PB-736_G-IW1
PB-1141-IW-3

THE QUAKER OATS COMPANY

Deep Injection Well System at the Belle Glade Plant

Permit No. I0-50-5168

VOLUME IV
APPENDICES

August 1983

THE QUAKER OATS COMPANY

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APPENDICES

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Appendix

APPENDIX A

AQUIFER TEST DATA

Appendix A
Aquifer Test Data

Black, Crow & Eidsness, Inc.
Engineers
Gainesville, Florida

IW-4/DMW-1 Pump Test

Project No. GN43201.53

Observation Well No. IW-4/DMW-1

Pumped Well No. IW-4/DMW-1

Location of Well Belle Glade

r = 3.5"

Sheet 1 of 4

Date	Hour	t (min)	t' (min)	t/t'	Depth to water (in feet)	s (unadjusted)	Adjustment Δs	s adjusted	Q (gpm)	Remarks
1/31/78	1240	0			9.20	0			0	Static Level
	1307	0			9.23	0			0	" "
	1315	0			9.21	0			0	" "
	1317	0			--	--			--	Start Pump
	1318	1			23.8	14.59			300	
	1320½	2.5			23.75	14.54			310	
		3.5			23.98	14.77			390	
		5			24.04	14.83			480	Pump Surging
		7			23.37	14.16			400	" "
		10			22.98	13.77			295	" "
		12			22.96	13.75			490	" "
		14			23.00	13.79			285	Adjusting Pump Rate
		16			22.80	13.59			375	Surging
		18			23.45	14.24			350	"
		20			22.74	13.53			365	"
		28			24.69	15.48			374	Adjust Pump Rate
	1348	30			24.97	15.76			250	
		35			24.93	15.72			300	
		40			24.95	15.74			425	
		45			24.96	15.75			405	
		50			24.98	15.77			300	

Black, Crow & Eidsness, Inc.
Engineers
Gainesville, Florida

Project No. GN43201.53

Observation Well No. IW-4/DMW-1

Pumped Well No. IW-4/DMW-1

Location of Well Belle Glade

r =

Date	Hour	t (min)	t' (min)	t/t'	Depth to water (in feet)	s (unadjusted)	Adjustment Δs	s adjusted	Q (gpm)	Remarks
1/31/78	1413	55			24.96	15.75			370	
		60			24.98	15.77			395	
		65			24.98	15.77			356	
		70			24.95	15.74			320	Flowmeter Failed
		72			24.97	15.76			320	
		75			24.96	15.75			320	
		80			24.98	15.77			320	
		85			24.98	15.77			320	
		90			24.97	15.76			320	
		95			24.95	15.74			320	
		100			24.95	15.74			320	
		105			24.97	15.76				
1/31/78	1513	115			24.96	15.75				
1/31/78	1515	0	PUMP	OFF					367	Average Pumping Rate
			BEGIN	RECOVERY						
		0.5			14.80	5.59				
		1.5			11.34	2.13				
		2			8.60	(-0.61)				Water Surging
		2.5			7.86	(-1.35)				In Well
		4			11.57	2.36				
		5			8.93	(-0.28)				

Black, Crow & Eidsness, Inc.
Engineers
Gainesville, Florida

Project No. GN43201.53

Observation Well No. IW-4/DMW-1

Pumped Well No. IW-4/DMW-1

Location of Well Belle Glade

r =

Sheet 3 of 4

Date	Hour	t (min)	t' (min)	t/t'	Depth to water (in feet)	s (unadjusted)	Adjustment Δs	s adjusted	Q (gpm)	Remarks
1/31/78		6			11.15	1.94				Recovery--continued
		7			7.33	(1.88)				Water Level Surging
		8			12.10	2.89				Water Level Surging
		9			11.16	1.95				Water Level Surging
		10			10.13	0.92				Water Level Surging
		11			10.23	1.02				Water Level Surging
		12			11.08	1.87				
		13			10.84	1.63				
		14			10.47	1.26				
		15			10.48	1.27				
		16			10.33	1.12				
		17			10.06	0.85				
		18			10.25	1.04				
	1534	19			10.05	0.84				
		20			10.03	0.82				
		23			10.00	0.79				
		25			9.94	0.73				
		30			9.93	0.72				
		35			9.95	0.44				
		40			9.95	0.74				
		46			9.95	0.74				

ENG-6/14/74-O

Black, Crow & Eidsness, Inc.
Engineers
Gainesville, Florida

Project No. GN43201.53

Observation Well No. IW-4/DMW-1

Pumped Well No. IW-4/DMW-1

Location of Well Belle Glade

r =

Sheet 4 of 4

Date	Hour	t (min)	t' (min)	t/t'	Depth to water (in feet)	s (unadjusted)	Adjustment Δs	s adjusted	Q (gpm)	Remarks
1/31/78	1605	50			9.94	0.73				Recovery--continued
		55			9.94	0.73				
		60			9.93	0.72				
		70			9.93	0.72				
		80			9.92	0.71				
		90			9.92	0.71				
		100			9.93	0.72				
		110			9.93	0.72				End of Test

Black, Crow & Eidsness, Inc.
Engineers
Gainesville, Florida

Project No. GN43201.53

Observation Well No. Annulus; 2,200' Zone

Pumped Well No. DMW-1

Location of Well Belle Glade

r =

Sheet 1 of 2

Date	Hour	t (min)	t' (min)	t/t'	Depth to water (in feet)	s (unadjusted)	Adjustment Δs	s adjusted	Q (gpm)	Remarks
1/31/78	1245	0			3.94				0	Static Condition
	1308	0			4.07					
	1315	0			4.06					Start Pump at 1318 hrs.
	1320	2			4.04	+.02				
		3			4.03	+.03				
		6			4.00	+.04				
		8			4.00	+.04				
		13			3.95	+.11				
		21			3.95	+.11				
	1350	32			3.95	+.11				Adjusting Pump Rate
		41			3.92	+.14				
		48			3.91	+.15				
		52			3.90	+.16				
		57			3.90	+.16				
		62			3.90	+.16				
		67			3.91	+.15				
		77			3.91	+.15				
		82			3.91	+.15				
		91			3.90	+.16				
		97			3.90	+.16				
	1501	103			3.91	+.15				

Black, Crow & Eidsness, Inc.
Engineers
Gainesville, Florida

Project No. GN43201.53

Observation Well No. Annulus; 2,200' Zone

Pumped Well No. DMW-1

Location of Well Belle Glade

r =

Sheet 2 of 2

Date	Hour	t (min)	t' (min)	t/t'	Depth to water (in feet)	s (unadjusted)	Adjustment Δs	s adjusted	Q (gpm)	Remarks
1/31/78	1505	107			3.91	+.15				Pump Off at 1515 hrs.
			START RECOVERY							
		21			4.03	+.03				Recovery
		29			4.04	+.02				
		41			4.08	-.02				
		83			4.07	-.01				
		111			4.07	-.01				

Table A-1
Well IW-3 Pumping Test

Hour	Time Since Pumping Began (min)	Depth to Water (feet from top of casing)	Drawdown (ft)	Pump Rate (gpm)
0836	0.0	7.90	0	0
	0.5	Missed	--	475
0837	1.0	Missed	--	450
	1.5	Missed	--	400
0838	2.0	7.50	-0.40	400
	2.5	Missed	--	375
0839	3.0	8.11	0.21	400
	3.5	Missed	--	450
0840	4.0	8.35	0.45	450
	4.5	8.88	0.98	400
0841	5.0	8.40	0.50	450
0842	6	8.33	0.43	425
0843	7	8.25	0.35	400
0844	8	8.53	0.63	425
0845	9	8.57	0.67	400
0846	10	8.42	0.52	425
0856	20	8.68	0.78	425
0906	30	9.12	1.22	425
0916	40	9.63	1.73	425
0926	50	10.13	2.23	425
0936	60	10.31	2.41	425
0946	70	10.41	2.51	425
0956	80	10.47	2.57	425

