is under cathodic control the corrosion rate may be slowed by removing oxygen or by covering the cathodic areas with protective coatings to reduce contact between those areas and dissolved oxygen (24, 25).

The Role of Velocity in Protective Coatings

A discussion of hydraulic velocity relates to both laminar and turbulent flow. Romeo (31) and coworkers, using Fick's law of diffusion for hydraulically smooth pipe in turbulent flow, found that: (1) the rate of oxygen supply to the pipe wall varied as the 0.875th power of the velocity in pipes of the same diameter and (2) the rate of oxygen supply to the pipe wall varied as the 0.125th power of the pipe diameter in flows of equal velocity. However, the rate of oxygen transfer increased with increasing turbulance.

McCauley (13) has shown through mathematical analysis and experimental work that a better protective Calcite coating can be developed at velocities of 3-13 fps. than at 0-1.5 fps. It is his opinion that the turbulence at the pipe surface contributes to the total energy requirements in the formation of Calcite protective coatings.

It is generally concluded that corrosion of bare metal increases with velocity and the associated oxygen availability at the pipe surface. However, in regions of low flow, the transfer of chemicals and dissolved gases must depend on diffusion. In a laminar flow, reactions at the pipe surface may diminish after depleting the available chemicals and therefore reduce the corrosion or protective coating reaction rate.

It has been concluded that waters that are not corrosive and aggressive under normal flow conditions may deposit a Calcite protective coating and be very aggressive and corrosive in dead ends of a water distribution system (32).

Protective Coating Using Polyphosphates

The use of hexametaphosphate as a corrosion inhibitor has been reported by Rice and Hatch (33). It was their opinion that the metaphosphates are absorbed on the metal surface.

Eliassen and Lamb (34, 35), from their experimental work on the inhibitive mechanism of metaphosphates, concluded that: (1) metaphosphates remove the corrosion products from the anode and deposit these same products on the cathode; (2) positively charged particles of hydrous ferric oxide and metaphosphate are formed near the anode and to some extent on the cathode; (3) the rate of metaphosphate deposition on the cathodes is increased by the presence of corrosion products or of iron in solution; and (4) the deposition may be termed an electrodeposition.

Physical investigations of the protective coating on the metal pipe surface indicates that there is a high ferric oxide-metaphosphate ratio and a minimum pH at the anode. However, the protective film on the cathode is

composed of colloidal metaphosphates, ferric oxide and other particles deposited from solution.

Rosenstein (36) discovered that a 1.0 ppm concentration of molecularly dehydrated phosphate effectively inhibited the foundation of calcium carbonate scale. Investigations by Reitemeier and Buehrer (37) on the inhibiting action of trace amounts of sodium hexametaphosphates found that a "threshold level" of 1.5 ppm of metaphosphate prevented deposition of calcium carbonate. Metaphosphates in concentrations below the "threshold level" interferred with the crystallization process of calcium carbonate, and produced large, grossly distorted crystals. Precipitated calcium carbonate was found to absorb the metaphosphate. Several workers have stated that threshold treatment tends to slowly remove old deposits of calcium carbonate chalk and corrosion products from the metal pipe surface. However, tests by Larson (38) found that megnesium hydroxide scale was not removed from the pipe surface by the addition of metaphosphates to a water.

McCauley (13) experimented to determine the optimum conditions for the development of pure Calcite protective coatings when using polyphosphates to control coating development. It was found that the addition of 0.02-3.2 ppm metaphosphate to a ground water

supersaturated with calcium carbonate resulted in a dense Calcite coating in two hours.

It has been reported by McCauley (39) that 1200 feet of six inch cast iron water main was successfully coated with a dense Calcite coating with the use of polyphosphate while varying the coating parameters to achieve a dense coating. Microscopic investigation of these coatings revealed a dense crystalline structure with practically no rust but with some pin holes; the coating appeared glass-like.

In studies conducted by Woodruff (40) the development of a protective Calcite coating was accomplished by use of threshold treatment (0.50 ppm polyphosphate). Microscopic investigation of the generally dense coatings revealed that the Calcite crystal structure was tightly bonded to the metal surface. In most cases the coating was continuous over the entire surface and was homogeneous. Polarigraphic studies when using 1.2" x 3.2" cast iron strips confirmed that the Calcite-metaphosphate coating was a cathodic inhibitor.

The Investigation of Protective Coatings

It has been shown by Evans (14) and others that calcium carbonate (Calcite) coatings can be formed. It is Evans' (14) opinion that a very soft water may attack a pipe indefinitely. Fortunately, most waters contain

a considerable level of calcium carbonate which is kept in solution by carbon dioxide. If the carbon dioxide excess is just sufficient to keep the calcium carbonate in solution, any incipient corrosion will increase the pH at the cathode region and lead to precipitation of calcium carbonate. As this layer is formed the cathode will be diverted elsewhere until the entire internal surface is covered with calcium carbonate. The calcium carbonate layer in the presence of sufficient oxygen will interact with iron salts formed below to give a clinging form of ferric oxide rust. The mixed layer, which often has a considerable protective character, can be described as chalky rust or rusty chalk. This layer may be more protective if oxygen is present in large amounts because the rust is then formed very close to the metal. The interaction between $CaCO_3$, CO_2 and ferrous salts first forms FeCO3 which is then oxidized. In the absence of oxygen, Magnetite often loose and not protective, is formed. Evans has quoted Baylis (17) that in a corrosion anode when the acid iron salts meet the relatively alkali water, the iron is precipitated, forming voluminous tubercles of incoherent magnetic oxide. Farther from the metal at the boundary of the region where dissolved oxygen is present in excess a relatively coherent membrane of hydrated ferric oxide appears.

It has been reported by Schikorr (18) as quoted by Evans (14) that rapid oxidation of ferrous hydroxide [FeO·H₂O or Fe(OH)₂] by oxygen forms the α form of hydrated ferric oxide, while slow oxidation yields first a Ferrosoferric body (regarded as ferrous-ferrite) which in turn yields the σ form of hydrated ferric oxide. Both α and σ forms have common chemistry [Fe₂O₃·H₂O or FeO(OH)]. X-ray examination has shown that the α form is crystallographically identical with the mineral Goethite and the σ form with the mineral Lepidocrocite. However, the common precipitation of both minerals is an aggregation of particles of colloidal size and shows no signs of crystal facets. Precipitated rust is very voluminous, containing far more water than iron oxide and tends to darken with age--probably due to water loses and the formation of ferric oxide (Fe₂O₃). The hydrated form of σ ferric oxide may have a marked blood red color and lose water, forming granular black Magnetite (Fe₃O₄)--usually very stable as pointed out by Bengough, Lee and Wormwell (19).

It has been noted by Girard (20) that for ferrous hydroxide formed on iron the outer portion is converted to the ferric condition in the presence of oxygen. The outer ferric portion can further react with the ferrous state to form a green intermediate hydrated Magnetite $[FeO \cdot Fe_2O_3 \cdot H_2O, Fe_3O_4 \text{ or } Fe(Fe_2O_3) \cdot H_2O]$. However, the diffusion of oxygen to the green body may convert it to

the ferric condition to yield either Geothite or Lepidocrocite, depending upon oxygen arrival rate. Loss of water and oxidation of these intermediate bodies may yield the trigonal ferric oxide (Fe_2O_3) Hematite. The formation of Magnetite is due to lack of oxygen and to further dehydration.

In the iron formation phenomena, as further confirmed by Obrecht and Pourbaix (26), corrosion first produces ferrous hydroxide $[Fe(OH)_2]$ and if oxygen is available, Magnetite $(FeO \cdot Fe_2O_3, Fe_3O_4 \text{ or } Fe \cdot Fe_2O_4)$ is formed (containing both ferrous and ferric iron). Upon further oxidation Limonite $(Fe_2O_3 \cdot nH_2O)$ where n = 3 then $2[Fe(OH)_3]$ is formed with an apparent amorphous structure.

It has been stated by Tillmans and co-workers (21) that hydrated oxide (FeO) is capable of taking up carbon dioxide from the air to form a basic carbonate (FeCO₃). Vernon (22) has strengthened this argument by stating that in both undersaturated and saturated atmospheres carbon dioxide reduces the rate of rusting by causing some change in the character of the rust and rendering it more protective. It has been shown by Baylis (24) that ferrous carbonate is produced in varying degrees as a product of corrosion either as free or half-bound carbon dioxide if the carbonic acid is present. The reaction may take place either directly with metallic iron or with iron oxides or hydroxides. Tests have

shown that ferrous carbonate (FeCO₃) in the absence of oxygen is practically insoluble at a pH and alkalinity close to the calcium carbonate saturation curve. However, solubility increases very rapidly if the pH is decreased below the level necessary for calcium carbonate equilibrium. Baylis (24) has stated that ferrous carbonate (FeCO₃) aids in protecting iron surfaces when the pH and alkalinity are above the calcium carbonate equilibrium levels, especially if the ferrous carbonate is overlaid by some kind of a coating that protects it from dissolved oxygen.

In studies conducted in 1935 by Mears and Evans (23) where water drops were placed on metal and the corrosion reaction observed, it was concluded that if the iron oxide coating over the metal was intact, ferrous hydroxide $[Fe(OH)_2]$ was formed so slowly that oxygen diffusing downward through the drop quickly converted the ferrous state to the ferric state to form hydrated ferric oxide. The hydrated ferric oxide appeared to stiffle further release of the (Fe⁺⁺) ion and the water drop remained rust free.

Camp (25) in his thermodynamic treatment of electrochemical corrosion has shown that ferrous hydroxide [Fe(OH)₂] does not form on iron unless the pH value of the solution exceeds 9.

The data of Strumm (28) on cast iron specimen exposed to oxygen saturated water of varying hardness and pH indicates that a high proportion of calcium carbonate in the film is more important in retarding corrosion than an increased film thickness. Coatings were found to contain a much higher percentage of calcium carbonate in the layers closest to the iron surface than the exterior layers which were predominately iron oxide.

It has been reported by McCauley and Abdullah (29) that the formation of protective Calcite coating was possible by varying the pH, hardness, momentary excess index and using various concentrations of colloidal calcium carbonate. The formations of the protective calcite coating on cast iron samples were mainly hydrous ferric oxide as Limonite with varying amounts of Calcite, usually 5-40%, and Siderate (FeCO₃) was usually observed close to the metal surface but in ridges. In addition, formation of a Limonite-Siderite protective Calcite coating occurred best when the specimens were corroded or when an external current was impressed through the specimen.

In experiments conducted by Pryor (27) on steel immersed in weak acid solutions from one to six months, the corrosion products, with time, varied as did the makeup within the blister. Two tests that provided interesting results were: (a) one month test using a

0.02N Na_2CO_3 solution and (b) one month test using a 0.01N Na_2HPO_4 solution. The description of the corrosion products for (a) are as follows: (1) bottom-loose material comprised mainly of γ and α [FeO(OH) or Fe₂O₃·nH₂O], (2) intermediate layer--greenish brown paste identified as α [FeO(OH) or Fe₂O₃nH₂O] plus unidentified material, and (3) blister shell-- α [FeO(OH) or Fe₂O₃·nH₂O]. The description of the corrosion products from (b) are as follows: (1) bottom--green paste identified as $Fe_3(PO_4)_2 \cdot 8H_2O$ or $3FeO \cdot P_2O_5 \cdot 8H_2O$, the mineral Vivianite, (2) intermediate layer--fine greenish needles with no apparent crystal structure (amorphous), and (3) blister shell--again no apparent crystal structure (amorphous). The material identification by Pryor was accomplished by X-ray diffraction equipment. The results show conclusively that corrosion products do form in layers--some with and some without crystal structure. However, the formation of Vivianite $[3FeO \cdot P_2O_5 \cdot 8H_2O]$ is an uncommon corrosion product and probably due to the phosphate concentration in the test water.

It is quite apparent from the work reported that protective coatings do form on a metal surface submerged in water. The protective coating composition or material varies with the ionic strength, gasses and salts in the aqueous solution. Coating investigative techniques

have varied from visual interpretation, chemical testing and the use of X-ray diffraction methods.

CHAPTER III

THEORETICAL CONSIDERATIONS

Introduction

The coatings that develop internally on water mains can be of two basic types. The first are those compounds or formations that contain the calcium ion. The second contain iron as the major ion concentration and are termed iron formations and coatings.

The former types are a coating that can be formed from random excess hardness (CaCO₃) in the aqueous solution or a coating developed through the use of precise chemical techniques such as developed by McCauley (13, 29, 39).

The latter types are coatings that exhibit a continuous rust formation or localized tuberculation. Depending on the coating type formed further corrosion may or may not continue. If these formations are not controlled a serious reduction in carrying capacity of the water main can evolve.

It is therefore necessary to adjust and control the chemistry of a water in order to predict which formation types will evolve and moreover determine the exact formation or formations that are present.



Two Typical Corrosion Cells

It is important to note that two distinct corrosion cells can form (14, 25, 26, 41). Figures 1 and 2 illustrate these types.



Figure 1 illustrates the effect when a differential electriode potential exists between the inside and outside of a tubercule. The current difference is caused by differential aeration and produces a highly localized corrosion. This tuberculation can be caused from a metal or a chemical protection over the cathode. Metals such as zinc or a substance such as Calcite provide this type of protection.

Figure 2 illustrates a chemical balance or equilibrium where excess carbon dioxide has escaped or been removed; calcium carbonate (Calcite) is over



saturated and reacts with the (OH⁻) ion to form a Calcite coating. This Calcite coating can form on the cathode and seal off further corrosion action or drive the precipitation reaction elsewhere.

Formation Chemistry

Protective Coatings

Protective coatings formed in water systems contain together with the calcium ion other ions in chemical composition or in solid solution. Ions other than calcium commonly found in these formations are: manganese, iron, phosphorus, carbonate, hydroxide and oxygen--all ions that are usually present in an aqueous-ion equilibrium phase. The chemistry of the coatings are as follows.

$\frac{\text{Calcium Carbonate--Calcite}}{\text{CaCO}_{3} \text{ or CaO} \cdot \text{CO}_{2}} (42)$

This chemical formation in the pure form contains by weight 40% as the calcium ion (Ca^{++}) and 60% as the carbonate ion (CO_3^{--}) (see Appendix A and B).
$\frac{\text{Calcium Carbonate--Aragonite}}{\text{CaCO}_{3} \text{ or CaO} \cdot \text{CO}_{2}} (42)$

This chemical formation in the pure form contains by weight the identical percentages as Calcite. However, the Aragonite formation is unstable at normal water works operating temperature and pressure and is not found in the normal water works operation. If formed, Aragonite is ready changed to Calcite (43) (see Appendix A).

$\frac{\text{Apatite} - 9\text{CaO} \cdot 3P_2O_5}{\text{Ca[Fe}_2(\text{OH})_2, \text{CO}_3\text{Cl}_2]} (42)$

The chemical analysis for Apatite requires a very careful isolation and testing procedure. Even though Apatite may be formed in a solid solution, alteration of any ion can alter the known percentages (see Appendix A).

$\underline{\text{Vivianite}-3\text{FeO}}_{2}\underline{O}_{5}\underline{\cdot8\text{H}}_{2}\underline{O}$ (42)

The exact chemical identification of Vivianite is difficult in that the percentages of each ion can change depending on the water of hydration attached to the mineral. Although this mineral does form in water systems, especially where phosphorus or phosphates are used in "threshold treatment," the actual protection for sealing of the cathode region is questioned because the hardness is only 2.0 on the Mohr scale. The soft nature of this material is due to the large water of hydration in the mineral structure (see Appendix A).

$\frac{\text{Ankerite}-\text{CaO}(Mg, Fe)}{0.2CO_2} \cdot$

The chemical determination of Ankerite is also difficult because the five ions involved can change in percentages (see Appendix A).

Iron Formations and Coatings

The iron formations are those that may in some instances provide a protective coating on a water pipe interior. In all cases iron is a major constituent. The iron in formation can be Fe^{++} (Ferrous) or Fe^{+++} (Ferric). The form of iron present in the mineral is due in a large part the level of oxygen present and to the kinetics of oxidation from the $Fe^{++} \rightarrow Fe^{+++}$ state.

In some minerals Fe⁺⁺ and Fe⁺⁺⁺ coexist. The presence of both iron types requires very careful chemical interpretation. Iron compounds most often found in pipe scale or coatings are as follows.

Hematite--Fe₂O₃ (42)

Hematite is a very stable form of ferric iron combined with oxygen. In pure form the Fe⁺⁺⁺ ferric percentage is 70% while oxygen contributes the remaining 30%. As will be discussed later, water of hydration can be attached to the Fe₂O₃ to yield different iron percentages (see Appendix A and B).

$\frac{\text{Magnetite}-\text{FeO}\cdot\text{Fe}_{2}\text{O}_{3} \text{ or}}{\text{Fe}(\text{Fe}_{2}\text{O}_{4})} (42)$

Magnetite contains both the Fe^{++} and Fe^{+++} iron forms. The latter formula (Fe_3O_4) is a common usage, however the iron or Fe valance, to balance the ion charges, would have to be +2.6. Since this intermediate valance cannot exist, the electro potential is satisfied when both Fe^{++} and Fe^{+++} are in the same mineral. Magnetite is usually undergoing oxidation of Fe^{++} and Fe^{+++} . The chemical testing of this mineral requires care and precision (see Appendix A).

Siderite--FeCO₃ or FeO·CO₂ (42)

Siderite is composed of the Fe⁺⁺ Ferrous iron. Depending on the ionic strength and equilibrium it is not uncommon to form:

Fe (OH)
$$_{2}$$
 + CO₂ + FeCO₃ + H₂O
(or) Fe⁺⁺ + CO₃⁻² + FeCO₃(44)

Although the above reactions do occur it may be impossible to test chemically because at a pH level above 6.0 the Fe^{++} is rapidly oxidized to Fe^{+++} (44). The Siderate iron form has been cited in the literature (27) as forming very close to the iron or metal surface and is reported to form a protective shield. This formation must be in the absence of oxygen or in an acid (below 6.0) environment. If the $FeCO_3$ is not oxidized the Fe^{++} percentage is 48.2% and the carbonate (CO₃) is 51.8% (see Appendix A and B).

$\underline{\text{Limonite}-\text{Fe}_{2}\text{O}_{3}\cdot\text{nH}_{2}\text{O}} (42)$

Limonite is a mineral that is formed as Hematite except that it has water of hydration attached. The nH_2O indicates that any number of molecules of hydrated water can be attached to the Fe_2O_3 structure. However, if the n = 1.0, 2.0 or 3.0, then the Fe component is 62.8%, 57.2% and 52.5% respectively. Although the mineral Limonite is amorphous (no crystal structure) the loss of some hydrated water will yield the crystal Goethite (see Appendix A and B).