Table A-1--Continued

Hour	Time Since Pumping Began (min)	Depth to Water (feet from top of casing)	Drawdown (ft)	Pump Rate (gpm)
1006	90	10.53	2.63	425
1016	100	10.57	2.67	425
1336	300	10.61	2.71	425
1445	360	10.61	2.71	425

Table A-2
Well IW-3 Recovery

Hour	Time Since Pumping Stopped (min)	Depth to Water (feet from top of casing)	Recovery
1445	0	10.61	0
Missed	5	--	--
1447	6	10.40	0.21
1448	7	10.85	--
Missed	8	--	--
1450	9	10.35	0.26
1451	10	10.35	0.26
1452	11	10.05	0.56
1502	20	10.15	0.46
1512	30	10.09	0.52
1522	40	10.09	0.52
1532	50	10.04	0.57
1542	60	10.01	0.60
1552	70	9.77	0.84
1602	80	9.60	1.01
1612	90	9.31	1.30
1622	100	9.18	1.43

APPENDIX B

GEOLOGIC DATA

Table B-1
Geologic Log of Well IW-4/DMW-1

Depth (feet)	Description
0-30	Limestone, coquinoidal, chalky, light tan, sandy. Sand is very fine, rounded quartz.
30-60	Sand, quartz, very fine, rounded. Numerous shell fragments and chalky limestone.
60-80	Shell fragments, no matrix, unaltered to completely altered. Fragments are white, tan to gray. Some rounded sand grains.
80-140	Limestone, grainy to chalky, light tan, sandy, cherty. Numerous altered shell fragments.
140-180	Limestone and sand as above. Some granular limestone in light green silty matrix.
180-220	Silt, sandy, soft, light olive-green. Numerous shell fragments as above.
220-240	Limestone, soft, chalky, light tan, sandy, silty. Numerous fragments of semialtered shell fragments.
240-320	Silt, sandy, light olive-green. Some shell fragments.
320-330	Limestone, silty, sandy, light olive-green. Some shell fragments.
330-340	Sand, quartz, fine. Some fine grains of dark accessory minerals. Some shell fragments.
340-350	Sand, quartz, silty, fine, light olive-green. Some recrystallized shell fragments, subhedral calcite crystals, and small well-rounded black grains of accessory minerals.

Table B-1--Continued

Depth (feet)	Description
350-370	Sand, quartz, silty, mostly fine, light olive-green. Numerous shell fragments; some recrystallized.
370-380	Sand and shell as above. More silty.
380-450	Sand, quartz, very silty, light green. Some shell fragments.
450-570	Sand, quartz, fine, calcareous, phosphatic, light gray. Some Foraminifera and shell fragments.
570-710	Sand, quartz, fine, silty, calcareous, phosphatic, light olive-green. Some Foraminifera and shell fragments. Less sandy and more calcareous with depth.
710-790	Limestone, soft, chalky, cream. Numerous shell fragments. Some free subhedral calcite crystals and rounded chert and phosphorite grains.
790-810	Limestone, soft, chalky to grainy, light gray. Numerous subhedral calcite crystals and rounded chert and phosphorite grains. Few shell fragments.
810-820	Limestone, soft, chalky to grainy, gray. Numerous dark brown, gray to black, rounded chert grains and subhedral calcite crystals.
820-850	Limestone, soft, chalky to grainy, light gray. Some partially altered shell fragments and aggregates to finely crystalline calcite.
Suwannee Limestone	
850-1,060	Limestone, soft, chalky to grainy, tan to light gray, sandy. Some recrystallized and partially altered shell fragments and very fine to coarse, rounded chert grains.

Table B-1--Continued

Depth (feet)	Description
1,060-1,070	Limestone, soft, grainy, light tan. Some Foraminifera. First appearance of *Dictyoconus*.
1,070-1,080	Sample missing.
Avon Park Limestone	
1,080-1,130	Limestone, soft, grainy, Foraminiferal, light tan.
1,130-1,170	Limestone, soft, chalky, white to cream.
1,170-1,260	Limestone, medium soft, chalky, Foraminiferal, cream. Some tan dolomite.
1,260-1,340	Limestone, soft, grainy to chalky, Foraminiferal, light tan.
1,340-1,370	Limestone, soft, grainy to chalky, Foraminiferal, light gray.
1,370-1,390	Sample missing.
1,390-1,650	Limestone, medium soft, grainy to chalky, Foraminiferal, light tan.
Lake City Limestone	
1,650-1,700	Limestone and dolomite. Limestone is medium soft, grainy to chalky, Foraminiferal, light tan. Dolomite is hard microcrystalline to sucrosic, light to medium brown.
1,700-1,720	Limestone, dolomite, medium soft, grainy to chalky, cream, abundant *Dictyoconus*. Some hard, subcrystalline to sucrosic, light brown dolomite.
1,720-1,730	Limestone, dolomite, grainy to chalky, cream. Cuttings very fine.
1,730-1,740	Limestone, dolomite, medium soft, grainy cream. Abundant *Dictyoconus*.

Table B-1--Continued

Depth (feet)	Description
1,740-1,750	Limestone, dolomite, soft grainy to chalky, cream. Cuttings very fine.
1,750-1,760	Limestone, dolomite, medium soft, grainy, cream. Abundant *Dictyoconus*.
1,760-1,770	Limestone, dolomite, grainy to chalky, cream. Abundant *Dictyoconus*. Some hard, subcrystalline to sucrosic, light brown to brown, dolomite.
1,770-1,790	Limestone, dolomite, medium soft, grainy to chalky, cream. Few *Dictyoconus*.
1,790-1,800	Limestone, medium soft, grainy to chalky, cream. Some hard subcrystalline, light brown, dolomite.
1,800-1,810	Limestone, soft, grainy to chalky, cream.
1,810-1,820	Limestone, medium soft, grainy to chalky, cream. Some dolomite, hard subcrystalline to sucrosic, brown to dark brown.
1,820-1,830	Limestone, medium soft, grainy, cream. Few *Dictyoconus*.
1,830-1,840	Limestone, soft, chalky, cream. Some dolomite, very hard, subcrystalline, brown.
1,840-1,850	Limestone, soft, chalky, cream.
1,850-1,860	Limestone, soft, chalky to grainy, cream. Some dolomite, subcrystalline, brown.
1,860-1,900	Dolomite, very hard, subcrystalline to sucrosic, brown to dark brown. Some limestone, soft, chalky to grainy, cream.
1,900-1,910	Dolomite, very hard, subcrystalline, brown.
1,910-1,930	Dolomite, very hard, microcrystalline, light brown.

Table B-1--Continued

Depth (feet)	Description
1,930-1,950	Dolomite, very hard, microcrystalline to subcrystalline, light brown to dark brown.
1,950-1,990	Dolomite, hard, microcrystalline, light brown.
1,990-2,010	Dolomite, hard, microcrystalline to sucrosic, light brown, brown to gray.
2,010-2,020	Dolomite, calcitic, medium hard, granular to chalky, light brown.
2,020-2,030	Dolomite, hard, microcrystalline to sucrosic, light brown, brown to gray.
2,030-2,040	Dolomite, calcitic, hard, microcrystalline, tan.
2,040-2,050	Dolomite, hard, microcrystalline to sucrosic, tan brown to gray. Weathered <u>Dictyoconus</u> present.
2,050-2,060	Dolomite, hard, microcrystalline to sucrosic, tan brown to gray.
2,060-2,090	Dolomite, hard, subcrystalline to sucrosic, tan brown to blue-gray. Some limestone, dolomitic, soft, grainy to chalky.
<u>Oldsmar Limestone</u>	
2,090-2,110	Dolomite as above. Sample is finely divided. Grains show extensive yellow iron stain. Some limestone, medium soft. Many loose well-developed rhombs.
2,110-2,120	Dolomite, hard, microcyrstalline to sucrosic, tan to blue-gray. Many fragments show yellow iron stain.
2,120-2,130	Dolomite, hard, sucrosic, tan.
2,130-2,230	Limestone, dolomitic, medium soft, grainy to chalky, white.
2,230-2,240	Dolomite, medium hard, sucrosic, light brown.

Table B-1--Continued

Depth (feet)	Description
2,240-2,250	Dolomite, medium hard, sucrosic, light brown. Some limestone, soft, chalky, white. Sample finely divided.
2,250-2,260	Dolomite, hard, sucrosic, light brown.
2,260-2,270	Dolomite, medium hard, subcrystalline to sucrosic, light brown. Some limestone, dolomitic, soft, white. Some pieces show both.
2,270-2,280	Dolomite, medium hard to hard, subcrystalline to sucrosic, light brown. Some limestone, dolomitic, soft, grainy to chalky, white.
2,280-2,300	Dolomite, hard, subcrystalline to sucrosic, light brown to dark brown. Some limestone, soft, grainy to chalky, white. Some pieces show both.
2,300-2,390	Dolomite, hard, subcrystalline to sucrosic, light brown.
2,390-2,400	Dolomite and limestone. Sample is finely divided. Dolomite is hard, sucrosic, light brown, mostly single rhombs. Limestone is medium soft, chalky pellets, white.
2,400-2,410	Dolomite, medium hard, sucrosic, tan.
2,410-2,450	Dolomite, medium hard, sucrosic to subcrystalline, tan. Some limestone, chalky, white. Some pieces show both.
2,450-2,460	Dolomite and limestone as above. Less limestone.
2,460-2,470	Dolomite and limestone as above. Less limestone. Dolomite is more subcrystalline.
2,470-2,480	Dolomite, medium hard, sucrosic to subcrystalline, tan. Some limestone, dolomitic, chalky, white.
2,480-2,520	Dolomite, medium hard, microsucrosic, tan.

Table B-1--Continued

Depth (feet)	Description
2,520-2,550	Dolomite, medium hard, microsucrosic to sucrosic, tan. Intermixed with limestone, dolomitic, chalky, white.
2,550-2,560	Limestone, dolomitic, medium hard, chalky, white. Some inclusions of microsucrosic dolomite.
2,560-2,570	Limestone, medium hard, granular to chalky, buff to white.
2,570-2,610	Limestone, dolomitic, medium hard to hard, buff to blue-white. Some fossil casts.
2,610-2,620	Limestone, dolomitic, medium hard, subcrystalline to chalky, blue-white.
2,620-2,630	Limestone, dolomitic, medium hard, tan to light gray. Some limestone, soft, chalky, light tan.
2,630-2,640	Limestone, dolomitic, medium hard to hard, light gray to tan.
2,640-2,660	Limestone, dolomitic, medium hard, light tan to gray. Some dolomite, hard, light brown, crystalline.
2,660-2,670	Limestone, as above. Cuttings finely divided.
2,670-2,680	Limestone, dolomitic, medium soft to medium hard, tan to gray. Some dolomite, hard, crystalline, light brown.
2,680-2,700	Limestone, dolomitic, medium soft, grainy, tan. Some limestone dolomitic, medium hard, gray to tan.
2,700-2,710	Limestone, dolomitic, medium hard, grainy, light tan. Some limestone, dolomitic, hard, light to dark gray. Some dolomite, hard, crystalline, light brown. Few small *Dictyoconus*.
2,710-2,730	Limestone, dolomitic, medium soft, grainy, light tan.

Table B-1--Continued

Depth (feet)	Description
2,730-2,790	Limestone, dolomitic, medium soft, grainy, cream.
2,790-2,800	Dolomite, medium hard, sucrosic, light brown. Some limestone as above.
2,800-2,820	Limestone, dolomitic, medium hard, grainy to subcrystalline, cream. Some dolomite as above.
2,820-2,830	Limestone, medium hard, grainy, light tan. Cuttings very finely divided.
2,830-2,870	Limestone, dolomitic, medium hard, grainy to chalky, cream.
2,870-2,900	Limestone, medium hard, grainy to chalky, cream. Some dolomite, hard, microcrystalline to sucrosic, light to medium brown.
2,900-2,930	Limestone, medium hard, grainy to chalky, cream.
2,930-3,200	Dolomite, very hard, microcrystalline to sucrosic, dark gray to medium brown. Some limestone, as above in parts.

Table B-2
Description of Cores from Well IW-4

Lithology	Depth of Cored Internal (ft)	Core Recovery (ft)	Largest Core Segment (in)	Air Permeability (millidarcys) Horizontal	Vertical	Porosity (Percent)	Remarks
Dolomite, cream to tan, hard microcrystalline, many vugs ≤1 mm diameter, some beds of brown crystalline dolomite 3 mm thick, no fossils.	1,970-1,974	1.7	5				
Dolomite, brown to gray, medium hard, limey at top, very hard microcyrstalline dolomite at bottom, many horizontal vugs, some 10 mm x 30 mm, no fossils.	1,974-1,978	3.5	9				
Dolomite, blue-gray, very hard microcyrstalline, some vugs <1 mm, peaty parting at top, no fossils.	1,978-1,982	4	12	<0.01	<0.01	2.8	
Dolomitic limestone, light brown to gray, very hard, microsucrosic texture, some recrystallization in abundant fossil casts, large cast present 50 mm x 35 mm.	2,100-2,104	3.3	17				
Limestone, cream to white, medium hard, microsucrosic texture, some fine beds of peat, abundant, vugs ≤1 mm diameter, microfossils present.	2,104-2,108	2.8	9	<0.01	<0.01	4.2	
Chalky limestone, white to cream, medium hard, grainy texture, porous, no vugs, microfossils present.	2,108-2,112	3.4	17				

Table B-2--Continued

Lithology	Depth of Cored Internal (ft)	Core Recovery (ft)	Largest Core Segment (in)	Air Permeability (millidarcys) Horizontal	Vertical	Porosity (Percent)	Remarks
Chalky limestone, cream to gray, soft, grainy texture, fine sand present, moderate porosity, microfossils present.	2,112-2,116	4	16	3.5	3.2	19.2	
Limestone, chalky, cream to gray, medium soft, fine sand present, microfossils present.	2,116-2,120	3.5	10	178	--	26.9	
Limestone, cream to yellow, soft, fossiliferous, some casts filled with fine sand and shell mix, solution vugs around shells, microfossils present.	2,215-2,219	2.8	5				
Limestone, cream to yellow, chalky, soft, grainy texture, fossiliferous at bottom, calcite-lined vugs, microfossils present.	2,219-2,223	3.4	4				
Limestone, tan to medium brown, medium hard, fossiliferous, abundant vugs ≤1 mm diameter, some calcite lined, moderately permeable, microfossils present.	2,223-2,227	3.3	4				
Limestone, tan to medium brown, medium hard, some vugs, moldic texture, large gastropod mold present, no microfossils.	2,227-2,228	0.3	3	40	41.3	19.6(H) 19.9(V)	

Table B-2--Continued

Lithology	Depth of Cored Internal (ft)	Core Recovery (ft)	Largest Core Segment (in)	Air Permeability (millidarcys)		Porosity (Percent)	Remarks
				Horizontal	Vertical		
Limestone, chalky, cream to tan, soft to medium hard, porous, moldic texture, microcrystalline in parts, fossils present.	2,404-2,418	3	6	5.4	--	19.4	
Limestone, cream to brown, medium hard, microcrystalline, no vugs, numerous filled molds of fossils, low permeability, horizontal peaty beds <1 mm thick through core.	2,542-2,546	3.4	12	0.31	<0.01	16.9(H) 19.4(V)	Different core segments used for vertical and horizontal porosity determinations.
Limestone, cream to light brown, medium hard, grainy texture, few vugs, fine peaty beds present, some fossils, microfossils present.	2,546-2,550	3.6	26				
Limestone, light brown, medium hard to very hard in dolomitized band through center of core. Lime is moldic, some vugs, moderate porosity, dolomite has low porosity, some vugs.	2,550-2,554	3.3	16				
Limestone, tan to cream, hard, no vugs, low porosity, some fossils, molds filled, some fine peaty beds at bottom.	2,554-2,558	3.6	20				
Dolomite, blue-gray to brown, very hard, microcrystalline, rhombic texture, few vugs, no porosity, no fossils.	2,940-2,946	3	5	<0.01	<0.01	<1	