$\frac{\text{Goethite} - \alpha \cdot \text{FeO} \cdot (\text{OH}) \text{ or}}{\text{Fe}_2 \underbrace{O}_3 \cdot n \underbrace{H_2 O}_2} (42)$

The mineral Goethite is an oxidation product from the original Fe⁺⁺ or magnetite structure. The formation is not totally stable and can lose water of hydration to form Hematite. This substance can also be obtained from the crystallation of Limonite (Amorphous). Goethite has a sister mineral γ form, Lepidocrocite. The two minerals are of the same crystal group and system, but the colors are completely different. The iron percentage is 62.3% and the oxygen and hydroxide percentage is 37.7%. These percentages are based on the formula FeO(OH) (see Appendix A and B).

Lepidocrocite-- γ FeO(OH) or $Fe_2O_3 \cdot nH_2O$ (42)

The mineral Lepidocrocite is of the same family as Goethite although the two forms (α and γ) are different. Lepidocrocite formation is from magnetite and formation of Lepidocrocite is by slow oxidation while Goethite is from rapid oxidation. The iron percentage is the same as for Goethite and Lepidocrocite. The oxidation rate is responsible for the difference of color for both the (γ and α) form of FeO(OH) (see Appendix A).

Chemical Isomorphism

The definition of isomorphism (43) is "Substances with analogous formulas in which the relative size of cations and anions are similar often have closely related crystal structures." This is true of the carbonate The anhydrous carbonates of the bivalent eleminerals. ment form two isomorphous groups, one orthorhombic and the other trigonal. The two groups are controlled by the cation radius Å (where Å is angstrum units) larger or smaller than the calcium ion (0.99Å). The mineral Aragonite (66) is orthorhombic and calcite (66) is trigonal as is Siderite (FeCO₃). CaCO₃ can therefore show the same tendency for Aragonite and Calcite and is said to be isomorphic. Also, Siderite (FeCO₂) and Calcite (CaCO3) are also isomorphic in that they are both trigonal and do exhibit isomorphism. The

relative size of Ca^{++} is 0.99Å while the Fe⁺⁺ is 0.74Å in size.

Chemical Solid Solution

It is the rule rather than the exception that atomic ions do in fact replace other ions. The replacement of one ion with another is common for ions of a similar radius, and atomic size is more important than the ion charge. It is not essential that ions with similar valance substitute but electronic integrity must be preserved. This may be accomplished by another ion substitution.

The extent to which solid solution takes place is determined by the nature of the structure, closeness of the ionic radii and the temperature of formation. Solid solution is important to the spinel group (Magnetite) and Apatite mineral.

The solid solution of migrating ions observe the radius size in that an ion 15% larger than the initial can be substituted. However, a large ion may substitute but distort the crystal lattice.

The other minerals that do exhibit solid solution are: Ankerite, Magnetite and Vivianite.

Chemical Changes

To understand the chemistry of the iron compounds it is necessary to review the oxidation and loss of hydrated water that can change one iron compound to another. The following reactions are based on completed reactions and not the kinetic structure in between changes:

Oxidation	Intermediate Oxidation	Complete Oxidation
2 Fe(OH) \rightarrow	Fe0.Fe203.nH20	$\rightarrow \qquad \stackrel{\alpha \text{FeO (OH)} *}{\rightarrow} \qquad \stackrel{\gamma \text{FeO (OH)} *}{\rightarrow} \qquad \stackrel{\text{Fe}_2\text{O}_3}{\rightarrow} \qquad (8)$
Ferrous hydroxide	hydrated Magnetite	*Goethite Hematite **Lepidocrocite
Oxidation		
FeCO ₃ →	Fe203 • nH20	\rightarrow Fe ₂ O ₃ (9)
Siderite	Limonite	Hematite
Oxidation		
3FeO + 1/202 →	FeO·Fe2 ⁰ 3 ^{•nH} 2 ⁰	$\rightarrow \qquad \begin{array}{c} \alpha \text{FeO(OH)} \star \\ \rightarrow \qquad \rightarrow \text{Fe}_2 \text{O}_3 (10) \\ \gamma \text{FeO(OH)} \star \star \qquad \end{array}$
Ferrous oxide	hydrated Magnetite	*Goethite Hematite **Lepidocrocite
*Based on Rapid oxi **Based on Slow oxid	dation lation	

X-ray Diffraction to Identify Internal Coatings in Water Mains

Crystal Structure and Lattice

Crystal Formation

Crystals are formed either in nature or in the laboratory. The crystal is formed wherever constituent atoms or ions are free to come together in the correct proportions to form a certain mineral under conditions which permit formation or growth of the mineral at a reasonably slow and steady rate. Regardless of the kinetics of formation, the well formed crystal and irregular grain of the same substance have the same orderly internal arrangement of constituents. Crystal forms are physically controlled by planar nets. Each planar net is defined by a unit parallelgram with adjacent sides equal or unequal in length and with the included angle not necessarily equal to 90°. See Figure 3 for an illustration of four separate types of net formations all in two dimension.



FIGURE 3 - SPECIAL TYPES OF PLANAR NETS

Lattice

Although the net does describe the two dimension aspect of the crystal, the crystal lattice identifies the crystal in three dimensions as on array of identical points. This array of points has an ordered arrangement such that all points fall on straight rows and are repeated at regular intervals along the row. Every pair then forms a lattice net-plane in which a unit parallelogram is repeated by translation throughout the net. The symmetry displayed by some lattices require that certain nonparallel sets of lattice planes be identical in spacing. Therefore, crystal faces developing parallel to these equivalent sets of lattice planes will be symmetrically equivalent and appear at regular intervals and this then constitutes crystal form. A typical lattice plane is as shown in Figure 4. Figure 4 shows that a lattice plane passes



FIGURE 4 - LATTICE PLANE

through NM' N'M in "a" where the P Pole is normal to the NM' N'M plane. In "b" of Figure 4 the Pole is normal to the page. However, R and Q are both normal to the arranged lattice. This illustrates the stacking at equal distance of lattice planes.

The crystal classes are listed at six. They are based primarily on symmetry although the names of the six systems are derived from the special dimensional properties of the lattices required by the symmetry. The length of the three lattice rows and the angles of the unit all serve to define a given lattice. These three lattice rows become the axes of reference for crystals.

The crystal systems are then; Triclinic, Monoclinic, Orthorhombic, Hexagonal, Tetragonal and Isometric.

The axis layout and crystal system as pertains to the minerals under investigation are as found in Appendix B.

Bragg's Law (42)

X-rays are produced when high speed electrons strike the atoms of any substance. An X-ray tube contains a heated element which provides a constant source of electrons that are directed at a metal target. The tube is an evacuated glass chamber fitted with a filament, a water cooled metal target and with several windows. The target is grounded and a rectified high voltage current is supplied to the filament.

The X-rays are emitted from the target in three wavelengths $K\alpha$, $K\alpha_2 < KB_1$. The intensity of $K\alpha$ is double $K\alpha_2$ and several times KB_1 . Because three X-ray intensity lines occur it is necessary to filter out the less intense x-ray line KB_1 .

X-ray Diffraction Theory

In crystals the planes of atoms are arranged parallel to one another at a regular repeat spacing, forming a crystal lattice. Figure 5 depicts a vertical section through a crystal lattice.



Each point row P-P', Q-Q' or R-R' in Figure 5 are equally spaced lattice crystal plans. It is shown that each single lattice plane may produce a diffracted X-ray beam incident at any angle. The X-ray beam is measured

in Angstron Å units. For a regular stacking of such planes to produce a diffracted beam the rays diffracted from the planes must reinforce one another. Thus, a diffracted beam results when the path difference between reflections from adjacent identical planes are equal to a whole number of wavelengths of the X-ray in use. The path difference AXD and BYE is GYH or by geometry

 $GY + YH = 2d \sin \theta$ (11)

The diffracted beam will follow the direction XD or YE if

$$\lambda = 2d \sin \theta \tag{12}$$

where d is the lattice spacing in Å and λ the wavelength in Å. This relationship is termed Bragg's Law.

Therefore Bragg's Law is $\lambda = 2d \sin \theta$ (12). (See Appendix D and E for X-ray, lattice spacing and sample calculations.)

Optical Crystallography

Introduction

The theory of optical crystallography includes several facets; light source, microscope, index oils and crystal index investigation. Each facet is important in itself and collectively they represent a large portion of optical crystallography. The overall concept is to identify crystals by identifying the respective refractive indexes.

Polarizing (Petrographic) Microscope

The polarizing (Petrographic) microscope is a very important tool in crystal investigation. The microscope is constructed for the specific measurement of refractive indexes while observing crystal structure. Figure 6 shows the general cross section of the Petrographic microscope.

Items that can be changed or interchanged are the lower fixed lenses of the condenser, objective lenses and the upper lenses. Items that can be hand adjusted are the revolving stage, the mirror to focus light, coarse and fine focus adjustment. It is possible to incline stage if required.

Light

Light is a form of radiant energy. Modern theory accepts the combined approach of electromagnetic-wave and particle concept and recognizes them as not necessarily contradictory but as complementary (45). Figure 7 illustrates a plane polarized electromagnetic wave.

Figure 7 shows an electric and magnetic vector oscillating in a perpendicular plane reaching maximum and minimum magnitudes. This wave is said to be plane









FIGURE 7 - PLANE - POLARIZED ELECTROMAGNETIC WAVE

polarized. In crystallograph work the emphasis is on the electric vector because this vector is the most important as regards optical phenomena. The electric wave aspect is as described by the following equation:

 $t = \frac{u}{\lambda}$ (13)

where: t = frequency in cycles per second u = velocity of propogation of energy waves λ in vacuum (186,000 miles/sec) = wave length in Angstrom units Å The visible light range is near a one micron wave length and 10¹⁵ frequency in cycles per second. Light of

aj li pla vac tha lea in t leng not in t resp light ^{the} alte or 0"N"] a particular wave length is described as monochromatic light. If light is traveling in a vacuum and a glass plate suspended so that the light passes through the vacuum and glass the velocity in the glass plate is less than in the vacuum. However, the same number of waves leave the glass plate as enter and accordingly, a change in the velocity must be accompanied by a change in wave length while the frequency remains a constant that does not change with any medium. An example of what can occur in two substances that are isotropic and anisotropic respectfully (do not alter the light ray and do alter the light ray) is shown in Figure 8.



As the light wave direction is altered as in <u>B</u> the altered wave does not move perpendicular along O'N'or O''N'' but along O'R'' and O''R''.

Passing of Light Through the Microscope

Light is passed through a microscope as illustrated in Figure 9.



Scattered light enters the polarizing filter (lower) (termed the lower filter) and the ray direction is resolved into one wave front. That is the lower filter only allows light through a directional slit. The light then passes through the condensing lenses to focus on the stage that contains an isotropic material (passes light without a wave front change). The light then enters the objective lens where a refocus is accomplished through the polarizing filter (upper) (termed the upper filter) and toward the ocular. The upper filter is rotated 90° from the lower filter and will not allow light to pass because the light ray is 90° out-of-phase. However, if an anisotropic material is on the stage, light will be omitted when the ray rotation is altered off 90° from the lower filter. Assuming then that light does pass the upper filter the light ray is refracted again, enters the eye and is focused on the eye retina where reversed enlarged image is seen by the observer.

Upper and Lower Filters

To illustrate how the upper and lower filters operate Figure 10 is included.

When the lower filter is inserted the light is passed in PP' direction only. However, when the upper filter is inserted the light path is A-A' turned at 90° from light path direction PP'. Therefore no light is passed to the ocular or the viewer's eye.



FIGURE 10-UPPER & LOWER FILTER

Magnification

The magnification of the petrographic microscope is based on the power or magnification of the objective lense and the ocular. The magnifying power of a microscope is obtained by multiplying the magnifying power of the objective lenses times that of the ocular. It is important to note that both the objective lense and ocular can be changed to adjust the microscope to the needs of the work involved.

For each particular microscope barrel or tube length only certain objective lenses or ocular are designed for insertion.

Index of Liquids

To determine the index of the crystals a reference must be established. A reference liquid is selected for crystal inmersion so that the solid can be contained in the liquid phase for microscope viewing.

Index Oils

A complete set of index oils for measuring crystal index can be obtained commercially (46) and the index oils come in sets that cover a specific range. The index is a unitless ratio of light in air to a substance. The range of liquids can vary from as high as 0.2 to as low as 0.002 units in a set. The variations may be above and below the actual index that is required. These limitations can be overcome by oil mixing in any ratio to yield the correct numerical index. The oil can be used with confidence and are stable over long periods of time. If an index oil set provides step increments of 0.002 and has been calibrated to 0.002 then accuracy of \pm 0.0005 is possible.

Temperature

Each oil set is referenced to 25°C temperature. It is not usually possible to conduct microscopic studies at 25°C, and it is necessary to correct the index oil to the investigation temperature. The <u>temperature coefficient</u> is on the label of the index oil and is multiplied by the

difference between 25°C and the working temperature. If the working temperature is lower than 25°C then the product is added to the index oil numerial value. The reverse is true if the working temperature is higher. Therefore

$$\frac{+}{dt} \frac{dn}{dt} = \text{temperature coefficient x (AT)}$$
(14)
When $\frac{dn}{dt} = + T < 25^{\circ}\text{C}$
or when $\frac{dn}{dt} = -25^{\circ}\text{C} > T$
Where ΔT = Temperature difference (T < 25^{\circ}\text{C} > T)

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T = Working temperature.
```

Crystal Refractive Index

The determination of the correct or exact crystal under investigation depends largely upon identifying corresponding refractive indexes. To accomplish this, several approaches have been developed. The refractive index is a unitless ratio of light in air to a substance. A discussion of several techniques is useful.

Emmersion

To investigate a crystal to determine optical properties the crystal must be emmersed in a known index oil. This is done by putting a drop of a known oil on a watch glass and sprinkling a minute quantity of comminuted crystal into the oil. It is possible to then put another watch glass over the index oil drop without interference. The top watch glass spreads the oil crystal phase out and allows for neat viewing. It is also possible to emmerse the objective lense into the oil and thereby view the crystal in close proximity.

Crystal Group

The crystals are broken down into two groups, uniaxial and biaxial. Each group will be discussed separately. However, the mineral system is as discussed in Appendix F.

Uniaxial

The uniaxial group as discussed by (42, 43, 45, 46) is a group with only two axes (see Appendix F) or two refractive indexes. The indexes are designated N_{ω} (ordinary ray) and N_{ε} (extraordinary ray). When a beam of ordinary light with equal vibrations in every direction passes into an anisotropic crystal it is broken into two rays vibrating at right angles to each other in planes representing the different refractive index directions. These rays are said to be polarized.

A uniaxial crystal is said to be either positive or negative. A positive uniaxial crystal is one for which the N_{ω} ray is smaller than the N_{ε} ray and for a negative crystal the opposite is true.

Biaxial

The biaxial group has three distinct axes or three refractive indexes. These are designated: N_{α} (alpha or lowest), N_{β} (Beta, intermediate), and N_{γ} (gamma, highest) indexes. As monochromatic light is passed through the C or main optic axes of the biaxial crystal, this ray is the N_{β} (Beta) and has only one index.

Like the uniaxial crystal the biaxial crystal has a positive or negative sign. For the positive biaxial crystal N_{β} is closer to N_{α}, for the negative crystal N_{β} is nearer to N_{γ}.

Extinction

To first investigate a refractive index a position of extension is necessary. The thin section crystal is first viewed with only the lower filter. The crystal is selected that appears to lie in a flat plane with very little distortion. The upper filter is then placed and the stage rotated until the crystal under investigation shows gray, white or black in any position of rotation. The extinction is then a lower filter polarizing the light ray. The crystal axis is oriented parallel to the microscope base to allow the polarized light to pass parallel to the axis without any distortion. The polarized light, although passed by the crystal, cannot pass through the upper filter because the upper filter

is at a 90° rotation to the lower filter. This condition is the extinction position of a crystal and a refractive index check can be made.

Crystal Refractive Index Determination

There are two methods commonly used to determine crystal refractive indexes. These methods are: (1) Becke line and (2) half or oblique illumination. The refractive index should only be attempted on crystals that show extinction. The two methods to determine extinction are as follows.

Lower Filter

When viewing crystals in thin section and when the lower filter (polarizer) is in place, as is always the case, a crystal shows extinction or darkens if the light ray passed by the lower filter is vibrating parallel or along one of the optic axes. This can apply for uniaxial or biaxial crystals.

Lower and Upper Filter

The insertion of the upper filter to view a well illuminated crystal may produce darkness or distinction. This can happen for either of the two crystal groups. This indicates that the light is passing parallel to one of three axes. The only way to check a refractive index is when the light is parallel to an axes.

Therefore, when extinction occurs a crystal index check can be undertaken.

Becke line method.--This method is based on the crystal immersion in a refractive oil and generally the two substances (crystal and oil) having difference refractive indices (45, 46). If the two materials (crystal and oil) do have different indices then a line will form around the crystal. As the barrel is raising this line appears to move in toward the crystal center or outside the crystal outline. However, if the crystal and oil have the same index value then the crystal outline, as the barrel is raised, does not move in or out. The illustration of Figure 11 is descriptive in terms of graphic display.



The depicted Figure 11 is based on the fact that when light rays from below encounter the higher index oil and strike the lower crystal medium the rays are deflected. Also as the rays pass through the crystal (lower index) and strike the oil (higher index) the light is refracted into the higher oil index medium. However, part of light rays 1 and 2 are reflected. It is important to note that as light rays 1 and 2 are refracted and light rays 3 and 4 reflected they enforce one another. When the microscope barrel is raised, very slightly, the edge of the crystal line appears to move outward giving the appearance that the crystal is getting larger. Conversely, if the crystal had a higher index than the oil and the microscope barrel is raised the crystal edge line outline appears to move in toward the crystal as if the crystal was getting smaller. The edge or line is termed the Becke line and can move in or out depending if the crystal has a higher or lower index value than the oil.

Half or oblique illumination method.--The half or oblique illumination method (45, 46) is determined by reflected or refracted light. This method uses only half the field of illumination so the light enters the crystaloil phase at a definite angle from the directed incoming light. As the light enters the crystal it is either reflected or refracted and as the light enters the oil at

the crystal-oil interface it is also reflected or refracted, depending on whether the oil or crystal has the higher index. As the light is reflected to enforce other light rays the light intensity at the crystal-oil interface appears dark. However if the light rays are deflected at the crystal-oil interface, this edge of the crystal portion then appears as a lighted area. Both Figure 12 and 13 illustrate the effect that takes place when using the half or oblique illumination method.

The half illumination of the microscope stage is accomplished by partially blocking the entering light by decentering the lower iris diaphram.



FIGURE 12 - HALF OR OBLIQUE ILLUMINATION

NOTE: A. INDEX OF FRAGMENT LOWER THAN THAT OF SURROUNDING MEDIUM B. INDEX OF FRAGMENT HIGHER THAN THAT OF SURROUNDING MEDIUM



Birefringence

The birefringence of a crystal is the numerical difference between the maximum and minimum indices of refraction. The birefringence are those colors as viewed when both the upper and lower filters are in place. Birefringence can also be as effected by crystal thickness and orientation. Two exact crystals with different thickness and orientation do in fact show different interference colors or birefringence. Thus the need to select, in all cases, a thin section of a specific crystal.

The larger the index separation, the higher the birefringence. For uniaxial crystals the difference is between the N_{μ} and N_{μ} rays. For biaxial crystals the

d i s i Re is sa la ,2 in in th <u>P1</u> fer Vie rem may Plea alth_C difference between the longest and smallest of the three indices is the birefringence.

Birefringence as viewed with both filters and the stage rotating will reveal a kaleidscope effect of changing colors.

Relief

When a crystal is at extension and one index ray is under investigation it is possible to quickly view the same crystal in 90° rotation to check the relief. A large relief at 90° rotation is an indication of the index separation. The greater the relief the wider the indices are apart. Very small relief is an indication then that the indices are close together.

Pleochrism

Certain nonopaque crystals absorb light differently in different directions of vibration. The viewing for pleochrism should be with the upper filter removed. For some crystals, in one optic direction light may be absorbed more than when the stage is turned 90°. Pleochrism may be described as for Goethite:

where x = clear yellow to brown
y = brown yellow
z = orange yellow

although many crystals do show pleochrism some do not.

CHAPTER IV

EXPERIMENTAL TEST APPARATUS

AND MATERIAL

Chemical Testing

The chemical testing approach was conducted by using <u>Standard Methods</u>, 12th edition. The ions or radicals tested for were: Ferrous Fe(II), Ferric Fe(III), Calcium Ca(II), Silica SiO₂ and Carbonate CO₃ radical. The equipment consisted of Corning Glassware and the following:

Balance--2 arm Pan Balance, Model #750-0 Serial No. M-12652 as manufactured by Voland and Sons, Inc.

pH meter--Model 76004 Expandometer as manufactured by Beckman Co.

Analysis--Hellige Aqua analyzer Photoelectric Colormeter including pre-calibrated concentration charts. Model 950-A Serial No. 137 as manufactured by Hellige Inc.

X-ray Diffraction

The X-ray investigation of the various minerals and crystal structures were as performed by the Norelco X-ray Diffractometer (Range 12045-60 cycles or 12048-50 cycles) wide range Goniometer (Range 12099- 60 cycles or 12048-50 cycles) Electronic Circuit panel manufactured by

Phillips Electronics Inc., Instrument Division, Mt. Vernon, New York. The unit is assembled in a two part module. The scanner, with X-ray gun, and receiver is in one module and the instrumentation plus paper strip recorder is in the second module.

Petrographic Microscope

To use the Petrographic Microscope on crystal identification several items of auxilliary equipment are necessary. The equipment, including the microscope, is as follows:

Microscope--Model 624681 biocular polarographic microscope as manufactured by Leitz-Wetzlar in Germany.

Light--Model 651, 60 cycle 115V with 5, 6 or 7.5 volt adjustment to include varying intensity (1-10) with adjustable focus. Manufactured by American Optical Company.

Standard Index Oils--Two sets of standard index oils were used to include one of intermediate range--1.4-1.8 in range increments of .015 and a second of a higher index with a range of 1.8-2.0 in variations of 0.02 units. The index oil refractive index is a unitless value in that it is the ratio of the speed of light in air to the speed of light in a particular substance. In this case the index liquid. The oils were as manufactured by Cargille Laboratories, New Jersey. Camera--To illustrate the various techniques and to present visual crystal review photographs of pertinent views were recorded. The camera was a Nikon F, No. 158755 with an "f" setting of 1.4 and focus length of 5.8 cm or 58 mm. Also equipped with Bellow attachment as manufactured by Nippon Kogaku, Japan. The camera was mounted above the microscope on a ring stand that could rotate over or away from the microscope focus.

Pedistal and Mortar--Used to comminute the samples to a fineness of 100 mesh or less.

Glass Plates--The glass plates are 3/4" x 2" x 1/32". The sample plus the index oil are placed on a glass plate in a small area and a cover glass is then placed over the sample and oil to secure the sample for viewing.

Test Specimens

Reagent Grade Chemical

Calcium Carbonate-Calcite--CaCO₃ or CaO·CO₂

Contained the following mineral percentages: SO₄ - .01%, Na - .01%, Fe - .001%, and magnesium - .01%.

Hematite--Fe₂03

Contained the following minerals:

SO₄ - .20% CN⁴ - .005% Zn - .005% with a molecular weight of 159.70 as manufactured by General Chemical Division.

$\frac{\text{Magnetite}-\text{Fe}_{3}\text{O}_{4} \text{ or FeO(Fe}_{2}\text{O}_{3})}{\text{or Fe(Fe}_{2}\text{O}_{4}) \text{ or Fe(Fe}_{2}\text{O}_{4})}$

As obtained from the inside of a fire Kiln where iron had been fired. The material formed on the inside wall is magnetite. The physical properties that identify magnetite are the magnetic property and the black color.

Siderite--FeCO3

It is impossible to purchase FeCO, commercially or chemically due to the instability of the compound. To obtain the FeCO₃ compound 2 grams of Ferrous Sulfate FeSO₄ were added to 50 ml. of demineralized water. Also, 2 grams of Sodium Carbonate Na₂CO₃ were added to 50 ml of demineralized water. Both the Ferrous Sulfate and Sodium Carbonate have large solubility and all the material was The two solutions were mixed to form siderite in solution. FeCO₃. Siderite has a low solubility (.0065 grams/100 ml.) and the precipitate is FeCO3. The precipitate was "Green" with an oatmeal texture. This precipitate was filtered through a Buchner funnel using 45 micron filter paper. As vacuum was applied to the receiving flask the green filtered material immediately turned Brownish-Black, as reported in the literature (14, 44). The Ferrous Fe (II) ion in the carbonate structure quickly oxidized to
Ferric Fe(III) state. The oxidized formation is the conversion of $2FeCO_3 + 3O_2 \rightarrow 2 Fe_2O_3 \cdot nH_2O + 2CO_2 \uparrow$. The immediate product is Limonite ($Fe_2O_3 \cdot nH_2O$) with no crystal structure. As will be discussed and illustrated later the oxidized form of $FeCO_3$ is in fact <u>Limonite</u>. This conversion of Siderite to Limonite was an immediate reaction and the long term oxidation of Limonite to Goethite did not take place at standard temperature or pressure. Also, the product was removed to a dessicator for drying. This removal did break the chemical reaction chain in that no new corrosion products were added to the system and altered corrosion products were not carried away.

Limonite--Fe₂O₃ · nH₂O

Limonite was the oxidized product of Ferrous Carbonate FeCO₃.

Calcite Protective Coatings--Laboratory Formation

In past work (29, 39, 40), the prediction of the Calcite coating and the formation evaluation were performed on cast iron strips that were 1" x 3" x 1/16" in size coated on the back to eliminate corrosion. The coating face was machine ground and then inserted into a static or dynamic testing program to receive a Calcite formation for testing. Several samples from work by Woodruff (40) were still available for scientific review. The cast iron test speciman had a dull gray Calcite coating or reported as a Calcite. The physical-chemical environment under which coatings were developed on the cast iron test speciman was as follows:

Run Time	-	2 Hrs.
Water Velocity	-	7.6 fps.
Water Temperature	-	14°C
рH	-	9.43
Alkalinity	-	430 ppm as CaCO,
Calcium	-	224 ppm as CaCO ₂
Carbonate	-	93 ppm as CaCO ₃
Total Dissolved		5
Solids	-	451 ppm
K's x 10^{10}	-	126
*M.E.	-	.92 ppm as CaCO,
**D.F.I.	-	165 3

*Momentary Excess **Driving Force Index

These cast iron test specimens were selected because the macroinspection of the coating indicated a Calcite coating, and because the cast iron test speciman could be placed into the X-ray equipment and yield ready results without transfer of the Calcite material from the cast iron test speciman to a glass plate.

Cast Iron Test Speciman

It is essential that an X-ray of the cast iron material be conducted to review the background effect of the cast iron speciman on the Calcite coating X-ray.

Iron Formations or Corrosion Products on a Cast Iron Pipe Surface

Several cast iron water pipes were available to allow an actual corrosion blister investigation. A 1" cast iron water pipe was extracted from a corrosion environment from the Fairmont, Minnesota Municipal Water System. The blister was intact and the entire pipe section was cut in half and a 4" long piece was stored in a dessicator until testing time. Figure 14 shows a photograph (M = 4x) of the half pipe and removed blister. The blister took the shape of a shoe print with the heel at top.



Figure 14.--1" Cast Iron Water Pipe Nipple with Corrosion Blister (M = 4x).

The blister top was removed and comminuted into 100 mesh size. The center or bottom material was scraped loose from the cast iron and also comminuted for sample preparation.

From the photograph the layer separation can be viewed--especially at the top (or heel) where the scale depth differential produces a shadow. It is estimated that the corrosion product scale depth was 1/32".

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CHAPTER V

EXPERIMENTAL PROCEDURE

Introduction

In previous and following chapters it is or will be apparent that discussion of the various compounds is separated into two distinct categories. These categories are those coatings or compounds that (1) contain the calcium Ca(II) or (2) contain iron (Fe II or III) ion as the common constituent. This was done in consideration of the fact that each category has similar characteristics and natural groupings.

In the following discussion of procedure the lack of category identification will be evident. This was necessary to eliminate duplication of discussion and for conservation of space. Although each category has unique characteristics the overall format procedure for known and unknown investigations is similar and in some cases identical.

Visual Inspection

The intent of this research is to provide a methodology on testing internal coating in water mains. In the past the determination of a coating was by visual

inspection, which is of real value. Visual inspection is <u>the</u> place to start an investigation of any protective coating or formation regardless of whether the coating contains calcium or iron as the common ion. The trained scientific eye can "get a handle" on the nature of the unknown coating and make valuable first-judgments by visual inspection.

Color

Materials that contain the calcium Ca(II) ion, and may be Calcite, appear white, gray or colorless and may, in fact, reflect the color of there surroundings when still attached to metal.

Compounds that contain a trace if iron impart a color trace to the crystal. As the iron concentration percentage increases in a crystal or compound a gray to brown to black color will be noted. As iron Fe(II) is oxidized to Fe(III) the color changes from brown to black, as for Magnetite. Hematite, however, is blood red and the iron phase is Fe(III). Therefore, a thorough knowledge of the calcium and iron compounds found in protective coatings is necessary (see Appendix A).

Hardness

The tighter and more stable the crystal lattice the harder is the compound. Hardness is based on numerical values of the Mohr Scale between 1-10 with 10 being

diamond. Numerical values are assigned to each compound. The thumbnail test on a coating is a good test of relative hardness because the thumbnail can scratch a surface with a 5.0 or less hardness. Most of the compounds investigated in this report have a 5.0 or less hardness. Hardness is a quick aid to general compound classification and of

Acid Test

specific value to coatings studied here (see Appendix A).

Many compounds will dissolve in acid, some in hot acid and others in a specific acid. Coatings may or may not effervesce on contact with acid. This visual test in general allows some decisions (see Appendix A).

Magnetism

A quick determination of Magnetite is a check for magnetism. The other 10 compounds considered here do not exhibit this tendency (see Appendix A).

Evaluation of Coatings or Compounds Using Chemical Identification

After the usual inspection of the known or unknown coating the chemical testing approach will be narrowed as to what general category is under investigation.

Sample Preparation

The sample amount should be sufficient to conduct three complete tests for a weighted average. The calcium

and iron test requires acid for dissolution and in the case of Magnetite the dissolution will require two-three days depending on how the comminution is handled. Therefore, chemical testing results may require several days away. The time frame of chemical testing must be considered.

Equipment Calibration

Results are as good as the equipment calibration and the scientific handling. The first consideration is a mechanical approach where the second consideration is familiarity and technique. At first, equipment calibration should be conducted each two-three days to note the sensitivity of the equipment. Once equipment sensitivity has been observed calibration can then be as needed.

The calibration of any equipment should be from known standards. The known standards are used to develop standardization curves for the equipment used in testing. See Figure 15 for equipment display.

Testing Format

The testing format is basically one of uniformity. That is, each test should be standard and identical to others of a series. Consistency relates to technique and to the reagents being used. Although not normally considered at a reagent, demineralized water should be



Figure 15.--Chemical Testing Equipment.

checked periodically for purity. Erratic data may be a function of deterioration of the laboratory demineralized water quality.

Testing is conducted to gather data and the data gathered must be recorded in an orderly manner. Recording is a function of data usage and the worker must, before beginning his work, decide his objective. Once the data arrangement is selected a data form can be devised to assist in data collection. The chemical test and results presented here were conducted as prescribed in Standard Methods, 12th edition, published by the American Public Health Association.

Evaluation of Coatings or Compounds Using X-ray Identification

When use of X-ray equipment is employed the format for testing is the same for both the calcium or iron based compounds. However, the radiation and filter selection is important. Some types of radiation cannot be used for iron detection--specifically, copper cannot be used. It is therefore necessary to select radiation and filters that yield usable results.

Sample Preparation

Known Reagents or Compounds

The use of X-ray equipment to test unknown compounds should be preceded by the testing of known compounds to observe characteristics or "thumb-present" patterns that in turn reflect the crystal habit and lattice. A glass test plate is used for testing of a known dry dessicated reagent grade compound or mineral. Glass is excellent for this purpose because it has no crystal structure (it is amorphous) and results in zero background interference).

The glass test plate can be 1" x 2" x 1/16". In the center of the plate a small rectangular area 1/2" wide x 1" long should be marked off. The enclosed area is considered the target area. A clear grease, of a type used to lubricate glass on glass surfaces, or silicone base as manufactured by Dow Chemical is used as an adhesive. The known test material is sprinkled on the grease to a depth and surface uniformity of 1/64". This loose sprinkled material then should be compressed by placing another piece of glass over the top and pressing down. The top glass may or may not be removed and if left in place allows the prepared sample to be handled without fear of disruption. This sample should be used as a standard and retained in a dessicator for future reference.

Cast Iron Test Specimen

The time saved by using a cast iron test specimen that has received a protective coating is appreciable. The cast iron test specimen can be extracted from the test cell, dried, dessicated and made ready for testing in a matter of hours. This time saving is two fold: (1) the coating, whether calcium or iron based, does not have to be disturbed for removal and (2) the plate size is compatible for X-ray use.

It is important that the cast iron X-ray pattern be known to check for background interference and when the pattern is known the X-ray data can be reviewed

accordingly. Should a corrosion blister form on the cast iron test plate, however, removal of the blister is necessary. The removal should be accomplished in layers because (27) the corrosion blister develops in layers that are, at best, difficult to define. An interface is present because the Fe(II) is being oxidized to Fe(III) and a change of state is observed as the blister enlarges.

The most valuable feature of cast iron specimens is the manner in which they can be removed from the test cell at random, be X-rayed for a protective coating or corrosion products and then reinserted into the test cell for further observation. Removal of the cast iron test specimen for X-rays do not alter or change the crystal structure or lattice nor destroy the integrity of the protective coating.