APPENDIX C

WATER QUALITY DATA

Table C-1
Water Quality Summary from Drilling of Test Holes

Depth (feet)	Conductivity (µmhos/cm)	SO_4 (mg/l)	Cl (mg/l)	Alkalinity (mg/l, as $CaCO_3$)	pH
		Well IW-4/DMW-1			
1,150	2,970	420	751	216	7.50
1,180	2,980	500	715	253	7.75
1,270	3,070	333	788	439	7.42
1,336	3,040	360	788	690	7.51
1,392	3,220	610	861	536	7.68
1,442	3,330	350	885	197	7.45
1,481	2,790	333	873	125	7.49
1,542	2,160	350	848	157	7.58
1,603	5,410	337	1,721	108	7.78
1,664	4,480	353	1,442	189	7.22
1,750	5,380	380	1,842	133	7.68
1,805	5,670	413	1,963	170	7.08
1,840	8,530	387	2,860	320	6.92
1,880	9,420	21	2,969	1,220	6.90
1,921	11,000	24	3,091	2,820	6.92
2,003	13,300	4.2	3,878	2,160	6.90
2,033	12,800	<2.0	3,878	1,850	6.97
2,050	13,400	<2.0	4,060	2,740	6.82
2,086	20,500	2.2	9,332	1,910	6.68
2,100	20,700	3.2	10,363	1,970	6.68
2,130	28,000	48	10,726	1,760	6.87
2,160	28,100	5.2	11,756	1,730	6.90
2,320	42,500	2,480	18,786	203	6.95

Table C-1--Continued

Depth (feet)	Conductivity (μmhos/cm)	SO_4 (mg/l)	Cl (mg/l)	Alkalinity (mg/l, as $CaCO_3$)	pH
2,338	35,200	790	14,786	1,480	6.88
2,368	39,100	1,370	16,726	960	6.92
2,399	39,500	1,980	17,210	582	6.72
2,429	36,900	2,050	15,998	541	7.04
2,458	36,800	2,050	15,635	388	7.11
2,489	37,300	1,680	16,241	790	7.05
2,520	38,600	1,470	16,120	1,030	7.04
2,542	38,300	1,200	16,120	950	7.08
2,554	37,500	2,080	17,332	410	6.95
2,586	39,500	1,980	18,180	440	7.41
2,617	39,600	1,960	18,442	417	7.22
2,649	38,900	1,800	17,210	800	7.03
2,680	40,600	2,120	18,301	490	6.80
2,712	40,500	3,600	18,301	820	6.90
2,744	41,900	2,010	19,392	500	6.87
2,775	41,800	2,220	19,150	406	6.90
2,806	41,700	2,010	19,513	502	7.07
2,838	38,500	2,220	19,877	414	7.12
2,869	41,200	2,018	19,513	430	6.97
2,900	42,900	2,340	20,362	228	7.09
2,932	42,300	2,320	19,756	242	7.10
2,940	43,900	2,480	20,604	196	7.19
2,963	43,600	2,440	20,968	167	7.29
2,995	44,400	2,580	21,452	142	7.47

Table C-1--Continued

Depth (feet)	Conductivity (µmhos/cm)	SO_4 (mg/l)	Cl (mg/l)	Alkalinity (mg/l, as $CaCO_3$)	pH
3,057	48,600	2,680	19,500	220	--
3,088	48,500	2,700	19,600	456	--
3,120	49,000	2,800	19,600	144	--
3,152	48,600	2,800	19,600	224	--
3,200	48,600	2,760	19,600	176	--
		Well IW-3			
1,400	4,800	360	1,010	414	7.6
1,500	4,600	376	910	488	7.4
1,600	4,500	398	920	455	6.59
1,700	4,600	390	905	458	6.58
1,800	5,100	424	1,050	505	6.49
1,900	5,000	448	1,030	469	6.56
1,921	10,000	190	795	2,290	6.4
1,944	10,500	152	825	2,350	6.15
1,955	10,800	142	1,040	3,220	6.05
1,960	10,800	142	930	3,180	6.15
1,975	10,500	98	890	2,260	6.2
2,005	10,250	167	960	2,270	6.25
2,037	11,500	54	1,540	2,140	6.25
2,068	16,000	89	3,630	2,100	7.1
2,130	19,500	198	5,820	2,070	6.9
2,161	21,000	397	5,870	2,030	6.6
2,180	20,000	270	5,920	1,900	6.45
2,225	19,000	326	5,050	4,960	6.7
2,253	19,000	192	5,690	1,810	6.45

Table C1--Continued

Depth (feet)	Conductivity (μmhos/cm)	SO_4 (mg/l)	Cl (mg/l)	Alkalinity (mg/l, as $CaCO_3$)	pH
2,280	41,000	2,550	17,100	Interference	7.6
2,315	40,000	2,300	16,900	Interference	7.65
2,347	40,000	3,700	16,900	Interference	7.35
2,374	42,000	2,940	16,700	Interference	7.4
2,409	43,000	1,060	16,200	900	7.4
2,446	45,000	2,270	17,300	430	7.0
2,470	46,000	2,270	17,800	377	7.05
2,503	47,000	2,310	16,900	292	7.5
2,535	45,000	2,360	16,400	755	7.25
2,566	45,000	2,330	16,400	574	7.1
2,596	45,500	2,140	16,400	592	7.55
2,628	45,500	2,170	16,200	618	7.35
2,658	48,000	2,250	16,600	531	7.25
2,692	49,000	2,360	17,400	354	7.35
2,720	49,000	2,500	17,700	Interference	7.55
2,750	49,000	2,270	17,300	425	7.45
2,782	50,000	2,590	17,800	200	7.9
2,817	48,000	2,460	17,500	330	7.35
2,847	49,500	2,390	17,800	251	7.45
2,875	49,500	2,700	17,600	181	7.5
2,908	49,500	2,560	17,700	190	7.65
2,940	49,000	2,690	17,600	272	7.7
2,972	51,000	2,790	18,600	172	7.65
3,000	55,000	2,830	19,400	140	7.9

Table C1--Continued

Depth (feet)	Conductivity (μmhos/cm)	SO_4 (mg/l)	Cl (mg/l)	Alkalinity (mg/l, as $CaCO_3$)	pH
3,033	52,000	2,900	18,800	223	7.75
3,051	52,000	2,740	19,700	154	8.15
3,090	53,000	2,860	19,300	140	8.05
3,130	54,000	2,720	19,400	162	7.9

Table C-2
Water Quality Data for Well IW-4/DMW-1

	Sample Point and Method at Collection					
Substance or Property	Test Hole to 2,200 ft from Drill Pipe	Test Hole to 2,338 ft from Drill Pipe	Monitor Zone 1,100-1,468 ft Flow	Test Hole 1,100-1,805 ft Pumped	Monitor Zone 2,240-2,281 ft Pumped	Injection Zone 2,989-3,200 ft Pumped
pH	6.95	8.05	8.15	7.25	6.8	7.6
Alkalinity, mg/l as $CaCO_3$	1,050	968	150	153	20	108
Calcium, mg/l	710	675	104	125	480	420
Magnesium, mg/l	805	965	92.5	99	1,200	1,300
Total hardness, mg/l as $CaCO_3$	--	--	--	742	6,100	6,400
Sodium, mg/l	7,600	8,700	500	950	10,200	10,600
Potassium, mg/l	--	--	--	19	360	404
Chloride	11,400	14,000	850	1,425	18,700	19,800
Sulfate	--	1,820	364	430	2,440	2,690
Sulfide	33.2	--	--	7.85	<0.01	<.01
Total phosphorus, mg/l	1.21	0.13	0.04	--	--	--
Iron	12.8	2.72	0.12	3.50	15.6	0.23

Table C-2-Continued

Substance or Property	Sample Point and Method at Collection					
	Test Hole to 2,200 ft from Drill Pipe	Test Hole to 2,338 ft from Drill Pipe	Monitor Zone 1,100-1,468 ft Flow	Test Hole 1,100-1,805 ft Pumped	Monitor Zone 2,240-2,281 ft Pumped	Injection Zone 2,989-3,200 ft Pumped
Nitrogen total, as N, mg/l	--	--	--	>0.01	--	0.05
$NO_3 + NO_2$	0.26	<0.01	0.22	--	--	0.05
TKN, mg/l	7.28	5.11	0.56	--	--	<0.02
COD,mg/l	2,070	935	93.4	--	--	1,400
TOC, mg/l	335	230	37.5	--	--	170
Color, APHA units	--	--	1	15	0	0
Conductivity, µmhos/cm	--	--	--	5,100	47,800	49,900
Dissolved solids, mg/l	--	--	--	3,690	--	--

APPENDIX D

AREA OF REVIEW DATA

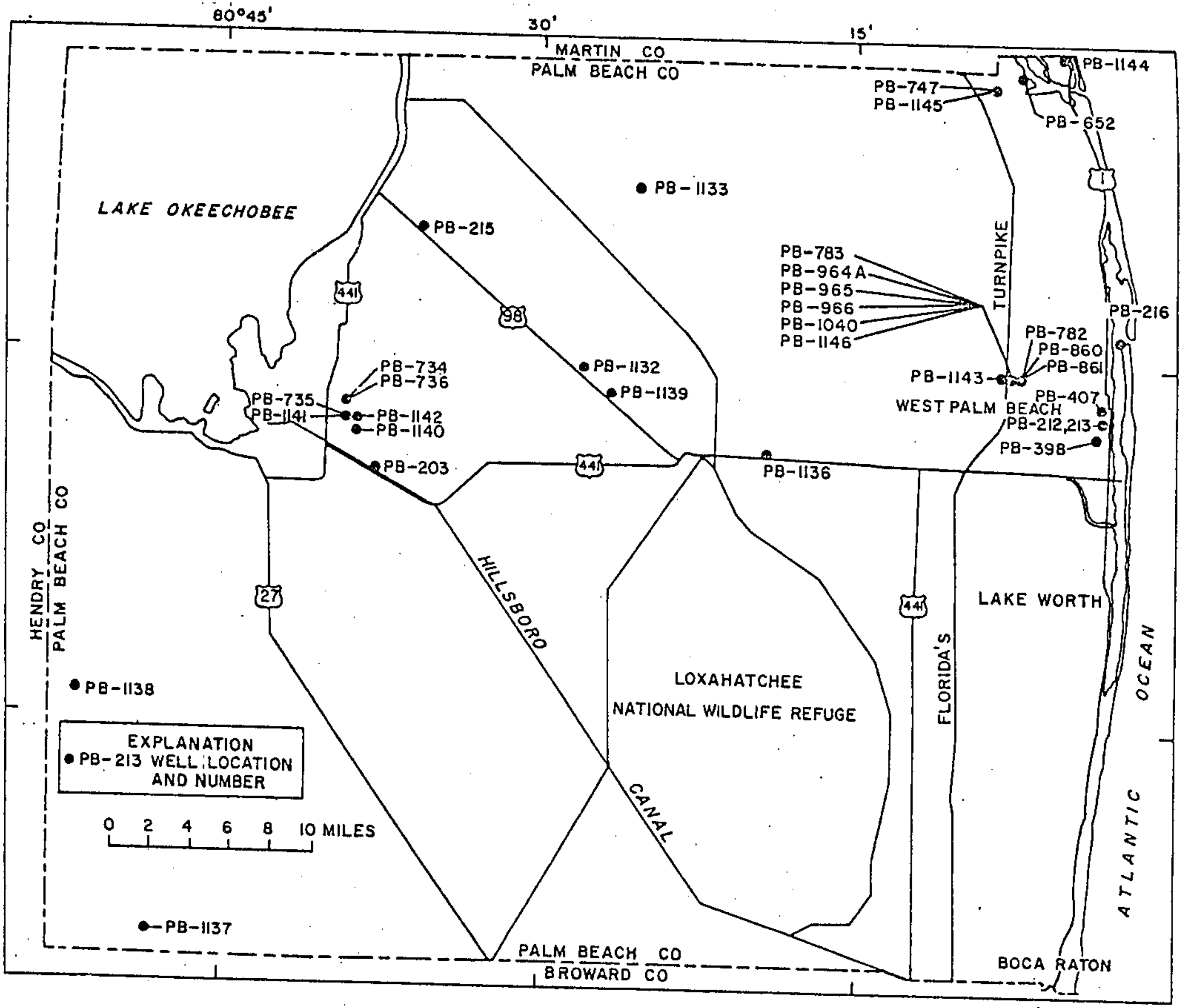


Figure 18.--Palm Beach County showing locations of deep wells.

Table 1.--Site identification and location data for selected deep wells in South Florida (continued)

Local well number	Other well identifier	Identification number	County code	Latitude	Longitude	Land net location	Well owner
MO - 133	W6118 S -1447	251913080165001	87	251914	801648	S07 T59S R41E	Ocean Reef Country Club
MO - 134	S -1447A	251913080165002	87	251914	801648	S07 T59S R41E	Ocean Reef Country Club
MO - 135	----------	251913080165003	87	251914	801648	S07 T59S R41E	Ocean Reef Country Club
MO - 136	----------	251913080165004	87	251914	801648	S07 T59S R41E	Ocean Reef Country Club
MO - 137	W12740	251913080165005	87	251914	801648	S07 T59S R41E	Ocean Reef Country Club
MO - 138	S - 396 W445	254247080574801	87	254247	805748	S06 T55S R34E	Peninsular Oil
MO - 139	W3011 permit 148 S -1259	251704080172901	87	251704	801729	S24 T59S R40E	Sinclair Oil
MO - 140	W5094	243659082022101	87	243659	820221	S-- T67S R22E	Gulf Oil
MO - 141	permit 564	254548080593201	87	254548	805932	S11 T54S R33E	Reynolds
MO - 142	permit 296 W6148	242610082293701	87	242610	822937	------------	Gulf-CALCO
MO - 143	permit 284 W5327	242700082214501	87	242700	822145	------------	Gulf-CALCO
MO - 144	W3174 permit 290	242517082360201	87	242517	823602	------------	Gulf-CALCO
MO - 145	permit 415	254548080550901	87	254548	805509	S15 T54S R34E	Triton
MO - 146	permit 754	254716080532801	87	254716	805328	S11 T54S R34E	Clinton
MW - 1	----------	262651082070301	71	262651	820703	S21 T46S R22E	Island Water Authority
NP - 100	W7363	252255080361101	25	252255	803611	S14 T58S R37E	USGS
PB - 203	S - 353	264000080375001	99	264002	803758	S03 T44S R37E	University of Florida
PB - 212	S - 382	264552080030601	99	264244	800323	S21 T43S R43E	Fla. Power & Light
PB - 213	S - 383	264552080030602	99	264244	800323	S21 T43S R43E	Fla. Power & Light
PB - 215	field 11 S - 399	265008080353801	99	265008	803542	S12 T42S R37E	U S Sugar
PB - 216	S - 400	264618080024501	99	264618	800545	S34 T42S R43E	U S Coast Guard
PB - 398	field 1175 PB- 439	264212080035001	99	264212	800350	S28 T43S R43E	City Ice
PB - 407	S -1184	264259080032001	99	264259	800320	S21 T43S R43E	Royal Palm Ice
PB - 652	----------	265642080072301	99	265642	800723	S35 T40S R42E	Wilson
PB - 734	1-shallow SMWP	264200080390001	99	264228	803905	S28 T43S R37E	Quaker Oats
PB - 735	2-deep	264200080390002	99	264222	803857	S28 T43S R37E	Quaker Oats