Magnetite

Magnetite forms in layers in an iron furnace. The layers can be striped off in sheets. An iron sheet 1/8" thick makes an excellent sample for X-ray testing. The sheet should be dessicated and then tested after being reduced in size to 1" x 3" x 1/64" thick.

Equipment Calibration

Calibration of the X-ray equipment is always necessary and must be done as per manufacturers recommendation. Once the equipment is calibrated the standards

used as controls should be tested and these standards should be retained as a baseline. During the testing program the standard should be tested from time to time to check calibration of the equipment. An identical X-ray pattern for a control standard is a positive indication that the equipment is still in calibration.

As X-ray patterns are recorded for known compounds it is important to record the base level of intensity. Some materials may record zero diffraction intensity while others exhibit a baseline intensity of 30 or 40 percent. The measurement is based on the observed diffraction angles and on the diffraction intensity peaks.

It is necessary that the technique used in testing the various compounds be consistent. Selection of the radiation and the filter equipment is important because calibration of equipment and test sample observations require a standard technique and use of the proper radiation and filter.

The X-ray equipment has one very important control termed the <u>Rate Meter</u>. This meter alters both the X-ray emission in conjunction with the filter material and also adjusts the receiver to coordinate physical aspects so as to yield specific results. This rate meter can be adjusted to vary or alter results to meet specific conditions. The X-ray experimental data, included in

the following section, was set at 16-1-1, meaning that all X-ray patterns are a result of constant rate meter control and the results can be compared with a valid data base.

Testing Format

Before any unknown coatings or compounds are tested the standards must be first tested to establish a thumbprint with which to review all subsequent data.

Broad Range

Any known or unknown should first be tested across the complete 20 range of 0-180°. This will display all diffraction angles and illustrate the diffraction intensities.

Selective Range

Upon completion of the Broad Range testing those diffraction intensities that exhibit the five highest values should be retested to redefine both the defraction angles (20) and intensities in that specific range. This is the X-ray range for future testing.

Only the three largest diffraction intensities are required to specifically identify a mineral or com-Pound.

Data Evaluation

Data is the key to identification. The recorder speed is slow and the diffraction intensity peaks can be recorded by the ink pen and the diffraction angle (2θ) can be noted. The Bragg equation (10) can then be employed for known radiation wave legnth (Å). As the data is printed the "d" lattice spacing can be calculated, and a search undertaken for comparing the data to the knowns can be implemented at once. Preliminary identification of unknown test coatings or compounds is possible immediately.

Evaluation of Coatings or Compounds Using the Petrographic Microscope for Identification

Sample Preparation

Each mineral or compound should be comminuted to 100 mesh. This comminution crushes any large masses to a finely divided powder which is easy to view in thin section.

It is not necessary to use a sample amount greater than 1.0 milligram, only a toothpick amount is used for each respective slide preparation. Once comminuted, the sample should be placed in a salt cup and marked with a grease pencil--as to data and amount and composition of iron. This cup should always be stored in a dessicator.

The preparation of the glass slide is accomplished by placing a drop of oil in the center of the glass slide and then adding to the oil the amount of material that can be perched on the thin end of a wood toothpick. A glass slide of identical size is then placed over the oil and sample, and the slides should then be squeezed together. It is wise to mark the index oil, date and material if known on the slide.

As the index of the material is checked it is advisable to make notations, on the glass slide, for future observations as required. Also, it is most helpful if the area being viewed is circled in red and the crystal orientation under investigation be recorded on the data sheet. This technique also allows for future observations.

Equipment Calibration

The calibration of a petrographic microscope is one of familiarization. It is important first to select the magnification that is to be used in the work. This is accomplished by multiplying the ocular power by the objective lense power. The higher the magnification the smaller the field of vision.

The arrangement of light source and microscope mirror is important and must be arranged to allow the operator to work freely around the microscope. Also, the intensity of the light should be selected for eye comfort in viewing. Figure 16 illustrates the microscope, light source and oil index set arrangement.



Figure 16.--Petrographic Microslope.

The operator of the microscope should become completely familiar with all the working parts of the petrographic microscope--especially the ocular, upper and lower filters, objective lense, etc.

The most significant calibration, in the identification of minerals by use of the petrographic microscope, is the index oils. This calibration is difficult to identify, and it is important that new, fresh calibrated oils be purchased at the start of any project. The index oils contain many organic materials that age and affect calibration.

Testing Format

General View

Once the sample has been prepared and is ready for investigation it is advisable to view the entire slide for crystal layout, thickness and habit with only the lower filter in place.

Many compounds exhibit a physical tendency that is a clue to the mineral or compound identification. A general view of the slide, for instance, provides background to pick out the crystal for color identification. Very small crystals may be ideal to work with, but can be too small. The larger crystals show up very distinctly, but may illustrate excessive thickness and exhibit birefringence. It is therefore advisable to select a crystal of intermediate size that apperas to lie horizontal (one axis) to the stage.

Oil Range

If after visual inspection the mineral or compound falls into a category the general refractive index group can then be estimated. This works well for the calcium or iron compounds. Calcium compounds have a

refractive index of less than 2.0 units, whereas the iron compounds have a refractive index near 2.0 units or above with the exception of Siderite which is 1.613 to 1.855 units. If the index is less than two (2.0) units and with brown to black color, the unknown is probably Siderite.

If the general group cannot be estimated, it is best to then try an intermediate oil to start.

Thin Section

A review of crystals in thin section using the lower filter can often shed light on the crystal type. It is best to look for general color arrangement for crystal comparison and to view for extension of a particular axis.

Crossed Filters

To convert from thin section to crossed filters the upper filter is added. The crossed filters allow the operator to look for extinction and birefringence. Extinction can be seen as two phenomenon. The first is total extinction when the crystal appears grey, white or black regardless of the stage rotation. Secondly, when viewing high birefringence the stage can be rotated to allow viewing of an extinction index. A rotation of 90° from this extinction index shows another extinction index of the crystal if it is in the uniaxial categories.

Crystal Groups

As has been discussed, crystals fall into two distinct categories: uniaxial and biaxial. The uniaxial group have only two index axes whereas the biaxial group have three axes. The following information allows a quick check on crystal group identification.

Uniaxial Group

- 1. Insert upper filter.
- Check for extinction (the crystal will appear grey, white or black regardless of crystal rotation).
- Identify the index axes with upper filter removed.
- 4. This axis will be omega without ray.
- 5. Once n has been determined insert the upper filter and select a crystal that shows high birefringence. Then use upper filter--turning the crystal to extinction and checking the index. Always be sure that the index is not the n_{ω} ray; if the index is not the n_{ω} ray, it must then be the Epsilon n_c ray.
- 6. When the n_{ε} ray is viewed check the index to see if the index is larger or lower than n_{ω} .
- 7. If $n_{\omega} > n_{\varepsilon}$ --Negative crystal if $n_{\varepsilon} > n_{\omega}$ --Positive crystal.

Biaxial Group

In the biaxial group there are three axes and therefore three index of refractions. By definition the three indexes are Alpha α (the lowest), Beta β (the intermediate) and Gamma γ (the highest). The following procedure is necessary to define a biaxial crystal.

- Observe, under crossed filters, a section that is grey (no birefringence) in any rotation.
- 2. Determine the index by removing the upper filter. The index is Beta β or the intermediate index of refraction.
- 3. With both filters in place observe crystals by rotating the stage for those which show the highest birefringence; determine the index using only the lower filter.
- 4. These two other indexes will be alpha α or gamma γ .
- 5. A mineral or crystal will be termed "positive" or "negative" when: Alpha α is closer to Beta β = Positive Gamma γ is closer to Beta β = Negative.

Determination of Index of Refraction

Although the procedure is very similar the determination of the index for each group will be discussed separately as Uniaxial and Biaxial.

Uniaxial

 If the crystal is unknown select a 1.50 index oil.

2. Insert both filters and select a "check" crystal with no birefringence at any rotation. The crystal will appear isotropic and the axis and index will be parallel to the microscope barrel at any stage rotation. 3. Determine the index of the crystal by use of the Becke line or the half or oblique illumination method, with only the lower filter in. The Becke Line Method is accomplished by raising the microscope barrel to unfocus the crystal fragment slightly. If the Becke line moves out away from the crystal the oil is higher than the index of refraction of the omega ray or n_{ω} (isotropic at any rotation). If the Becke line moves in toward the crystal center and the crystal center appears to brighten then the crystal index is higher than the oil (see Figure 11). Depending on results, it is necessary to make another slide mount and again utilize the Becke Line Procedure to narrow the crystal n_{ω} index.

Before a new mount is made it is wise to check the Becke Line findings by using the half or oblique illumination method. This is accomplished by a refocus of the crystal to cut off half of the light entering the crystal. To this end, insert a plate below the stage in a slot especially designed for this purpose. If the crystal shows a dark shadow toward the dark half, the oil refractive index is lower than the crystal (see Figure 13). If the opposite is true the oil is higher than the crystal. Now is the proper time to make a new slide mount using another index oil.

4. Continue to make slide mounts until the n_{ω} ray has been determined.

5. Using the slide with an index oil of the n_{ω} , insert the upper filter and select a crystal with large birefringence. Remove the upper filter and turn the crystal to an extinction angle. Now check to determine whether the index of refraction is identical to the n_{ω} or higher or lower than the n_{ω} . If the refraction index is identical, the extinction is for the n_{ω} ray; if above or below the slide oil n_{ω} value the extinction position is the Epsilon n_{ε} ray. If the n_{ε} is lower than n_{ω} select another mount with a lower oil and if higher select a higher oil. When the oil and index are identical rotate the crystal 90° to view the n_{ε} extinction position.

6. Pursue the n_{ε} ray identification by making new mounts with different oils and using the Becke Line or half oblique illumination methods.

7. When n_{ϵ} has been determined the unknown crystal can be identified by the uniaxial group sign (positive or negative), n_{ω} ray and n_{ϵ} ray index of refractions.

Biaxial

 If the crystal is unknown, mount in an oil of intermediate range such as 1.5 units.

2. The Orthorhombic, Monoclinic and Triclinic mineral systems have three indices of refraction.

3. Of the three axes, the Beta β will show extinction (grey) when viewed under crossed filters. This section should be selected and the index determined using the Becke Line or half-oblique illumination methods (as per description 3 under Uniaxial, p. 77). Several mounts must be made for exact index determination.

4. Remount a sample in an index oil lower than for Beta β . View the new mount using crossed filters. Select a crystal with the greatest birefringence and determine the index. The fact that a lower oil than Beta β is being used automatically means that the alpha α ray index is being investigated. In this determination it is important that for the observed index, no other crystal has a lower index than alpha α .

5. Select an index oil that is higher than the oil used to determine the Beta β ray index. This index of refraction is termed the gamma γ index and is larger than Beta β . Follow the procedure as above in step 4 but no other crystal may have a larger index than gamma γ .

6. Once the three Biaxial indices have been determined then the unknown crystal can be identified by the group (biaxial) sign (positive or negative) beta β , alpha α , and gamma γ indexes of refraction.

Data

The collection of data for the Petrographic microscope when identifying crystals requires a careful

recording of the oil used and the manner in which the Becke Line or illumination methods reacted. Also record each new oil selection when it is necessary to select a higher or lower index oil. The data shown in Figure 17 is a typical "trackdown" record for crystal identification.

DATA SHEET FOR REFRACTIVE

INDEX DETERMINATION

Date: Sample: Temperature:

-dn +dt

Index* Oil Ref Temp.	Index Oil (+,-) Temp. Change	Becke Line Method	Half-Oblique Illumination Method

* The refractive index is a unitless ratio of the speed of light in air to a substance.

Figure 17 - Data Sheet.

CHAPTER VI

DATA

Remarks on Data Format and Notation

The data format isolates the minerals under investigation into two groupings. The first grouping is the <u>Protective Coatings</u> group that contain the Calcium Ca(II) ion as the common crystal or agent. The second group <u>Iron Compounds and Coatings</u> contains the iron Fe(II or III) ion as the common crystal or agent. The <u>Protective</u> <u>Coatings</u> include the following minerals: Calcite, Aragonite, Apatite, Vivianite and Ankerite. The <u>Iron Compounds and</u> <u>Coatings</u> group contain the following minerals: Hematite, Magnetite, Siderite, Limonite, Goethite, and Lepidocrocite.

The data consists of the following categories: (a) Chemistry, (b) X-ray, and (c) use of the Petrographic Microscope. The Chemistry data is from the investigation of the two principal common ions to the coatings group, mainly the Calcium Ca(II) and Iron Fe(II and III). The X-ray data includes the investigation of the various known and unknown minerals in both coating groups by comparison of known lattice crystal patterns. The Petrographic Microscope data includes the verbal description of the minerals and, as a supplement, photographs were taken of selected minerals to illustrate detection techniques.

The following notations are used for data display: Chemical; X-ray; Petrographic Microscope.

1, 2 ... are used for mineral group identification
with an a, b, or c array.

1-A, 1-B ... are individual mineral identification breakdown within a grouping.

I-A-I, 2-A-II ... are used to identify the data included in the Petrographic Microscope Section. the I, II ... designate the respective photographic and visual descriptions. Because the same I, II ... are also used to identify the photograph and descriptive work, the words "photo" and "description" are written immediately below the number-letter-number data designation.

The valance of an ion always follows the ion notation with (I), (II), (III), etc. The letter notations used are as follows:

- d = Lattice distance spacing in Angstrom units.
- A = Angstrom units.
- L = Light source setting for microscope from 1-10.
- M = Magnification of microscope. For instance 6x10-60 times magnification of camera (4) and total magnification is 240x.
- "f" = Camera appature setting.
 - T = Camera time setting.
- T.S. = Crystal view in thin section using only the bottom polarizing filter.
- C.F. = Crystal view in thin section using the bottom and top polarizing filters.

Bire = Birefringence.

Rhomb = Rhombohedral crystal.

Appendix material has been referenced for the data as follows:

Chemical

Appendix A - Data for nonopaque minerals.

Appendix B - Calcium (Ca) and Iron (Fe) percentages in various compounds.

X-ray

Appendix C - X-ray diffraction data.

Appendix D - Some calculations of "d" spacings for calcite (CaCO₃ or CaO.CO₂) using Bragg's equation.

Petrographic Microscope

- Appendix E Data on minerals for use of petrographic microscope.
- Appendix F Crystal group data.

Protective Coatings

These are minerals that contain calcium Ca(II) as a common ion. The discussion of the protective coatinglaboratory formations can be found on page Chemical

l. Calcite (CaCO ₃)	
<u>1-A</u>	<u>1-B</u>
Calcite (CaCO ₃) Reagent grade	Protective Coating Laboratory Formation
39.6 % as Ca(II) 39.5 % as Ca(II)	37.8% as Ca(II) 38.0% as Ca(II) <u>3</u> 8.0% as Ca(II)
Average 39.55% as Ca(II)	Average 37.9% as Ca(II)
X-r	ау
1. Calcite (CaCO ₃)	
<u>l-A</u> (See Figure 18)	<u>l-B</u> (See Figure 19)
Calcite (CaCO ₃) Reagent Grade	Protective Coating Laboratory Formation
<u>l-C</u> (See Figure 20)	
Cast Iron	
Petrographic	Microscope
l. Calcite (CaCO ₃) (See Figur	res 21-27)

<u>1-A</u>

1-B

Calcite (CaCO₃) Reagent Grade³ *Protective Coating Laboratory Formation

^{*} In complete petrographic microscope testing of the referenced sample, the identification of the No - 1.658 and Ne - 1.486 index rays were tested and confirmed on three distinct and different samples. From this, it can be concluded that the referenced sample is a Calcite (CaCO₃) formation.

Figure 18 - Calcite: 1-A.

20	26.71	29.68	31.70	36.28	39.65	43.42	47.39	47.71	48.75
Radiation	Iron								
d-Å	4.19	3.78	3.55	3.11	2.86	2.62	2.40	2.40	2.35
Correcțed D*-A	3.34	3.014	2.82	2.47	2.28	2.08	1.92	1.90	1.87
\$ Intensity	6.9	100.0	5.0	15.0	17.6	17.6	7.5	16.3	17.5

* Corrected d spacing ratio of copper radiation to iron radiation = .796.

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Figure 19 - Protective Coating: 1-B.

* From cast iron test specimen.

** Corrected d spacing ratio of copper radiation to iron radiation = .796.

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Figure 20 - Cast Iron: 1-C.*

48.78	Iron	2.35	I	59.0
47.75	Iron	2.39	ı	65.0
44.90	Iron	2.53	,	95.5
29.65	Iron	3.78	I	100.
20	Radiation	d-ð	Corrected d-Å**	\$ Intensity

^{*} The same iron plate on which the protective coating was formed in the laboratory. The backside of the Cast Iron Test plate was used. During the coating the test plate backside was coated with a paint and therefore, did not rust or corrode. The paint was removed before X-ray.

** No need to correct as Iron radiation can be used as the standard.


Legend:

C.F. = Crossed polarizing filters. T.S. = Thin section. L = Light. M = Magnification of microscope and camera. "f" = Camera appature setting. T = Camera time setting. bire = Birefringence.

Iron Compounds and Coatings

Those minerals contain Fe(II) or Fe(III) as a common ion. It is possible that Fe(II) can be in an oxidization state to Fe(III).

Chemical

1. Hematite (Fe ₂ O ₃) Reagent Grade	
<u>1-A</u>	<u>1-B</u>
Fe ₂ O ₃ (Pure)	Fe ₂ O3 (Pure) @ l Hr 500°C
69.7 % as Fe(III) 70.4 % as Fe(III) 69.7 % as Fe(III) 70.4 % as Fe(III)	70.2 % as Fe(III) 71.0 % as Fe(III) 70.6 % as Fe(III)
Average 70.05% as Fe(III)	Average 70.60% as Fe(III)
<u>1-C</u>	<u>1-D</u>

Fe ₂ 0 ₃	Fe ₂ O ₃
(Pure) +	(Pure) +
water	water @
	1 Hr 500°C

Figure 21 - Calcite 1-A-I. CaCO (Pure), Index Oil -1.55, m - 240 x. 1-A-I Photo--1-A-I Description: Focus calcite crystal in E-ray position: 1 - 5.0; "f" - 5.6; T - 60; M - 240x. T.S. - perfect Rhomb colorless crystal. C.F. - shows slight blue and orange bire due to crystal thickness.

10. 10 an



Figure 22 - Calcite 1-A-II. CaCO₃ (Pure), Index Oil -1.55, m - 240x.

1-A-II Photo--1-A-II Description:

(See Description 1-A-1). This photograph illustrated the effect of crystal index identification using the Becke Line Method. Oil - 1.55; Ne = 1.486. The microscope barrel is raised and in that the oil is higher than the Ne. The Becke Line moves out into the higher oil--the crystal appears to enlarge.



Figure 23 - Calcite 1-A-III. CaCO₃ (Pure), Index Oil - 1.55, M 240x.

1-A-III Photo--1-A-III Description:

Rotation of 90° of crystal in Figure 21 and 22 focus of crystal to observe O-ray. Notice crystal appears darker at edges. L = 5.0; "f" - 2.8; T - 250; M = 240x.



Figure 24 - Calcite 1-A-IV. CaCO₃ (Pure), Index Oil - 1.55, M - 240x.

1-A-IV Photo--1-A-IV Description:

(See Description 1-A-III). Oil is 1.55 and N_{ω} - 1.658. The <u>Becke Line Method</u> shows that the lines move in toward the crystal--the crystal edge actually darkens. This indicated the O-ray is larger than the oil index.



Figure 25 - Calcite 1-A-V. CaCO₃ (Pure), Index Oil - 1.55, M - 240x.

1-A-V Photo--1-A-V Description:

*See Description 1-A-III). The Half or Oblique Method is employed. Oil is 1.55 and O-ray 1.658. Darkening one-half of the light source the crystal shows dark toward the dark and light toward the light. The illustration that the crystal index is higher than oil.



Figure 26 - Protective Coating 1-B-I. Laboratory Formation Index Oil - 1.55, M - 240x.

1-B-I Photo--1-B-I Description:

Focus on Rhomb crystal that has the appearance of Calcite. The entire sample appeared as Calcite except that the individual crystals were smaller and some nonopaque material was present. This position allows observation of the O-ray, No - 1.658 with; L=5; "f" - 2.8; T - 250; M - 240x; index oil - 1.55. T.S. - small perfect Rhomb that are colorless, with some blue and orange appearing. However, some massing of crystal structure to form vitreous mass. C.F. - black is black with bire colors from the large masses.



Figure 27 - Protective Coating 1-B-II. Laboratory Formation Index Oil - 1.55, M - 240x.

1. 1. 2.4

1-B-II Photo--1-B-II Description:

(See Description 1-B-I). The illustration here is that in observing the O-ray the Becke Line <u>Method</u> is used. Notice the black rises on the crystal when the microscope barrel is raised. Also, observe the "light" spot in the center of the crystal--this phenomena occurs sometimes in conjunction with a <u>Becke Line</u> illustrating that the crystal fragment is higher than the oil index.





67.0% 66.0% 66.0%	as Fe(III) as Fe(III) as Fe(III)		70.0 % as Fe(III) 71.5 % as Fe(III) 71.6 % as Fe(III)
*Average 66.6%	as Fe(III)	Average	71.03% as Fe(III)
2. Magnetite (F Fe ₃ O ₄ or Fe	<u>e0.Fe₂03) or</u> (Fe ₂ 04)		
<u>2-A</u>			<u>2-B</u>
FeO.Fe2 ^O 3		Fe0.Fe2	⁰ 3

	Average	72.03%	as Fe	e (total	Average	71.46%	as F	'e (total
3	. Sideri	ite or 1	Ferrou	is Carboi	nate-			
	FeCOa	(format	tion f	rom mix:	ing			

73.6 % as Fe (to+al)

72.3 % as Fe (total)

70.2 % as Fe (total)

52.5 % as Fe (total)

55.5 % as Fe (total)

56.2 % as Fe (total)

55.7 % as Fe (total)

53.5 % as Fe (total)

54.2 % as Fe (total)

52.2 % as Fe (total)

FecO₃ (formation from mixing Ferrous Sulfate and Sodium Carbonate)

3-A

FeCO₃ (Formation)

<u>3-B</u>

1 Hr. - 500°C

FeCO₃ (Formation) 1 Hr. - 500°C 61.8% as Fe (total) 62.4% as Fe (total) 61.5% as Fe (total) 63.0% as Fe (total)

72.0 % as Fe (total

71.84% as Fe (total

70.54% as Fe (total)

61.7% as Fe (total) 61.1% as Fe (total) 60.3% as Fe (total)

Average 54.25% as Fe (total) Average 61.7% as Fe (total)

^{*} The sample had a roisture content of 5.33% as water. The water was added to the sample then filtered through .45 micron filter paper and disiccated before testing.