Table 1.--Site identification and location data for selected deep wells in South Florida (continued)

Local well number	Other well identifier	Identification number	County code	Latitude	Longitude	Land net location	Well owner
PB - 736	PB - 505 PB - 600 PB - 493 IW1 PB - 546	264227080390701	99	264229	803905	S28 T43S R37E	Quaker Oats
PB - 747	PB - 733 injection	265604080082601	99	265604	800826	S03 T41S R42E	SFWMD
PB - 782	test well	264421080073201	99	264421	800732	S11 T43S R42E	West Palm Beach
PB - 783	monitor	264419080073301	99	264420	800738	S11 T43S R42E	West Palm Beach
PB - 860	test monitor	264421080073204	99	264421	800732	S11 T43S R42E	West Palm Beach
PB - 861	test monitor	264421080073205	99	264421	800732	S11 T43S R42E	West Palm Beach
PB - 964A	DW1A W13012	264416080074401	99	264416	800745	S11 T43S R42E	West Palm Beach
PB - 965	W13690 DW2	264413080074801	99	264412	800748	S11 T43S R42E	West Palm Beach
PB - 966	DW3 W13691	264416080075001	99	264416	800750	S11 T43S R42E	West Palm Beach
PB -1040	DW4	264412080075301	99	264412	800753	S11 T44S R42E	West Palm Beach
PB -1132	----------	264438080281101	99	264438	802811	S08 T43S R39E	Hughes & Hughes
PB -1133	permit 235	265146080253501	99	265152	802513	S34 T41S R39E	Amerada
PB -1136	W1471 permit 47	264056080190901	99	264056	801909	S02 T48S R35E	Humble Oil
PB -1137	permit 265 W4661	262039080484201	99	262013	804841	S02 T48S R35E	Humble Oil
PB -1138	permit 740	263039080515101	99	263003	805227	S07 T46S R35E	Shell Oil
PB -1139	W8322 permit 385	264313080265801	99	264322	802652	S21 T43S R39E	Amerada
PB -1140	SMW2	264148080384001	99	264148	803840	S28 T43S R37E	Quaker Oats
PB -1141	IW3	264224080390401	99	264224	803904	S28 T43S R37E	Quaker Oats
PB -1142	IW4	264220080384801	99	264220	803848	S28 T43S R37E	Quaker Oats
PB -1143	DW5	264417080075601	99	264417	800756	S11 T43S R42E	West Palm Beach
PB -1144	PBF1	265800080051301	99	265811	800513	S30 T40S R43E	Broadview Condominiums
PB -1145	monitor	265608080082301	99	265608	800823	S03 T41S R42E	SFWMD
PB -1146	DW1	264416080074502	99	264416	800745	S11 T43S R42E	West Palm Beach
S - 125	----------	254717080113001	25	254717	801143	S36 T53S R41E	City Ice
S - 142	WGI70	254646080113501	25	254647	801143	S37 T54S R41E	Fla. Power & Light
S - 144	WGI71	254440080125001	25	254447	801252	S40 T54S R41E	Deering

CH2M HILL
engineers
planners
economists
scientists

August 21, 1981

FC43202.A2

Mr. Robert V. Raessler
The Quaker Oats Company
Belle Glade, Florida

Dear Bob:

Subject: Plugging Wells IW-1, IW-2, and SMW-1

The attached report describes the permanent plugging of the above-referenced wells at the Belle Glade plant.

The wells were plugged essentially in accordance with the specifications for this work, with minor modifications to accommodate field conditions.

The only deviation occurred in IW-1, where safety considerations dictated a change in plugging procedure. However, the changes did not affect the outcome of the plugging operation or the integrity of the resulting plugging of the well.

Please review the attached, and if you have any questions or comments, please call.

Very truly yours,

C. Ross Sproul

67/a
Enclosure
xc: Jose Calas
Ron LaRovier
Frank Reynolds
Dave Snyder

Gainesville Office
7201 N.W. 11th Place, P.O. Box 1647, Gainesville, Florida 32602 904/377-2442
In the Southeast, CH2M HILL was formerly known as Black, Crow and Eidsness

REPORT ON THE PLUGGING OF IW-1, IW-2, AND SMW-1

This report documents the permanent plugging of two injection wells and one monitor well at the Quaker Oats plant at Belle Glade, Florida. These wells, designated IW-1, IW-2, and SMW-1, were the original wells of the disposal system which became operational in the latter part of 1966.

Since the completion of the replacement injection Well IW-3 in 1977, Well IW-1 has been inactive. Well SMW-1 was in use during this period as a monitoring well, and Well IW-2 was the source of water for the backflow study.

Plugging of these wells was determined to be advisable due to the presence of high concentrations of hydrogen sulfide gas in the wells and suspected deteriorated condition of the liners and casings.

The wells were plugged in accordance with the "Project Manual for Abandoning Two Waste Disposal Wells at The Quaker Oats Company, Belle Glade, Florida." The technical specifications for well plugging were prepared by CH2M HILL. The specifications were reviewed and approved by the appropriate regulatory agencies. The plugging of SMW-1 was added to the work after the project started, also with the concurrence of these agencies.

Figures 1, 2, and 3 of this report show the present construction and plugging of the wells.

PRELIMINARY ACTIVITIES

Prior to work on the wells, ESSE International, specialists in H_2S gas safety, was retained by The Quaker Oats Company to establish a safety program for personnel working in the area of the wells. ESSE personnel remained onsite throughout the project to act as safety consultants.

In addition to personal safety equipment, a liquid-gas separator and its associated flare stack was installed at each well location during each plugging operation to deal with any gas-laden fluid flows. All fluid wastes were piped to the active injection Well IW-3 for disposal. No fluids or gases were released during the project.

WELL PLUGGING OPERATIONS

Plugging of the wells proceeded generally as outlined in the specifications. Any deviations from the specified procedure are discussed below. The quantities of cement and other materials used are summarized in Table 1 and the placement of the materials noted on Figures 1, 2, and 3. Since the plugging of IW-2 and SMW-1 proceeded in a straightforward manner, with no significant deviations from the specifications, the description of those operations is brief. The only deviations occurred during the plugging of IW-1, as described later in this report.

IW-2

The plugging of this well was accomplished by the direct injection of cement into the open hole and liner. The cement was preceded by a gelling agent (Halliburton Flow-Check®) to aid in plugging the cavernous injection zone.

Cement was placed in the annular space outside the liner and in the remainder of the liner using grout pipe. The operation proceeded smoothly without incident. Pressure tests conducted on the liner after the initial cementing stage indicated a sound plug in the liner. Pressure tests on the annulus indicated no communication to the aquifer.

SMW-1

Prior to plugging the well, geophysical logs were run on the well. The log suite consisted of a natural gamma ray, static temperature, and caliper. No logs had been run on this well prior to this time.

The plugging procedure agreed upon by the regulatory agencies and Quaker Oats called for the initial injection of cement through grout pipe placed to near the bottom of the borehole. The lower portion of this grout pipe would be left cemented in the hole, with the upper part retrieved by separating it at one of two left-hand thread joints. However, neither one of these joints (placed at 606 feet and 854 feet below the surface) would unscrew following placement of the first cement stage up to 696 feet. The pipe finally separated 63 feet below the surface, leaving 1,260 feet of 2" pipe in the well. Cement was tagged in the annulus between the 6-inch hole and the grout pipe at a depth of 696 feet below the surface. A second string of tubing was inserted in the annulus to a depth of 684 feet, and cementing was completed, in three stages, to the suface.

A 1-inch grout pipe was used to cement the original 2-inch grout pipe, from the bottom up to the surface. Return fluids from the well were passed through the liquid-gas separator and piped to IW-3 for disposal. The presence of gas in the fluid was not observed, and no fluid spills occurred during the operation.

IW-1

The first step in the plugging of IW-1 was the pumping of 3,360 gallons of heavy drilling mud into the annulus, which was under artesian pressure of approximately 20 psi. The quantity and density of the mud was theoretically sufficient to depress the fluid level in the annulus to 30 feet below the surface (it was not possible to measure directly the fluid level at this stage).

The liner of IW-1 was then cemented completely to the surface according to the procedure in the specifications. The initial stage of cement, which was preceded by the gelling agent described above, was injected directly into the liner filling the open hole and liner up to a depth of 162 feet. The remainder of the liner was then filled to the surface by injecting the cement through a grout pipe installed in the liner..

Immediately following the liner cementing, approximately 350 gallons of water was pumped into the annulus to reconfirm its connection to the formation.

The original intent was to plug the annulus via a grout pipe. However, an evaluation of the relative risks and benefits of opening up the annulus to allow installing grout pipe versus injecting cement directly into the annulus from the surface resulted in a concensus of opinion between Quaker Oats personnel, the safety consultants (ESSE), and CH2M HILL that cement placement from the surface would be safer and would result in at least as good a seal as could be achieved by placement through grout pipe. The reasons for this conclusion were as follows:

1. There was no way to maintain positive control of the annulus, which had been under artesian pressure, during running-in of the grout pipe.

2. In any case, the grout pipe could not be set below about 626 feet, where a 12-inch casing is telescoped inside the 16-inch casing.

3. It had been confirmed, both via placement of the mud used to kill the annulus, and the water which followed, that the annulus would take fluid.

Subsequently, cement was placed in the annulus through a 4-inch access pipe. After a total of 180 cubic feet of API Class H cement with 2 percent bentonite had been pumped in, the pressure at the well head rose rapidly, reaching 400 psi before pumping could be stopped. Some upward movement (5 to 6 inches) of the liner occurred simultaneously with the pressure rise in the annulus. The annulus was then shut in and the cement allowed to set.

The amount of cement pumped was sufficient to produce approximately 210 feet of fill in the 8-inch by 16-inch annulus. The quantity of heavy fluid pumped prior to the cementing is sufficient to fill approximately 720 feet of the annulus. The character of the material in the annulus below about 950 feet cannot be conclusively known. However, based on the following observations, we believe that at least part of this interval contains cement, the presence of which was responsible for the "squeeze" which occurred during annulus cementing:

1. The upward movement of the liner which accompanied the squeeze indicates that the liner had probably parted near the surface in the section where the cement had not set. Some cement may have entered the annulus at this depth if a partial break existed before cementing. This material probably helped to bridge off the annulus' path of communication with the outside, resulting in the pressurization observed during the cementing.

2. One of the two tieback packers near the bottom of the 12-inch casing is believed to be damaged or unseated (see Figure 1A). It is likely that some of the cement placed in the liner entered the zone between 1,500 and 1,600 feet during the cementing of the liner. The presence of such material in the lower part of the well probably contributed further to the premature squeezing off of the annulus during cementing.

In our opinion the three wells were plugged in a manner which will ensure that upward migration of waste and waste products will not occur.

67b

SUMMARY OF PLUGGING MATERIAL
IW-1, IW-2, AND SMW-1

IW-1

LINER

STAGE 1

535 cu ft Haliburton Flow Check (gel)
1,000 cu ft API Class H "thixotropic" cement

STAGE 2

67 cu ft API Class H with 2 percent bentonite

ANNULUS

180 cu ft API Class H with 2 percent bentonite

IW-2

LINER

STAGE 1

535 cu ft Haliburton Flow Check (gel)
1,500 cu ft API Class H "thixotropic" cement

STAGE 2

56 cu ft API Class H with 2 percent bentonite

ANNULUS

STAGE 1

247 cu ft API Class H with 2 percent bentonite

STAGE 2

103 cu ft API Class H with 2 percent bentonite

SMW-1

STAGE 1

170 cu ft API Class H "thixotropic" cement

STAGE 2

50 cu ft API Class H with 2 percent bentonite

STAGE 3

30 cu ft API Class H with 2 percent bentonite

STAGE 4

20 cu ft API Class H with 2 percent bentonite (inside 2-inch tubing)

STAGE 5

40 cu ft API Class H with 2 percent bentonite

NOTE: API Class H "thixotropic" cement is formulated as follows:

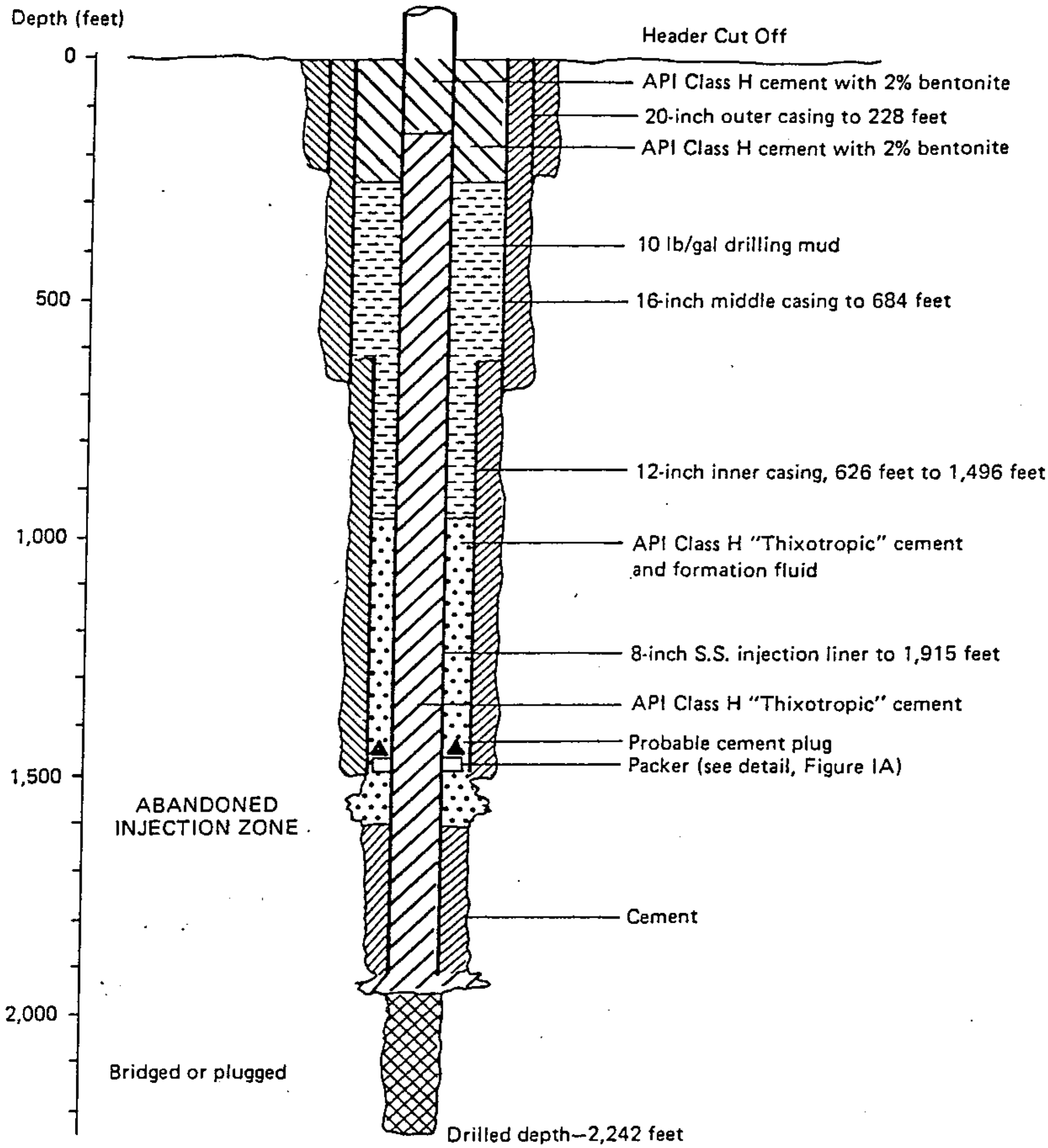
1. API Class H cement
2. 25 percent bentonite
3. 25 pounds per sack gilsonite
4. 10 pounds per sack Calseal (gypsum cement)
5. 4 percent calcium chloride