4. Corrosion Sample-Pipe Nipple; The sample was removed from the nipple in layers--top to bottom and will be discussed in that sequence. 4-A **4**–B bottom top 63.0% as Fe (total) 57.0% as Fe (total) 64.0% as Fe (total) 59.5% as Fe (total) 65.0% as Fe (total) 57.0% as Fe (total) 64.0% as Fe (total) 59.5% as Fe (total) 65.2% as Fe (total) 58.8% as Fe (total) 59.5% as Fe (total) Average 64.2% as Fe (total) Average 58.2% as Fe (total) 4-C 4-D top bottom @ 1 Hr. - 500°C 1 Hr. - 500° C 67.0% as Fe (total 60.0% as Fe (total) 67.0% as Fe (total) 60.5% as Fe (total) 66.2% as Fe (total) 59.8% as Fe (total) Average 66.7% as Fe (total Average 60.1% as Fe (total X-ray 1. Hematite (Fe₂O₃) Reagent Grade 1-B (See Figure 29) 1-A (See Figure 28) Fe_2O_3 Fe₂0₃ (Pure) @ (Pure) 1 Hr. - 500°C 1-C (See Figure 30) 1-D (See Figure 31) Fe₂0₃ Fe₂0₃ (Pure) (Pure) plus nH₂O plus nH₂O @ 1 Hr. - 500°C

(Pure).
Fe_2O_3
F
28
Figure

20	24.32	33.34	35.8	41.09	49.61	54.21
Radiation	Iron	Iron	Iron	Iron	Iron	Iron
d-Å	4.61	3.37	3.14	2.76	2.30	2.12
Corrected d-Å		NO	t Neces	sary		
% Intensity	37.7	100.0	71.0	29.0	40.0	48.4



20	24.32	33.34	35.8	41.09	49.61	54.21
Radiation	Iron	Iron	Iron	Iron	Iron	Iron
d-A	4.61	3.37	3.14	2.76	2.30	2.12
Corrected d-A		NO	t Neces	sary		
% Intensity	37.7	100.0	71.0	29.0	40.0	48.4

Figure 29 - Fe₂O₃ (Pure) @ 1 Hr. - 500°C.



$nH_20.$
plus
(Pure)
$Fe_{2}O_{3}$
- Fe ₂ 0 ₃
30 - Fe ₂ 0 ₃

20	24.69	33.70	36.70	41.40	50.0	54.56
Radiation	Iron	Iron	Iron	Iron	Iron	Iron
d-Å	4.53	3.34	3.07	2.74	2.29	2.11
Corrected d-Å		NO	t Neces	sary		
% Intensity	39.6	100.0	74.2	25.0	41.6	48.0

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plus
(Pure)
Fe_{203}
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31
Figure

20	24.5	33.55	36.0	41.20	49.8	54.5
Radiation	Iron	Iron	Iron	Iron	Iron	Iron
d-Å	4.56	3.38	3.13	2.75	2.29	2.11
Corrected d-Å		Not	Necess	ary		
% Intensity	41.5	0.001	69.7	29.1	44.5	45.3

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2. Magnetite (FeO. Fe₂O₃)
or Fe₃O₄ or Fe(Fe₂O₄)

$$2-A$$
 (See Figure 32)
FeO. Fe₂O₃ or Fe₃O₄
 $e \ 1 \ Hr. - 500^{\circ}C$
3. Siderite or Ferrous Carbonate-
FeCO₃ (formation from mixing
Ferrous Sulfate and Sodium
Carbonate)

FeCO₃ (Formation FeCO₃ (Formation) at

3-B-I (See Figure 37)

- $1 \text{ Hr.} 500^{\circ}\text{C}$ $3-A-II \text{ (See Figure 35)} \qquad 3-B-II \text{ (See Figure 38)}$ $FeCO_3 \text{ (Formation)} \qquad FeCO_3 \text{ (Formation) at}$ $1 \text{ Hr.} 500^{\circ}\text{C}$ $3-A-III \text{ (See Figure 36)} \qquad 3-B-III \text{ (See Figure 39)}$ $1 \text{ Hr.} 500^{\circ}\text{C}$
- 4. Corrosion Sample-Pipe Nipple; The sample was removed from the nipple in layers--top to bottom and will be discussed in that manner.

FeCO3

3-A-I (See Figure 34)

4-A (See Figure 40)4-B (See Figure 41)Corrosion Sample - TopCorrosion Sample - Bottom4-C (See Figure 42)4-D (See Figure 43)Corrosion Sample - TopCorrosion Sample - Bottom@ 1 Hr. - 500°C@ 1 Hr. - 500°C

Figure 32 - FeO. Fe₂O₃ or Fe₃O₄.

×....

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36.4	Iron	3.10	Necess	92.4
35.8	Iron	3.15	Not	83.0
20	Radiation	d-å	Corrected c-A	% Intensity

2 θ	33.3	35.64	36.30	42.20	43.4	57.1	58.9	61.04	62.65
Radiation	Iron	Iron	Iron	Iron	Iron	Iron	Iron	Iron	Iron
d-Å	3.38	3.16	3.05	2.69	2.62	2.03	1.96	1.90	1.86
Corrected d-Å				Not Nec	essary				
\$ Intensity	67.8	0.06	71.0	100.0	72.5	72.5	71.0	73.3	76.0

Figure 33 - FeO. Fe $_2O_3$ or Fe $_3O_4$ @ 1 Hr. - 500°C.

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Figure 34 - No "d" spacing as the material tested was amorphous (without crystal structure).

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Figure 35 - No "d" spacing as the material tested was amorphous (without crystal structure).

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- No "d" spacing as the material tested was amorphous (without crystal structure). Figures 36

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20	24.4	33.49	35.9	41.12	49.8	54.50
Radiation	Iron	Iron	Iron	Iron	Iron	Iron
d-A	4.58	3.36	3.14	2.76	2.30	2.112
Corrected d-Å		NO	t Neces	sary		
å Entensity	83.3	100.0	93.0	83.3	82.5	84.2

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20	33.40	35.90	49.8	54.30
Radiation	Iron	Iron	Iron	Iron
d-Å	3.34	3.14	2.30	2.12
Corrected d-A	Z	ot Nece	ssary	
% Intensity	100.0	94.5	84.0	87.0

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Figure 39 - FeCO₃ @ 1 Hr. - 500°C.

20	24.26	25.96	28.28	33.30	35.72	49.62	54.18
Radiation	Iron	Iron	Iron	Iron	Iron	Iron	Iron
d-Å	4.61	4.33	3.97	3.39	3.16	2.30	2.12
Corrected d-Å			Not Nec	essary			
% Intensity	83.0	86.0	83.0	100.0	97.0	85.0	88.4

20 - 41.00° not shown, considered marginal.

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Figure 41 - Corrosion Sample - Bottom

20 = 35.64 Radiation = Iron d-Å = 3.157 Corrected d = Not Necessary % Intensity = 100

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Petrographic Microscope

<u>Hematite (Fe₂O₃)</u> Reagent Grade 1-B* 1-A $Fe_{2}O_{3}$ (See Figure 44) Fe203 (Pure) (Pure) plus heat 1 Hr. - 500°C <u>1-C</u>* 1-D* Fe203 Fe₂⁰3 (Pure) (Pure) plus water of hydration plus water and heat 1 Hr. - 500°C 2. Magnetite (FeO. Fe_2O_3) or Fe_3O_4 or $Fe(Fe_2O_4)$ 2-A FeO. Fe_2O_3 (See Figure 45) (taken from iron furnace)

3. Siderite or Ferrous Carbonate-FeCO3 (formation from mixing Ferrous Sulfate and Sodium Carbonate).

<u>3-A</u>

FeCO₃ (formation) (See Figures 46 and 47) FeCO₃ (formation) plus heat 1 Hr. - 500°C

(See Figures 48 and 49)

3-в

^{*} No description or photo as the X-ray pattern Figures 29, 30 and 31 were all identical to Fe₂O₃ reagent grade Figure 28.



4. Corrosion Sample-Pipe Nipple; The sample was removed from the nipple in layers--top to bottom and will be discussed in that manner.

<u>4-A</u>

<u>4-B</u>

Top (See Figure 50)

Bottom (See Figure 51)

<u>4-C</u>

Top 1 Hr. @ 500°C (See Figure 52)

<u>4-D</u>

Bottom 1.0 Hr. @ 500°C (See Figure 53)



Figure 44 - Hematite - Fe₂O₃, Reagent Grade, Index Oil - 2.00, M - 240x.

1-A Photo--1-A Description:

Focus on large center mass where L - 7.0; "f" - 5.6; T - 60; M - 240x. The general appearance is an occasional large mass or blob and the remainder is a background of very fine particles. The large mass appears earthy and compact with little evidence of crystal structure. However, notice (by arrow) a vitrious crystal right of the large mass. The index oil is 2.00 and the compound appears to have an index higher than the oil. Under C.F. the color is blood red. In T.S. the color is black.



Figure 45 - Magnetite - FeO. Fe₂O₃ Taken from Iron Furnace Index Oil - 2.00, M - 240x.

2-A Photo--2-A Description:

Focus on center crystal mass group using oil index of 2.00 and L - 7.5; "f" - 5.6; T - 60; M - 240x. The crystal formation was rotated with and without C.F. and the sections were opaque. It is possible on occasion to see some red and blue in the rotation. This may be due to impurities created from firing. Observe (by arrow) the clear vitrious edge on the right edge of the center crystal group. Generally, the crystals were massive with very few fines. The crystal index appears higher than the oil. Inasmuch as this mineral is difficult to identify by using the microscope, a magnet passed over filings of this material identifies the magnetic character and thus we conclude Magnetite.



Figure 46 - Siderite - FeCO₃ (Formation) Index Oil - 2.00, M - 240x.

3-A-I Photo--3-A-I Description:

Viewing a sample of Siderite in an index oil of 1.95 using L - 6.0; "f" - 4.0; T - 125; M - 240x. The crystals are large with a few small pieces. The crystal mass observed is as located (by arrow). There are two types of crystals on the glass plate, opaque and clear. Importantly, the opaque crystals have an index lower than the oil, whereas, the clear crystals have a higher index than the oil. In T.S. the opaque section is orange to orange red. The clear or vitrious sections, however, are orange. In C.F. opaque sections are orange to orange red to brownish. It is not uncommon to find in other samples the large earthy clumps as associated with Hematite. A physical test tried wigh HCl acid--the sample did effervese.



Figure 47 - Siderite - FeCO₃ Formation - Becke Line Index Oil - 2.0, M - 240x

3-A-II Photo--3-A-II Description:

(See Description 3-A-I). The crystal viewed is located (by arrow). The section is opaque and the Becke Line has moved out into the oil, indicating that the crystal has a lower index or that the oil has the higher index. A very good Becke.





Figure 48 - Siderite - FeCO3
Formation - Heat 1 Hr. @ 500°C
Index Oil - 2.00, M - 240x
3-B-I Photo--3-B-I Description:
Submerged in 2.00 oil with; L-7.0; "f" - 4.0;
T - 125; M - 240x and heated for 1.0 Hr.
@ 500°C. The sample appeared very much like
Hematite (see Figure 44) with large earthy
crystals and enormous amounts of fine particle
material. In T.S. black mass opaque. In
C.F. the large masses are blood red. The oil
had a higher index than the crystals.

NOTE: These two samples do not resemble each other in appearance at all. The granular characteristic (Figure 49) may be due to the lack of comminution.


Figure 49 - Siderite - FeCO₃ Formation - Heat 1 Hr. @ 500°C Index Oil - 2.00, M - 240x

3-B-II--3-B-II Description:

Submerged in 1.95 oil with; L - 5.0; "f" - 5.6; T - 60.0; M - 240x and heated for 1.0 Hr. @ 500°C. The sample contained large particles with very little small crystals. In view the crystal mass is both opaque and clear. The opaque section has an index lower than the oil, whereas, the clear section has a higher index than the oil. Under C.F. some of the crystals appear yellow to green yellow, others with blood red color.

NOTE: These two samples do not resemble each other in appearance at all. The granular characteristic (Figure 49) may be due to the lack of comminution.



Figure 50 - Corrosion Sample - Pipe Nipple Taken from Top Index Oil - 1.95, M - 240x.

4-A Photo--4-A Description:

Sample submerged in index oil 1.95 with; L - 5.0; "f" - 4.0; T - 125 and M - 240x. It can be observed from the figure that there are many Rhombohedral clear crystals (by arrow) in addition to the masses of opaque mineral structure. Under C.F. observation, the opaque sections, if thin enough, are red outside and some are completely red-orange. However, some crystals exhibit varying color to include purple, blue, yellow, and green. In T.S. clear crystals are Rhombohedral shape (as in Calcite) with a vitreous orange mass. In observing the indexes, the clear crystal has a higher index than the oil, whereas, opaque crystals have a lower index than oil.



Figure 51 - Corrosion Sample - Pipe Nipple Taken from Bottom Index Oil - 1.95, M - 240x

4-B Photo--4-B Description:

Sample in 1.95 index oil with; L - 5.0; "f" - 4.0; T - 125 and M - 240x. Again the clear Rhombohedral crystals can be observed. The clear Rhombohedral appear as salt on a plate in this figure. Under C.F. the opaque section is orange on outside or entire depending on thickness--if thin all orange. Again, there are some greenish-yellow crystals. In T.S. the clear Rhombohedrals are orange to red and the opaque sections are dark orange to red.



Figure 52 - Corrosion Sample - Pipe Nipple Taken from Top 1.0 Hr. @ 500°C Index Oil - 1.95, M - 240x

4-C Photo--4-C Description:

The index oil is 1.95 with; L - 6.0; "f" - 4.0; T - 125; M - 240x. The clear Rhombohedral crystals are gone and the normal opaque mass (by arrow) and many vitreous masses are visible. The clear crystals have a higher index, whereas the reverse is true for the opaque sections. In T.S. a definite red color appears at the large opaque masses that somewhat resemble Hematite-especially true in thin section. In thick section a black appearance is evident. As the stage is rotated in T.S., the colors yellow, green and blue appear; disappear, and reappear.



Figure 53 - Corrosion Sample - Pipe Nipple Taken from Bottom 1.0 Hr. @ 500°C Index Oil - 1.95, M - 250x

4-D Photo--4-D Description:

The index oil is 1.95 with; L - 6.0; "f" - 4.0; T - 125; M - 240x. The opaque crystals have a lower index than the oil, whereas, the clear crystals have a higher index than the oil. Generally, the Rhombohedrals are absent with mass and vitreous (by arrow) being the bulk for observing. In T.S., most crystals are opaque with some clear vitreous masses. Under C.F. the vitreous mass appears greenish-yellow.



CHAPTER VII

DISCUSSION OF RESULTS

General

Discussion of the data will take the following format: the <u>Protective Coatings</u> will be discussed separately as will the <u>Iron Compounds and Coatings</u> (a. Chemical, b. X-ray, and c. Petrographic Microscope). A summary will follow coordinating all three test results.

Protective Coatings

Chemical

The data for Calcite (CaCO₃) Reagent grade and Protective Coating--laboratory formation relate quite well, 39.55% and 37.9% Ca(II) respectively for the two as compared to the theoretical value of 40% Ca(II) (Appendix B) of pure CaCO₃.

In any chemical test, the accuracy depends on the technique, reagents, and the interferences as described by Standard Methods. The limitations of chemical testing when Ca(II) ion is determined relate to other ions such as Carbonate (CO₃) or ions in Solid Solution.

X-ray

1. Calcite (CaCO₃)

1-A: Reagent Grade

The X-ray pattern as illustrated in Figure 18 is very clear and precise. The important measurement is the diffraction angle and intensity. It is important to note the very low background base level of intensity 2.0+ %.

When comparing the data, Figure 18, with the X-ray data Appendix C and D, the identification is complete. Actually, Appendix D identifies the X-ray pattern with the known X-ray data by the ratio of the two radiations (Copper to Iron). The three principle angles and "d" spacings are: 29.68° - 3.04 > 3.014Å; 39.65° - 2.29 > 2.28Å; and 43.12° - 2.10 > 2.08Å.

The X-ray pattern of Calcite (CaCO₃) is standard and is used as a match to identify other X-rays.

1-B: Protective Coating, Laboratory Formation

The Calcite $(CaCO_3)$ X-ray pattern was determined and comparison of Figure 19, Protective Coating, to Figure 18 identified Calcite in the coating. It should be noted that the X-ray was conducted on a Calcite formation $(CaCO_3)$ as formed on a cast iron test plate and the entire unit (coating and plate) was tested as companions.

The results point to a formation of Calcite $(CaCO_3)$ when comparing Figures 18 and 19. However, the intensities are generally lower. Conversely, two diffraction angles and their intensities are higher or $2\theta = 31.6^{\circ}$ and 47.7° . In addition, a new diffraction angle appears with value of 44.9° . The explanation of the new $2\theta = 44.9^{\circ}$ can be found in Figure 20, Cast Iron X-ray pattern. This angle is approximately 96.0% of the 100.0% intensity value and indicates that the Cast Iron background did exhibit some influence on the X-ray pattern.

The Cast Iron test plate with the Protective Coating (expected Calcite (CaCO₃) was used because removing the coating might also remove small pieces of Cast Iron which would contaminate the sample. Also, during the coating formation one or several ions may have formed in solid solution to slightly alter the X-ray pattern.

It may be concluded that the X-ray pattern of Figure 19 generally fits Figure 18 in angle and inteisity comparisons.

1-C: Cast Iron

The X-ray pattern of the Cast Iron test plate was made to assist in identifying any diffraction angles that might occur in the testing of specimen 1-B Protective Coating, laboratory formation. As discussed above, at least one diffraction angle was identified as showing through the protective coating.

The Cast Iron X-ray is used to interpret other X-rays when the coating is formed on Cast Iron and tested as companions.

Petrographic Microscope

1. Calcite (CaCO₃)

1-A: Reagent Grade

<u>1-A-I</u>.--From Figure 21, the pure Calcite crystals are rhombohedral in shape. The sizes vary from large to small. The crystal under study as identified by the arrow shows shadow on one side and the edge blends in on the other (this particular crystal is identified to Figure 54, Calcite located in Appendix F). The identified crystal is aligned with one of the optic axis. The crystal is noted to have all the characteristics of Calcite (CaCO₃)-especially the blue and orange color when viewing with both polarizing filters in place (see Appendix E).

<u>1-A-II</u>.--A view of the same crystal as 1-A-I except that one axis is parallel to the lower filter axis and a crystal index investigation can be made. The Becke Line Method will be employed.

The index oil is 1.55 and when raising the barrel a very dark outline appears on the crystal edge and has moved out as shown by the arrow of Figure 22. The darkness is more apparent on the side, where before the edge

was difficult to determine. Darkening at the outer edge indicates that the liquid has a higher index than the crystal in this particular axis alignment. As per Appendix E, the axis in view is the n_{ε} or extraordinary ray axis. The ray n_{ε} is 1.486 < 1.55.

<u>1-A-III</u>.--In viewing the crystal in Figure 23, it is apparent that the crystal has been rotated 90°. The crystal takes on a different cast (dark) at the edges than for Figure 21. The darkness is due in part to the crystal depth and also to the large birefringents (0.172) of the crystal (Appendix E). The 90° rotation allows observation of the n_{ω} - 1.658 from the previous n_{ε} -1.486 ray.

<u>1-A-IV</u>.--The observation of Figure 24 immediately reveals that the crystal rotation is as for Figure 23. No ray is now in focus and the Becke Line Method is being used to determine the closeness of the index oil to the n_{ω} ray. The oil has an index of 1.55, and the n_{ω} ray index is 1.658. Therefore, when the microscope barrel is raised--the dark edge outline moves into the crystal-indicating that the oil has a lower index that the crystal 1.55 < 1.658. Darkness surrounds the sides and leaves only the apparent flat top undarkened. <u>1-A-V</u>.--This sample is identical to the others except the view is as per Figure 23-24. The illustration is for an index determination using the Half or Oblique Method. The oil is 1.55 and the n_{ω} ray is being viewed N_{ω} -1.658.

The light source to the crystal mounting is onehalf blocked and therefore, the half method. The dark side of the stage and the crystal (as per arrow) are dark, and the light side is facing the lighted area of the stage. For this, as for Figures 12 and 13, the crystal index is higher than the oil--that is N_{ω} -1.658 < 1.55.

1-B: Protective Coating, Laboratory Formation

<u>1-B-I</u>.--Figure 26 is of a suspected Calcite crystal. The crystal is a rhombohedral and is difficult to observe even though an arrow is pointing directly toward it. There is one noticeable difference from the reagent grade Calcite; most crystals are generally smaller and less perfect in shape though in some cases, the individual crystals are perfect to observe and to work with.

<u>1-B-II</u>.--Figure 27 is of the same crystal observed in Figure 26 and the photograph was taken to observe the Becke Line Method in testing a small, apparent Calcite crystal. As the barrel is raised, the dark moves up into the crystal and a <u>light</u> spot appears in the crystal center. The dark movement into the crystal indicates that the crystal has a larger index than the 1.55 index oil, and it is suspected that the ray being observed is the $N_{\rm w}$ -1.658.

Summary of Protective Coatings

The data for the Calcite (CaCO₃) Reagent grade compare quite well for chemical, X-ray with the microscope. Comparison of the chemical, X-ray and microscope work of the Protective Coating, laboratory formation, also appear to coincide and the X-ray pattern of the protective coating attached to the Cast Iron plate is valid. Knowledge of the Cast Iron X-ray is of course important in this technique.

Differences should be noted, however, when comparing the Calcite Reagent grade with the Protective Coating. The chemical tests vary slightly, X-ray intensities are either less or (in two cases) greater, and although the crystal structure is always rhombohedral the crystal formation size of the Protective Coating is smaller.

From this it is concluded that the formation coating is Calcite, though not in pure form.

Iron Compounds and Coatings

Chemical

It has been reported that the Ferrous Fe(II) oxidized to the Ferric Fe(III) state with time and under proper conditions. Laboratory testing did not allow natural oxidation of the Fe(II) to (III) and various samples were heated to promote rapid oxidation. The oxidation of the Fe(II) to Fe(III) in some minerals may force an alteration of the crystal structure and mineral This oxidation is illustrated in equations 8, 9, type. and 10 and especially in equations 8 and 10. The conversion of hydrated Magnetite (FeO.Fe,O, •nH,O)--Goethite [aFeO(OH)] by rapid oxidation has been reported and, in the interest of time, heating for 1.0 Hr. @ 500°C was selected to promote rapid oxidation.

1. Hematite (Fe₂O₃)

1-A: Reagent Grade

Pure Hematite has an Fe(III) of 70.0% as per Appendix B. The test results average 70.05% Fe(III), which is very good.

1-B: Reagent Grade @ 1.0 Hr. - 500°C

This check was performed to observe any changes that might occur. The data show that Fe(III) was greater than 70.0%. As noted in Appendix B, the Fe(III) of Hematite is 70.0%. 1-C: Reagent Grade Plus Water

Water was added to the sample to observe the effect, if any; that is, would the water become bound or water of hydration. The average Fe(III) percentages of 66.6% appear to indicate that some water was chemically bound. The value is 66.6%, and falls between the 62.8% or 57.2% for Fe_2O_3 with 1 or 2 moles of hydrated water (Appendix B).

1-D: Reagent Grade Plus Water @ 1 Hr. - 500°C

Sample 1-C was heated for 1 Hr. @ 500°C to drive off the bound hydrated water and restore the reagentgrade-plus-water to the original Hematite. Within the chemical testing limits, the Fe(III) average percentage was 71.03%, higher than expected but assuming that the bound water was eliminated, reasonable.

2. Magnetite (Fe₃O₄)

2-A and 2-B: Fe₃O₄ and 1 Hr. - 500°C

This sample, as extracted from an iron kiln, was chemically tested to determine Fe(III) both with and without heat (1 Hr. @ 500°C). The values for the unheated sample was 72.03%, and with heat was 71.46%. As per Appendix B, the value of Fe(III) for FeO.Fe₂O₃ is 72.4%.

It is important to note that the Magnetite dissolved very slowly in the acid solution (hydrochloric), and it is then not surprising that the Fe(III) values are not exactly 72.4%.

3. Siderite (FeCO₃)

3-A: Laboratory Formation

The laboratory formation exhibited no characteristics of Siderite. Chemical testing revealed that the Fe(total) percentage was higher than that of Appendix B Fe(total) for which FeCO₃ → 48.2%. The formation was observed to oxidize immediately from FeCO₃ → to Fe₂O₃•nH₂O. The 54.25% Fe(total) places the compound somewhere between Fe₂O₃•2H₂O - 57.2% or Fe₂O₃•3H₂O - 52.5%. Oxidation from the FeCO₃ to the Fe₂O₃•nH₂O is as predicted.

$$FeCO_3 \rightarrow Fe_2O_3 \cdot nH_2O \rightarrow Fe_2O_3$$
 (9)
Siderite Limonite Hematite*

From the above, the Siderite oxidized quickly to form Limonite. Limonite is an intermediate step toward Hematite, and the physical appearance of Limonite changed immediately from greenish-gray to brown-yellow.

^{*}With water of hydration can be termed Goethite.

3-B: Laboratory Formation @ 1 Hr. - 500°C

The sample from 3-A was in an oxidized state and heated to force further oxidation. Fe(total) percentage increased from heating to 61.7%. The oxidation level altered the crystal and mineral structure, approaching either Goethite (20) (Appendix B) Fe(III) 62.3%, or Hematite plus water of hydration $Fe_2O_3 \cdot 1H_2O$ Fe(III) of 62.8%.

4. Corrosion Sample

The sample was removed from the nipple in layers-top to bottom--and will be discussed in that manner.

4-A: Pipe Nipple--Top

The sample tested and the percentage recorded 64.2% Fe(total) indicates that the oxidation state is between Hematite (Fe_2O_3) and Hematite plus water with Fe(III) of 70.0% and 62.8%, respectively. The top layer of the blister was a green-gray, and a layer effect was apparent.

4-B: Pipe Nipple--Bottom

The bottom layer when removed from the pipe nipple was similar to the top layer in physical appearance and color. Testing showed that the (total) Fe was less for the bottom layer. Average percent Iron was 58.2% indicating that the oxidation state was between the $Fe_2O_3 \cdot 1H_2O = 62.8\%$ and $Fe_2O_3 \cdot 2H_2O = 57.2\%$ of Appendix B.

These observations were surprising because it has been reported (42) that the top layers are of a porous nature and that the oxidation state is predicted as per equation (8); that is, the percentage of iron should increase with depth.

```
4-C: Pipe Nipple--Top
@ 1 Hr. - 500°C
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Upon heating, the total iron percentage increased in Sample 1-A from 64.2% to 66.7% Fe(total). Some of the water of hydration was driven off, but not all. Hematite (Fe₂O₃) has an iron content of 70.0% and Fe₂O₃·1H₂O is 62.8% Iron.

4-D: Pipe Nipple--Bottom @ 1.0 Hr. - 500°C

This sample from 4-B was heated to drive off water of hydration and Fe(total) increased from 58.2% to 60.1%. This oxidation state approaches Goethite α [FeO(OH)] Fe(total) of 62.3%. Goethite was more probable than Lepidocrocite because Goethite is formed by rapid oxidation, and the latter is formed by slow oxidation (see equations 8 and 10).

The possibility that sample 4-D being Fe_2O_3 with hydrated water cannot be ruled out. The range would then be $Fe_2O_3 \cdot 3H_2O = 52.5$ % and $Fe_2O_3 \cdot 2H_2O = 62.8$ %. It is important to note that the baseline level of interference for all the iron compounds is higher than the levels for the Calcite coatings. There is no interference with testing or observation, however, so long as an altered baseline is observed.

1. Hematite (Fe₂O₃)

1-A: Reagent Grade

Hematite was selected as a compound that would serve as a reference for other X-ray comparisons. Hematite (Fe_2O_3) was especially appropriate because this compound is present in many of the other altered forms and/or oxidation states.

In Figure 28, reagent grade Hematite was tested using Iron radiation with a nickel filter. The radiation angles are as tabulated below the figure.

The three radiation angles (20) with the largest intensities respectively are: 33.34° - 100.0%; 35.8° -71.0% and 54.21° - 48.4%. Radiation peaks are very sharp and recognizable. Inasmuch as Hematite plays a large role in protective coatings, tests were conducted to observe any changes.

1-B: Reagent Grade @ 1.0 Hr. - 500°C

Pure Hematite was heated to observe any change and to duplicate rapid oxidation. The result of this testing is shown in Figure 29. Figure 29 is identical to Figure 28, showing Hematite (Fe_2O_3) to be a very stable form.

1-C: Reagent Grade Plus Water

Water was added to Sample 1-A to observe any water of hydration. The sample was mixed, allowed to sit, dissicated and prepared on the glass plate for X-ray testing.

Figure 30 is the X-ray pattern. The pattern is identical to Figure 28, Hematite reagent grade (Fe_2O_3) , and no hydration was experienced.

1-D: Reagent Grade Water Added Plus 1.0 Hr. - 500°C

Sample 1-C was heated and then X-rayed. No change in the X-ray patterns from Figures 28 and 30 was noted, and there was no water of hydration.

2. Magnetite (Fe₃O₄)

2-A: Fe₃0₄

The Magnetite was taken from an iron furnace, and chemical testing showed Fe(total) 72.0% and 71.46% as compared to 72.4% for Appendix B.

The X-ray pattern of Figure 32 is for the sample of Magnetite. When compared to Figure 28, the only radiation angle that corresponded was $2\theta - 35.8^{\circ}$ or d = 3.15Å. 2-B: Fe₃O₄ 1 Hr. - 500°C

Magnetite is unstable and can be oxidized. A sample of Magnetite was heated for one hour at 500°C and X-rayed.

Figure 33 and the table indicates the change that took place after heating. The three 20 angles in Figure 32 were repeated in Figure 33. Angles 35.8° and 42.4° were more intense. However, 20 - 36.3° diminished in intensity. Heating altered the entire crystal structure and six new diffraction angles appeared: 33.3°, 43.40°, 57.10°, 58.90°, 61.04°, and 62.65°.

In comparing Figure 28 with Figure 33, the 20 angles that match are 33.34° and 35.64°. This is some improvement over the unheated Magnetite for which one angle only coincided 20 - 35.8°. The oxidized material did not take on the form of Hematite, probably because there was no water of hydration.

3. Siderite (FeCO₃)

3-A: Laboratory Formation

<u>3-A-I, II, III</u>.--X-ray pattern for Siderite, Figures 34, 35, and 36 are identical. The formation is amorphous (no crystal structure) and could be only one iron compound, <u>Limonite</u>, not Siderite. As per equation (9),

$$FeCO_3 \rightarrow Fe_2O_3 \cdot nH_2O \rightarrow Fe_2O_3$$
 (9)
Siderite Limonite Hematite

Siderite is oxidized to form Limonite and the X-ray provides perfect identification.

3-B: Laboratory Formation 1 Hr. - 500°C

<u>3-B-I</u>.--Use of heat to speed the kinetics of oxidation was successful. The <u>Limonite</u> formation (FeCO₃ oxidized) plus heat formed Hematite (Fe₂O₃) as predicted by equation (9). The formation of Hematite (Fe₂O₃) is evident when comparing Figure 37 with Figure 28 Hematite (Fe₂O₃) pure reagent grade.

The diffraction intensities are not quite as sharp or large but comparison in terms of the diffraction angles (20) is almost perfect.

<u>3-B-II</u>.--Here, the match between Figures 38 and 28 is not perfect. The diffraction angles (20) do not match and in fact; $2\theta - 24.32^{\circ}$ and $2\theta - 41.09^{\circ}$ did not appear. In addition, 2θ angles 49.80° and $2\theta - 54.30^{\circ}$ are of very low intensity, barely discernible.

It is suspected that the oxidation of the FeCO₃ \rightarrow Fe₂O₃ \cdot nH₂O \rightarrow Fe₂O₃ was not complete; it could well be that the heating period should have been longer. However, the change toward Hematite (Fe₂O₃) is evident.

<u>3-B-III</u>.--Comparison of Figure 39 to Figure 28 reveals that the pattern generally matches that of Hematite (Fe_2O_3) pure reagent grade. The 20 angle -41.0° is evident, but barely so. Two new comers have arrived and may be a false background reading or an impurity. Intensities of these new lines are difficult to detect.

In spite of imperfections, the compound represents Hematite (Fe $_2O_3$).

4. Corrosion Sample

The sample was removed from the nipple in layers-top to bottom--and will be discussed in that manner.

4-A: Pipe Nipple--Top

Figure 40 reveals that there is only one diffraction angle; $2\theta - 35.72^{\circ}$. This angle corresponds to $2\theta - 35.80^{\circ}$ in Figure 28. However, it is noteworthy that the angle 35.72° is not the 100% intensity angle of Figure 28 (angle $2\theta - 33.34^{\circ}$).

From Appendix C, Lepidocrocite $[\gamma-\text{FeO} \cdot (\text{OH})]$ the 100% intensity and the corresponding 20 angle 34.40° with d - 3.27Å, generally matches the 100% intensity of Figure 40 with a 20 angle 35.72° where d - 3.16Å.

The corrosion sample oxidized over a long period of time and the compound X-rayed is organizing toward the formation of Lepidocrocite $[\gamma-FeO \cdot (OH)]$ as per equations (8) and (10).

4-B: Pipe Nipple--Bottom

Samples 4-A and 4-B appear to be identical in X-ray pattern. The 2 θ angle 35.64° from Figure 41 is only .08° different from the 2 θ - 35.72° in Figure 40.

The conclusions are identical to that for 4-A and the compounds appear to be oxidizing toward the formation of Lepidocrocite [γ -FeO·(OH)].

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4-C: Pipe Nipple--Top
@ 1 Hr. - 500°C
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If the top and bottom corrosion samples are organizing toward Lepidocrocite, heating for 1 Hr. -500°C should force oxidation toward Hematite (Fe₂O₃).

In Figure 42, the X-ray pattern is starting to exhibit Hematite (Fe₂O₃) tendencies. When comparing to Figure 28 all the 20 angles are observed except $20 - 24.32^{\circ}$.

Diffraction intensities and peaks are less sharp and defined than for Figure 28, but the 20 angles are present. The angle in question is $20 - 41.00^{\circ}$, though excitation of this angle is marginal.

From this, we may assume that the heated sample was converted to Hematite (Fe_2O_3) and not Lepidocrocite.

It can be safely presumed that Lepidocrocite did not form inasmuch as the 100% intensity is for a $35.-^{\circ}$ angle and the 100% intensity in Figure 42 is $2\theta - 33.0^{\circ}$ range.

4-D: Pipe Nipple--Bottom @ 1 Hr. - 500°C

In Figure 43, the X-ray pattern is approaching Hematite (Fe₂O₃) and the only angle not in appearance is $2\theta - 41.09^{\circ}$. For this pattern the $2\theta - 24.48^{\circ}$ did appear over that of Figure 42.

It is concluded that the compound X-rayed is exhibiting the near normal pattern of Hematite (Fe $_2$ O $_3$).

Petrographic Microscope

1. Hematite (Fe₂O₃)

1-A: Reagent Grade

Figure 44 illustrates the general appearance of (Pure) Hematite (Fe_2O_3). The overwhelming color--red-is an outstanding identification. The random distribution of a vitreous mass--note Figure 44--is important and will be referenced to in later text. Also, it is common to see a "glob" of material, even though the sample has been comminuted. 1-B, 1-C, and 1-D: Reagent Grade (1 Hr. - 500°C; with Plus Water and 1 Hr. - 500°C

In the testing of 1-B, 1-C, and 1-D, it was learned from X-ray pattern of these respective samples that each is identical to Hematite (Fe_2O_3) reagent grade. The petrographic microscope verified the reagent grade status. Duplication of data has been omitted because Figure 44 is representative of the Sample 1-B, 1-C, and 1-D.

2. Magnetite (Fe₃O₄)

2-A: Fe₃O₄ (taken from kiln)

The identification of Magnetite can almost be determined by visual inspection. The material is unique, and the magnetic property is a specific identification.

Review of Figure 45 illustrates the crystal mass. Some vitreous material is evident--note arrow. It is difficult to check the crystal index because selection of a proper crystal is impaired by the fact that the crystal color (Appendix E) is either black or opaque in nature. A more thorough comminution should assist in crystal viewing and identification.

3. Siderite (FeCO₃)

3-A: Laboratory Formation

<u>3-A-I</u>.--It was hoped that the compound Siderite would result because Siderite has been cited in the literature as forming an outer protective coating over other materials. Instead, X-ray and microscopic tests showed the compound had no crystal structure and appeared to be Limonite.

Figure 46 shows the lack of real fine crystal material and predominance of large gross crystals.

An index check (see arrow) was made because for an opaque compound the index is lower than for the oil. A small percentage of this sample is vitreous and has a higher index than the oil. This compound has a reddish to brownish cast when viewing and the compound appears to be Limonite.

<u>3-A-II</u>.--Figure 47 is from an index check of the opaque crystals. This figure indicates that as the microscope barrel was raised (slightly out of focus) the Becke Line moved out and away from the crystal as shown by the arrow.

Note the light and almost white outer crystal edge. A Becke Line allows a positive confident crystal index oil check. The oil has a higher index than the compound, suspected to be Limonite.

3-B: Laboratory Formation @ 1 Hr. - 500°C

<u>3-B-I</u>.--Microscope work on the heated Siderite samples showed that two materials may look and appear

different but be the same compound or crystal. In comparins Figure 48 to Figure 44 - Hematite (Fe_2O_3) pure, it becomes obvious that the heated sample is Hematite. The two figures (48 and 44) depict the same material type; that is, the earth compact "blobs" and the blood red color.

<u>3-B-II</u>.--This sample was prepared using the same techniques as of preparation as for the previous sample for Figure 48. Comparison of Figures 48 and 49 shows that in appearance the materials looked dissimilar. However, that is not the case. The materials are similar, but not identical, and the X-ray and microscope work indicate this uniformity.

In Figure 37, 38, and 39 (X-ray patterns), it can be seen that the heated sample does not in all cases coincide with the crystal Hematite (Fe_2O_3), but is being oxidized toward Hematite (Fe_2O_3). This is also true of this sample. There is a very dominant theme of Hematite (Fe_2O_3) black opaque crystals with the blood red showing under crossed filters. However, there are also yellow to greenish-yellow crystals in this material and this could be <u>Goethite</u>, suggesting that this material was being oxidized toward Hematite (Fe_2O_3). Goethite is suspected because this material is formed under rapid oxidation conditions.

4. Corrosion Sample

4-A: Pipe Nipple--Top

Figure 50 illustrates two types of formation. Large masses dominate the sample, but upon close review of the photograph, it is evident that small-clear-fine particles are common. The fine material is rhombohedral in shape and appears to have a higher index than the oil. The opaque crystals have a lower index that the oil. The overriding color of the mass or clear material is the red or orange-red indicating that the compound under investigation is Lepidocrocite [γ -FeO·(OH)].

4-B: Pipe Nipple--Bottom

Figure 51 is much the same as Figure 50, a large mass with a great number of fine particles. There are clear rhombohedral crystals, generally very fine. A crystal index of the two types indicated that the clear crystals have a higher index than the oil, whereas, the opaque crystals have a lower crystal index than the oil. The color red is vivid both in the clear and opaque crystals. It would also seem that this compound, as in 4-A, is Lepidocrocite.

4-C: Pipe Nipple--Top @ 1 Hr. - 500°C

Figure 52 indicates that the sample has changed when compared with 4-A, Figure 50. There are very few

fines, although more large vitreous masses (see arrow). The opaque material is not as large as in 4-A but there are more smaller opaque pieces. The crystal index of the clear vitreous material is higher than the oil, whereas the reverse is true for the opaque material.

The appearance of Figure 52 can be compared with Figure 44 [Hematite (Fe₂O₃) reagent grade]. The identification is not perfect, but the trend is apparent. The compound or crystal under investigation has the appearance of Hematite.

4-D: Pipe Nipple--Bottom @ 1 Hr. - 500°C

After heating sample 4-B, the oxidized material has the appearance of Hematite. The red color of the clear and opaque material is one identifying feature. The comparable appearance between Figure 52 and Figure 44 [Hematite (Fe_2O_3) reagent grade] also assists in identifying sample 4-D.

Comparison of the X-rays of sample 4-A and 4-D indicate that the sample was being oxidized toward Hema-tite. The X-ray figures for 4-C and 4-D are $\underline{42}$ and $\underline{43}$ respectively.

Summary of Iron Compounds and Coatings

1. Hematite (Fe₂O₃) Reagent Grade

It can be stated that the data as regards testing of Fe_2O_3 (Pure) from a chemical, X-ray and microscope standpoint correlates very well. One accurate method to correlate data is by use of X-ray diffraction. This procedure positively identified Hematite (Fe_2O_3) regardless of added water or rapid oxidation from heat (1 Hr. - 500°C).

2. Magnetite [Fe0·Fe₂O₃ or Fe_3O_4 or $Fe(Fe_2O_4)$]

The identification of Magnetite can be accomplished by chemical testing if the proper time and precautions are observed. The X-ray illustrates a perfect thumb print of the crystal, and this is confirmed by the microscope, though the dominance of opaque material is somewhat limiting. The correlation, however, is solid evidence that the material tested is Magnetite.

3. Siderite or Ferrous Carbonate (FeCO3) (Formation From Mixing Ferrous Sulfate and Sodium Carbonate)

The complete testing of Siderite (FeCO₃) (chemical, X-ray and microscope) illustrates that Siderite was oxidized to form <u>Limonite</u>. Limonite was identified by
the chemical percentages, the amorphous structure from X-ray and confirmation of the microscope work, especially the brownish color as described in Appendix E and under Petrographic Microscope, 3-A.

The heating of the Siderite (actually Limonite) revealed a change, that is from Limonite toward Hematite. Correlation of this by chemical, X-ray and microscope work is good. X-ray patterns match very well with a few exceptions. However, data from the chemical tests and microscope indicate that oxidation toward Hematite is not complete. The chemical Iron percentage was 61.7 which was less than 70.0%. Also, the microscope work revealed something less than pure Hematite (Fe₂O₃).

4. Corrosion Sample--Pipe Nipple

Тор

The chemical testing of this material revealed an iron percentage of 64.2 which was higher than the suspected Lepidocrocite. The percentage is somewhere between $Fe_2O_3 \cdot 1H_2O$ and Fe_2O_3 and X-ray pattern, as compared with Appendix C, revealed Lepidocrocite. Microscopic testing of this compound also identified Lepidocrocite from the blood red color. The X-ray and microscope work identified the unkonwn material which then conformed with chemical testing. Bottom

Testing for this unkonwn resulted in about the same results as above. That is, X-ray and microscopic data reinforced for identification even though chemical testing suggested another crystal. The X-ray data as compared with Appendix C and the microscopic data as compared with Appendix E provide sufficient proof that the material was oxidizing toward Lepidocrocite.

Top--1 Hr. - 500°C and Bottom--1 Hr. - 500°C

These two substances are grouped together because they are similar materials. The chemical testing data do not conform, 66.7% as compared to 60.1%. The X-ray patterns are quite close and are sufficiently matched to insure that both heated samples are in an oxidation state toward Hematite (Fe_2O_3). Microscopic data reinforce the identification as Hematite.

Corrosion samples for top and bottom layers were apparently the same material or the strip removal techniques were not effective. The heated samples are identical and the observation of the oxidation from Lepidocrocite toward Hematite is apparent. Though oxidation of the sample is not complete, the appearance and likeness provide sufficient evidence to identify the material as Hematite.

CHAPTER VIII

CONCLUSIONS

The thesis is a format or methodology for the investigation of any internal coatings in water mains. These coatings range from Calcite to any of several iron coatings. Coatings vary widely because each water system is unique in water chemistry. The positive and negative ion balance reveals many types in solution.

It should be noted that any trace ion can form in solid solution. In addition, iron released from corrosion often forms in solid solution. Therefore, a complete water chemistry profile of a water system is important when investigating an internal coating of a water main.

 The visual observation technique is useful for quick identification. However, the reporting of color, hardness and appearance packing is only one clue in the total identification of a coating. Chemical, X-ray and microscope testing collectively are the real key to correct identification of a coating.

2. The identification of the unknown coating under investigation should start with properly calibrated standard data, especially for Calcite (CaCO₃) and

Hematite (Fe₂0₃). Reagent grade materials, or laboratory produced standards, after complete testing for correctness, can be used.

Standards for chemical tests are as important as the standards used for testing by X-ray and with the microscope. These two latter forms of testing can quickly reveal the nature of an unknown material. The X-ray patterns of Calcite and Hematite, for instance, allow visual comparison with unknown coatings. A quick and accurate method for preliminary checking is to produce an X-ray pattern for comparison with a known X-ray pattern.

3. It is possible to form a protective Calcite coating $(CaCO_3)$ formation on a test Cast Iron speciman and to quickly check this coating by X-ray methods. This is called the "companion testing method." The standard X-ray pattern for Cast Iron and the pattern for Reagent grade Calcite $(CaCO_3)$ provide a visual X-ray review of a coating for a preliminary check.

The "companion testing method" can be used in dynamic testing for Calcite coatings. At designated time intervals, the companion test sample can be dried, dessicated and an X-ray check conducted. The companion may be checked immediately after blot drying; water retained on the sample should not interfere with the X-ray pattern.

4. The testing of the Calcite laboratory formation reveals Calcite, but not in pure form. The crystal formations, although rhombohedral in shape, were very much smaller than for reagent grade Calcite. One or more substances in solution in the water system may retard or alter the formation and reduce crystal size. However, the formation is Calcite and affords a protective coating.

It has been reported (14, 21, 22, 24, and 29) 5. that Siderite (Ferrous Carbonate FeCO₂) forms a protective coating over a Calcite coating on the water main metal, or over another iron compound. It was necessary to attempt formation of Siderite (FeCO3) in the laboratory because Reagent grade was impossible to obtain. The laboratory formation immediately oxidized to Limonite (amorphous). The X-ray best illustrates this no-crystal structure. It can therefore be concluded that Siderite oxidizes quickly in the presence of oxygen making it very difficult to develop a standard for testing. The oxidation of Siderite to Limonite is in accordance with equation (9) and was expected.

The formation of Siderite in a Nitrogen atmosphere could be used to provide a standard, but kinetics of oxidation after formation in a water system would be helpful. Again, if a water system has some dissolved oxygen, whether this is sufficient to allow oxidation

to form Limonite from Siderite is questionable. It seems doubtful that Siderite could be observed in a protective coating!

6. The oxidation of Siderite to form Limonite and the X-ray patterns revealed no crystal structure (amorphous).

Testing of Limonite then took another path. From equation (9), Limonite oxidizes to form Hematite (Fe_2O_3) and in fact, the X-ray pattern is a close comparison to Hematite (Fe_2O_3) , Reagent grade. The similarity is not perfect and formation as per equation (9) could be Hematite plus hydrated water or Goethite.

The application of heat speeds oxidation. Oxidation did take place, but the kinetics under normal conditions are not known for formation of Hematite.

7. The investigation of the corrosion formed on the pipe nipple was interesting. The dessicated form had little crystal structure and inasmuch as it was formed slowly, was probably Lepidocrocite. However, to expidite oxidation, heat was applied (1 Hr.-500 C).

The X-ray of the heated unknown sample resembled Hematite. It can be concluded that the water of hydration was driven off and the crystal structure changed to form Hematite (Fe_2O_3). The X-ray pattern is not perfect, but the general characteristics are apparent. 8. Care should be taken in using the microscope for identifying iron bearing compounds. The black or opaque sections make it difficult to observe the crystal index, but with care and patience, a reliable crystal index can be obtained.

In summary, most of the test data did reveal that a Calcite coating can be formed on a Cast Iron test specimen tested by X-ray. Various forms of Iron were revealed in testing and the oxidation of several compounds indicated formation of another crystal structure. No attempt was made to test the capacity of various coatings for inhibiting corrosion.

X-ray tests should be the first checks considered for unknown coatings. Once the X-ray check has provided a lead, other testing techniques can follow, including use of the microscope and chemical testing.

CHAPTER IX

RECOMMENDATIONS

The following recommendations are proposed for refining the methodology of investigation for coatings in water mains.

1. All testing should be conducted on coatings that have been formed in a water system, that is, a formation that has been formed under field conditions. The testing should include the chemical and polarization studies to determine how effective a formation may be for providing a protective coating.

2. Use x-ray as the first check on any unknown compounds or crystals and comparison with the standards will provide good initial direction.

3. Proper radiation and filter are required for best comparison results. Radiation and filter are suggested in Appendix C.

4. When testing for a specific ion concentration, an atomic absorption machine is recommended. A complete ion check can be conducted to reveal the ions bound in the compound or in solid solution. It is proposed that, in addition to Iron and Calcium tests,

checks for other positive ions such as Magnesium and Phosphorus be made.

5. Use great care in removing the specific layers of coating formation. The peeling or removing of specific layers will allow the specific investigation of an oxidation layer for the iron compounds. Disturbing the layers reveals only one common compound, and does not represent the true nature of the coating.

6. It is proposed to form a Calcite coating and to then specifically allow some rusting to take place, causing iron formation to adhere to the Calcite coating. Observe the two in tandum for solid solution or increased protective capacity. Use of atomic absorption may be the only reliable test for the degree of solid solution.

7. More tests on the "companion testing method" to determine the thickness of Calcite (CaCO₃) necessary to screen out the Cast Iron radiation pattern.

8. Form Siderite (Ferrous Carbonate FeCO₃) in a nitrogen atmosphere to observe the crystal characteriistics from X-ray and microscope standpoint. This formation can be used for oxidation studies. More importantly, it could permit kinetics study to determine oxidation from the Siderite form to Limonite or beyond. A kinetics study should be performed under conditions of normal water temperature, normal water pressures and normal chemical quality found in a water main.

9. When Limonite is formed observation of the change of crystal structure and the kinetics involved are suggested. The change is reported to form Hematite or, with some water of hydration, Goethite. Again, the formation of a study should be in a water system near normal as compared to general water conditions in a municipal water distribution system.

10. A formation of Calcite (CaCO₃) with several ions in solid solution would reveal much on the protective coating on water mains. The formation of solid solutions could be useful in future interpretation. BIBLIOGRAPHY

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APPENDICES

Mineral Name and Composition	Group	Mineral System	Color	Hardness, Specific Gravity & Fusibility	Remarks
Calcite CaCO ₃	Uniaxial	Hexagonal	Colorless to Green to Blue to Brown	H-3 G-2.715 Infusiable	Effervesces in acid CaCO ₃ - 100% Termed CaO. CO ₂
Aragonite Ca0.CO_2	Biaxial Negative	Orthorhombic	Colorless to Green to Blue to Brown	H-4 G-2.94 Infusiable	Soluble in dilute acid CaCO3 - 99.91% stains red when boiled in CaNo3; (Calcite Doesn't)
Apatite 9CaO. 3P ₂ O ₅ Ca[F ₂ (OH) ₂ CO ₃ ,Cl ₂]	Uniaxial Negative	Hexagonal	Colorless to Green to Blue to Brown	H-5.0 G-3.16 F-5	Sol. in Acid contains F-3.31%, CL37%, H ₂ O71%, CO ₂ 57%
Vivianite 3FeO.P ₂ O5.8H ₂ O	Biaxial Positive	Monoclinic	Colorless to Green, Blue	H-2.0 G-2.6 F-1.5	Soluble in HCl Colorless if fresh, but on powdering turns to deep blue.
Ankerite CaO(mg,Fe)O.2CO_2	Uniaxial Negative	Hexagonal Trigonal	Coloriess to Dark Brown	H-3.0 G-2.94 Infusiable	Data for mineral with caco ₃ -52.6%, mgcO ₃ -36.7%, FeCO ₃ -10.7% soluble in Acid
Hematite Fe ₂ 0 ₃	Uni ax ial Negative	Hexagonal Trigonal	Gray to Black	H-5 G-5.2 Infusiable	Soluble in acid, streak yellow

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APPENDIX A - Data for Nonopaque Minerals.*

Magnetite FeO.Fe ₂ 0 ₃	Spinel	Isometric	Black, Opaque	H-5.5-6.5 G-5.17	Can be termed-Fe ₃ 0 ₄ , Fe(Fe ₂ 0 ₄) Magnetic
Siderite FeCO ₃	Uni ax ial Negative	Hexagonal Trigonal	Gray Yellow to Gray to Greenish Gray	H-4.0 G-3.78 Infusiable	Soluble in acid, data for FeCO ₃ -90%, mgCO ₃ -5%, CaCO ₃ -5%. Can be termed FeO.CO ₂
Limonite Fe ₂ 0 ₃ .nH ₂ 0	Isotropic	Amorphous	Brown Brown to Black	H-4.0± G-3.8± Infusiable	Soluble in HCl crystallized to form Goethite
Goethite α-FeO.(OH)	Biaxial Negative	Orthorhombic	Yellow or Brown to Black	H-5-5.5 G-4-4.4	Soluble in HCl Can be termed Fe ₂ 0 ₃ .H ₂ 0
Lepidocrocite À-FeO(OH)	Biaxial Negative	Orthorhombic	Blood Red	H-4 G-4.1	Streak Dull Orange Can be termed Fe ₂ 0 ₃ .H ₂ 0
•					

* Taken from Larsen, Esper S., and Berman, Harry. The Microscopic Determination of Nonopaque 2nd Ed., Geological Survey Bulletin 848, U.S. Department of the Interior, 1964. Minerals,

APPENDIX B

CALCIUM (Ca) AND IRON (Fe) PERCENTAGES

IN VARIOUS COMPOUNDS

Calcite - CaCO ₃	40% Ca
Iron Oxide - FeO	77.9% Fe(II)
Hematite - Fe ₂ 0 ₃	70.0% Fe(III)
plus water - Fe ₂ 0 ₃ ·lH ₂ 0	62.8% Fe(III)
plus water - Fe ₂ 0 ₃ •2H ₂ 0	57.2% Fe(III)
plus water - Fe ₂ 0 ₃ •3H ₂ 0	52.5% Fe - Limonite - 2[Fe(OH ₃)](III)
Magnetite - FeO·Fe ₂ 0 ₃	72.4% Fe (Total) or $\text{Fe}_3^{O_4}$
Siderite - FeCO ₃	48.2% Fe(II)
Ferrous hydroxide - Fe(OH) ₂	62.3% Fe(II)
Goethite - a[FeO(OH)]	62.3% Fe(III)
Lepidocrocite - γ[FeO(OH)]	62.3% Fe(III)

;

APPENDIX C

X-RAY DIFFRACTION DATA*

The following data is as pertains to the three highest reflection-intensity ratios as per X-ray dif-fraction techniques.

Material, Composition and Radiation	"d" spacing in A units	I/I.%	20 Angles in degrees
Calcite			
CaCO ₃	3.04	100	29.68°
Radiation = CuK_{q}	0.00	•	
$\lambda = 1.5405A$	2.29	18	39.65
Nickel Filter	2.10	18	43.12°
Aragonite	2 40	100	_
Radiation =	3.40	100	*
$\lambda =$	1.98	65	
Filter	3.27	52	
Apatite			
9CaO•3P205	2.82	100	*
$Ca[Fe_2(OH)_2, CO_3, Cl_2]$			
$\lambda =$	3.45	75	
Filter	3.11	75	
Vivianite			
3FeO P205•8H2O	6.80	100	*
Radiation =			
$\lambda =$	2.97	67	
Filter	2.91	67	

*Data not available.

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Appendix C.--Cont.

Material, Composition and Radiation	"d" spacing in À units	I/I°8	2θ Angles in Degrees
$\frac{\text{Ankerite}}{\text{CaO} \cdot (\text{Mg,Fe}) \text{O} \cdot 2\text{CO}_2}$ Radiation = CuK_{α} , $\lambda = 1.5405\text{\AA}$ Nickel Filter			*
$\frac{\text{Hematite}}{\text{Fe}_2\text{O}_3}$ Radiation = FeK _{\alpha} , λ = 1.93597Å	2.69 2.51	100 80	42.20° 45.20°
Calcite Filter	1.69	80	70.00°
$\frac{\text{Magnetite}}{(\text{Fe0} \cdot \text{Fe}_2\text{O}_3) \text{ or } (\text{Fe}_3\text{O}_4)}$ Radiation = FeK_{α} , λ = 1.93597Å Calcite Filter	2.53 1.48 2.97	100 70 60	44.80° 81.60° 38.00°
$\frac{\text{Siderite}}{\text{FeCO}_3}$ Radiation = FeK _{\alpha} , λ = 1.93597Å Calcite Filter	2.79 1.73 3.59	100 80 60	40.60° 68.00° 31.20°
$\frac{\text{Limonite}}{\text{Fe}_2\text{O}_3 \cdot \text{nH}_2\text{O}}$ Radiation = λ = not recessary Filter	Amorph Amorph Amorph	nous nous nous	0 ° 0 ° 0 °
$\frac{\text{Goethite}}{\alpha - \text{FeO} \cdot (\text{OH})}$ Radiation = CoK _{\alpha} , λ = 1.7889Å No Filter	4.18 2.44 2.69	100 80 70	24.73° 43.00° 39.47°

*Data not available.

Appendix C.--Cont.

Material, Composition and Radiation	"d" spacing in A units	I/I°8	2θ Angles in Degrees
Lepidocrocite y-FeQ•(QH)	3.27	100	34.40°
Radiation = FeK_{α} , $\lambda = 1.93597Å$	7.30	90	15.00°
Calcite Filter	2.56	80	44.40°

*As compiled from:

A. N. Winchel and N. H. Winchel, <u>Elements of</u> Optical <u>Mineralogy</u> (4th ed.; New York: John Wiley & Sons, 1927).

Horace Winchel, Optical Properties of Minerals--A Determinative Table (New York: Academic Press, 1965).

Handbook of Chemistry, Physics (36th ed.; New York: Chemical Rubber Publishing Company, n.d.).

X-Ray Power Data File Set 1-5, ASTM Special Technical Publication 48-J (New York: American Society for Testing Materials, 1960).

X-Ray Power Data File Set 1-5, ASTM Special Technical Publication 48-I (New York: American Society for Testing Materials, 1960).

APPENDIX D

SOME CALCULATIONS OF "d" SPACING FOR CALCITE (CaCO₃ or CaO·CO₂) USING BRAGG'S EQUATION*

$$\lambda = 2d \sin \theta \tag{12}$$

where

Use:

- a) Iron radiation where $k\alpha_1 = 1.93596$ = 1.936Å
- b) Nickel filter w/ 0.021mm thickness

Therefore

 $\lambda = 2d \sin \theta \tag{12}$

Select the reflection angle 2 θ = 29.68° from Figure 18. Therefore 2 θ = 29.68° or θ = 14.84 (sin 14.84° = .256).

$$d = \frac{1.936}{2(.256)} = 3.78\text{\AA}$$

*As referenced from:

L. G. Berry and Brian Mason, <u>Mineralogy Concepts</u>, <u>Description, Determinations</u> (San Francisco and London: W. H. Freeman and Company, 1959).

4.00

20	^I 1 ^{/I} o	Calculated "d" spacing
26.71°	6.9%	4.21Å
29.68°*	100.0%	3.78Å*
31.70°	5.0% <u>+</u>	3.54Å
36.28°	15.0% <u>+</u>	3.11Å
39.65°**	17.6% <u>+</u>	2.68Å**
43.42°***	17.6%	2.62Å***
47.39°	7.5%	2.42Å
47.71°	16.3%	2.40Å
48.75°	17.5%	2.35Å

As per Figure 18 the 20 angles, ratio percent intensity and calculated "d" spacing:

However, as per ASTM Data Sheet for calcium carbonate (Calcite) Appendix C the "d" spacing for the lattices yielding the highest reflection ratio is as per astericked above.

20		^I l ^{/I} o		d	۵d	corrected
*29.68°	-	100%	-	3.04Å	>	3.014Å
**39 .6 5°	-	18% <u>+</u>	-	2.29Å	>	2.28Å
***43.12°	-	18% <u>+</u>	-	2.10Å	>	2.08Å

∆The correction factor is a ratio of the "d" spacing as calculated using copper radiation of 1.54Å and the iron radiation of 1.935Å or

$$\frac{1.54\text{\AA}}{1.935\text{\AA}} = .796$$

$$*3.78\text{\AA} \times .796 = 3.014\text{\AA}$$

$$**2.86\text{\AA} \times .796 = 2.280\text{\AA}$$

$$***2.62\text{\AA} \times .796 = 2.085\text{\AA}$$

APPENDIX E

DATA ON MINERALS FOR USE OF PETROGRAPHIC MICROSCOPE*

The color of crystal is as viewing without any polarizing filters and isolating one single crystal. The color of mass is the same as above except that the crystal is in mass. The color of thin section is as viewed with both polarizing filters in place viewing a single crystal.

Legend:

- Δ Based on various concentrations of ions
- * Apply only to uniaxial mineral group
- † Difference between refractive indexes for uniaxial
 group when n > n mineral considered
- Ø Difference between n and n refractive indexes for biaxial group is the refractive index.

*Based on

Esper S. Larsen and Harry Berman, <u>The Micro-</u> scope Determination of Nonopaque Minerals, Geological Survey Bulletin 848 (2d. ed.; Washington, D.C.: U.S. Department of the Interior, 1964).

L. G. Berry and Brian Mason, <u>Mineralogy Concepts</u>, <u>Description</u>, <u>Determinations</u> (San Francisco and London: W. H. Freeman and Company, 1959).

A. N. Winchel and N. H. Winchel, <u>Elements of</u> <u>Optical Mineralogy</u> (2d. and 4th eds.; New York: John Wiley & Sons, 1927). Calcite - CaCO3 Group--Uniaxial, Negative System--Hexagonal Trigonal Habit--Rhombohedral Color of Crystal--Colorless Color of Mass--Vitreous Color of Thin Section--blue and orange Isotropin--No *Pleochrism--Refractive Indexes: Aragonite - CaCO₂ Group--Biaxial Negative System--Orthorhombic Habit--Acicular or chisel shaped Color of Crystal--Colorless Color of Mass--Transparent to translucent *Color of Thin Section --Isotropic--No *Pleochrism--Refractive Indexes: $n_{x} = \alpha = 1.530$ $n_{z} = \gamma = 1.685$ $n_{y} = \beta = 1.680$ ØBirefringent Index = -.155

```
<u>Apatite</u> - 9CaO·3P<sub>2</sub>O<sub>5</sub>Ca[Fe<sub>2</sub>(OH)<sub>2</sub>, CO<sub>3</sub>·Cl<sub>2</sub>]
     Group--Uniaxial, Negative
     System--Hexagonal
     Habit--Prismatic
    AColor of Crystal--Colorless to Green to Blue to Brown
     Color of Mass--Colorless to Green to Blue to Brown
     Color of Thin Section--Transparent to opaque
     Isotropic--No
    *Pleochrism--
     Refractive Indexes:
          n = w = Ordinary ray = 1.649
n_{\varepsilon}^{O} = \varepsilon = Extraordinary ray = <u>1.644</u>
                                           = -.005
          Birefringent Index
Vivianite - 3FeO.P.O.5.8H.O
     Group--Biaxial, Positive
     System--Monoclinic
     Habit--Prismatic
     Color of Crystal--Colorless to green, blue
     Color of Mass--Black to opaque
     Color of Thin Section--Vitreous
     Isotropic--No
     Pleochrism--Colorless mineral upon powdering
          x = Dark Blue, y = Colorless, z = Olive green
                                                    to brownish
     Refractive Indexes:
         n_{x} = \alpha = n_{x} = \gamma =
                                    1.579
         n'z
                                    1.633
         n
Y
             = β =
                                    1.603
          Birefringent Index = +.054
```



```
Ankerite - CaO·(Mg,Fe)O·2CO,
    Group--Uniaxial, Negative
    System--Hexagonal
             Trigonal
    Habit--Rhombohedral
   △Color of Crystal--Colorless to Dark Brown
    Color in Mass--Colorless to Dark Brown
    Color of Thin Section--Brown to opaque
    Isotropic--No
   *Pleochrism--
    Refractive Indexes:
        n = w = Ordinary ray = 1.698

n_{\varepsilon}^{O} = \varepsilon = Extraordinary ray = 1.518

Birefringent Index = -.18
       †Birefringent Index
Hematite - Fe<sub>2</sub>O<sub>3</sub>
    Group--Uniaxial, Negative
    System--Hexagonal
             Trigonal
    Habit--Rhombohedral
    Color of Crystal--Gray to Black
    Color of Mass--Deep Red
    Color of Thin Section--Opaque except in very thin
         section which is blood red with x = yellowish
         red and z = brownish red
    Isotropic--No
    Pleochrism--Slight to faint
    Refractive Indexes:
        Birefringent Index
```

```
Magnetite - FeO·Fe2O3 or Fe3O4 or Fe(Fe2O4)
Group--Spinel
System--Isometric
Habit--Octahedral
Color of Crystal--Black, opaque
Color of Mass--Black, Opaque
Color of Thin Section--Blue-Black
Isotropic--Yes
Pleochrism--No
Refractive Index
n = 2.42
Siderite - FeCO3
Group--Uniaxial Negative
System--Hexagonal
```

```
Trigonal
```

Habit--Rhombohedral

```
Color of Crystal--Gray, yellowish gray to greenish gray
```

```
Color of Mass--Vitreous
```

```
Color of Thin Section--Translucent to brownish
```

```
Isotropic--No
```

*Pleochrism--

Refractive Indexes:

```
Limonite - Fe<sub>2</sub>O<sub>3</sub> nH<sub>2</sub>O
    Group--Isotropic
    System--Amorphous--No crystal structure
    Habit--Massive to earthy
    Color of Crystal--Yellow Brown-Brown
    Color of Mass--Yellow, Brown or Brownish Black
    Color or Thin Section--Translucent yellow (to brownish)
    Isotropic--Yes
    Pleochrism--No
    Refractive Index:
         n = 2.05 +
         Birefringent Index = 0.04
<u>Goethite</u> - \alpha-FeO·(OH) or Fe<sub>2</sub>O<sub>3</sub>·H<sub>2</sub>O
    Group--Biaxial, Negative
    System--Orthorhombic
    Habit--Fiberous
    Color of Crystal--Yellow to Brown to Black
    Color of Mass--Brown to Black
    Color of Thin Section--Gray
    Isotropic--No
    Pleochrism--Variable with x = clear yellow to brown,
         y = brown yellow, z = orange yellow
    Refractive Indexes:
         n_{x} = \alpha =
n_{x} = \gamma =
n_{y} = \beta =
                                    2.21
                                    2.35
                                    2.35
         Birefringent Index = -0.140
```

```
<u>Lepidocrocite</u> - \gamma-FeO·(OH) or Fe<sub>2</sub>O<sub>3</sub>·H<sub>2</sub>O
    Group--Biaxial, Negative
     System--Orthorhombic
    Habit--Blades
     Color of Crystal--Blood Red
     Color of Mass--Blood Red to Opaque
   *Color of Thin Section--
     Isotropic--No
    Pleochrism--Strong with x = clear yellow, y = red-
         orange, z = orange-red
     Refractive Indexes:
        n = n
n = n
z = n
                                   1.94
             = \alpha =
            = γ =
                                   2.51
         n'
Y
                β =
                                   2.21
```

```
Birefringent Index = -.57
```

APPENDIX F

CRYSTAL GROUP DATA

Since reference has been made to birefringence, in discussing the determination of more than one refractive index, a brief explanation of optical principles and crystalline structure is included. Minerals and chemicals can all be structurally classed in two groups: <u>amorphous</u> and <u>crystalline</u>. The first, meaning "without form," has no regular molecular structure. Glass is an example of such, as is Limonite.

All crystalline substances have definite molecular structure. They can all be classed into six groups or systems which, for simplicity, can be related to their length, breadth, and thickness. These three directions are called crystallographic axes, which are imaginary lines running through the crystal and intersecting at its center.

The first, and simplest, group is known as the <u>isometric</u>, or <u>cubic system</u>; all axes are of equal length and cross each other at right angles. The molecular structure is such that no matter what direction light passes through it, its path is the same, as though the crystal were a sphere. Thus, it has a single refractive

index (also true of amorphous substances) and light will not be polarized.

The second system differs from the cubic in that one crystallographic axis (designated "C" and considered the vertical axis) is either longer or shorter than the other two (designated "A" and "B") which are of equal length and constitute the horizontal axes; all three axes are still at right angles to each other. This is known as the tetragonal system. It can be likened to a cylinder, either longer or shorter than its diameter. The difference in the shape of the crystal reflects the difference in the shape of its molecules. It becomes evident the molecular path offers a different resistance to light crossing the diameter of the cylinder than passing through from top to bottom, i.e., along the vertical or "C" axis. This means that it will possess two refractive indexes, and therefore is uniaxial. These axes are known as n_{ij} (omega) and n_{c} (epsilon). The first, ω or ordinary ray, corresponds to the index for any ray crossing the diameter of the cylinder, since axes A and B are equal. n_c, or extraordinary ray, corresponds to the index for a ray parallel to the "C" axis. The mineral can be either positive or negative depending on whether the length of the cylinder is longer or shorter than the diameter.

The third system is similar to the second except, instead of two equal axes (A and B) at 90° to each other, it has three at 60° forming a hexagonal body instead of a cylindrical one. It is known as the <u>hexagonal (including trigonal) system</u>. It too has two refractive indexes. Both the tetrahedral and hexagonal systems, while birefringent, are optically uniaxial.

The fourth system, <u>orthorhombic</u>, differs from the tetragonal in that the three axes, while at right angles to each other, all have different lengths. Such crystals have three refractive indexes known as n_{α} (alpha), n_{β} (beta), and n_{γ} (gamma). Instead of a single vertical optical axis parallel to the C crystallographic axis, it has two optical axes, located symmetrically on each side of one of the three crystallographic axes. The angle which the two optical axes made with each other varies in different minerals and can amount to anything from near zero to practically 90°. The system is biaxial.

The fifth system, <u>monoclinic</u>, differs from the orthorhombic in that the crystallographic axes no longer cross at right angles, but one of the three is rotated to an angle other than 90° to the other two, which are still at right angles to each other. The system is biaxial.
Finally, for the <u>triclinic system</u>, all the axes are of different lengths and all three crystallographic axes are at other than right angles to the others. This system is complicated as to the positions of the three optical axes and is biaxial.

It is necessary to display the mineral crystal habit and form of the respective compounds that have been discussed in the text. The following information* is to assist in identification of the various compounds.

^{*}As compiled from L. G. Berry and Brian Mason, <u>Mineralogy Concepts</u>, <u>Descriptions</u>, <u>Determinations</u> (San Francisco and London: W. H. Freeman and Company, 1959).



FIGURE 54- CALCITE





FIGURE 55- ARAGONITE

System--Orthorhombic Habit--Acicular or chisel shaped





System--Hexagonal Habit--Prismatic





System--Monoclinic Habit--Prismatic



FIGURE 58- ANKERITE

System--Hexagonal Trigonal Habit--Rhombohedral



FIGURE 59-HEMATITE

System--Hexagonal Trigonal Habit--Rhombohedral



FIGURE 60 - MAGNETITE

System--Isometric Habit--Octahedral



FIGURE 61 - SIDERITE

System--Hexagonal Trigonal Habit--Rhombohedral

Limonite -
$$Fe_2^{O_3} \cdot nH_2^{O_3}$$

System--Amorphous No Crystal Structure (Is sometimes identified with crystalline Goethite)



FIGURE 62 - GOETHITE

System--Orthorhombic Habit--Fibrous



FIGURE 63-LEPIDOCROCITE

System--Orthorhombic Habit--Blades