Slurry weight: 11.7 pounds per gallons

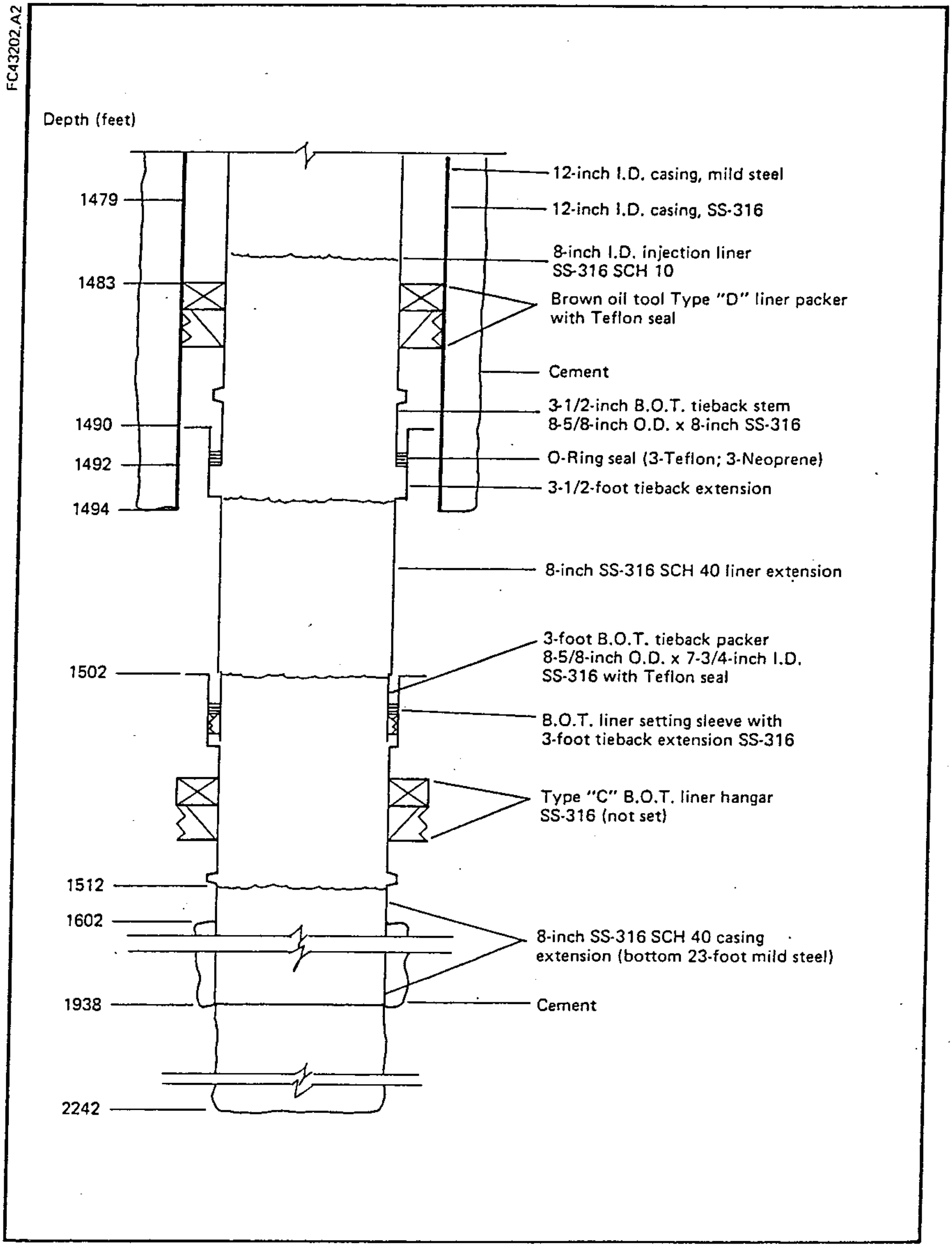
Yield: 3.46 cu ft per sack

67/b

FC43202.A2

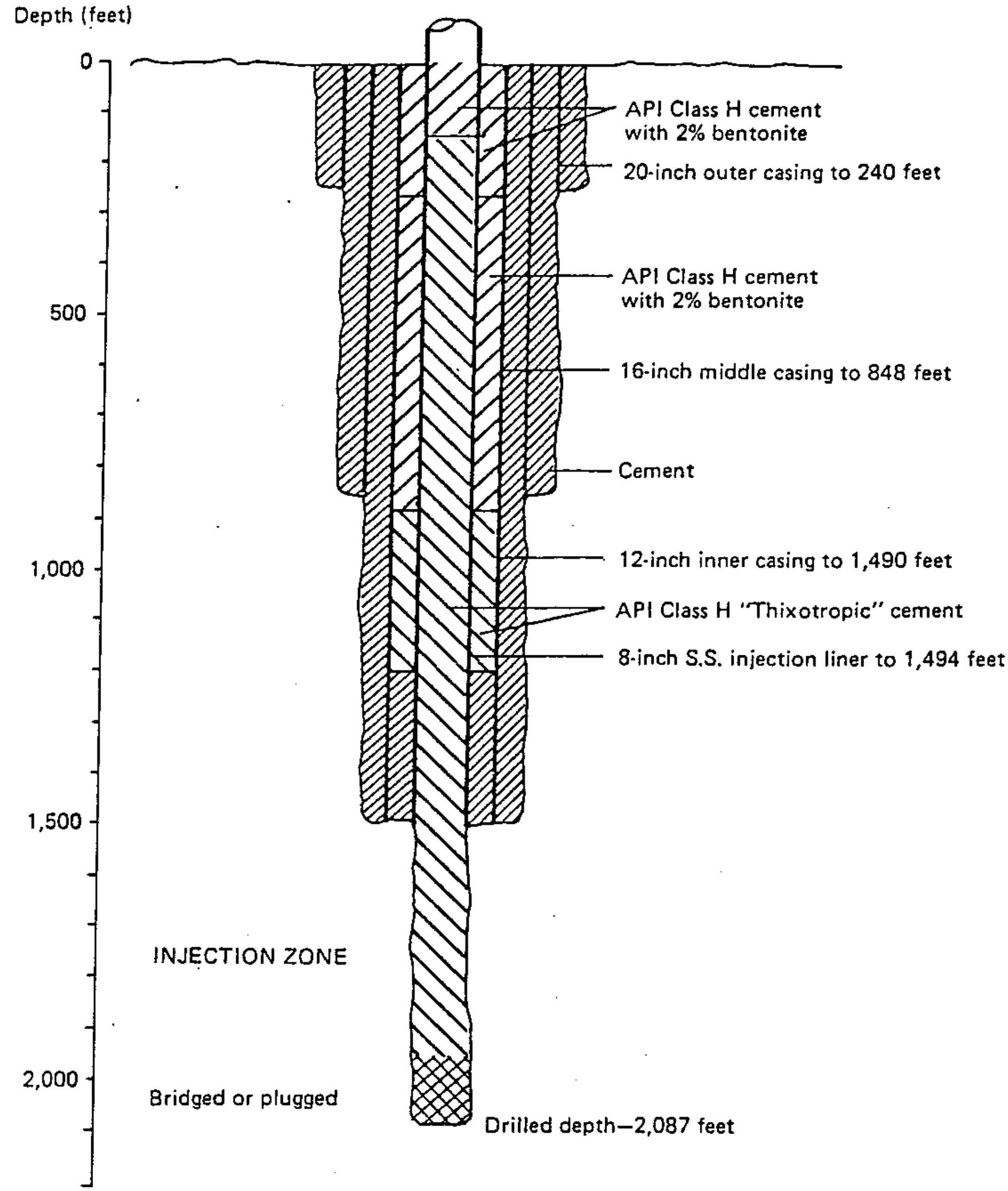


DRAWING NO. 1. WELL PLUGGING DIAGRAM—IW-1.

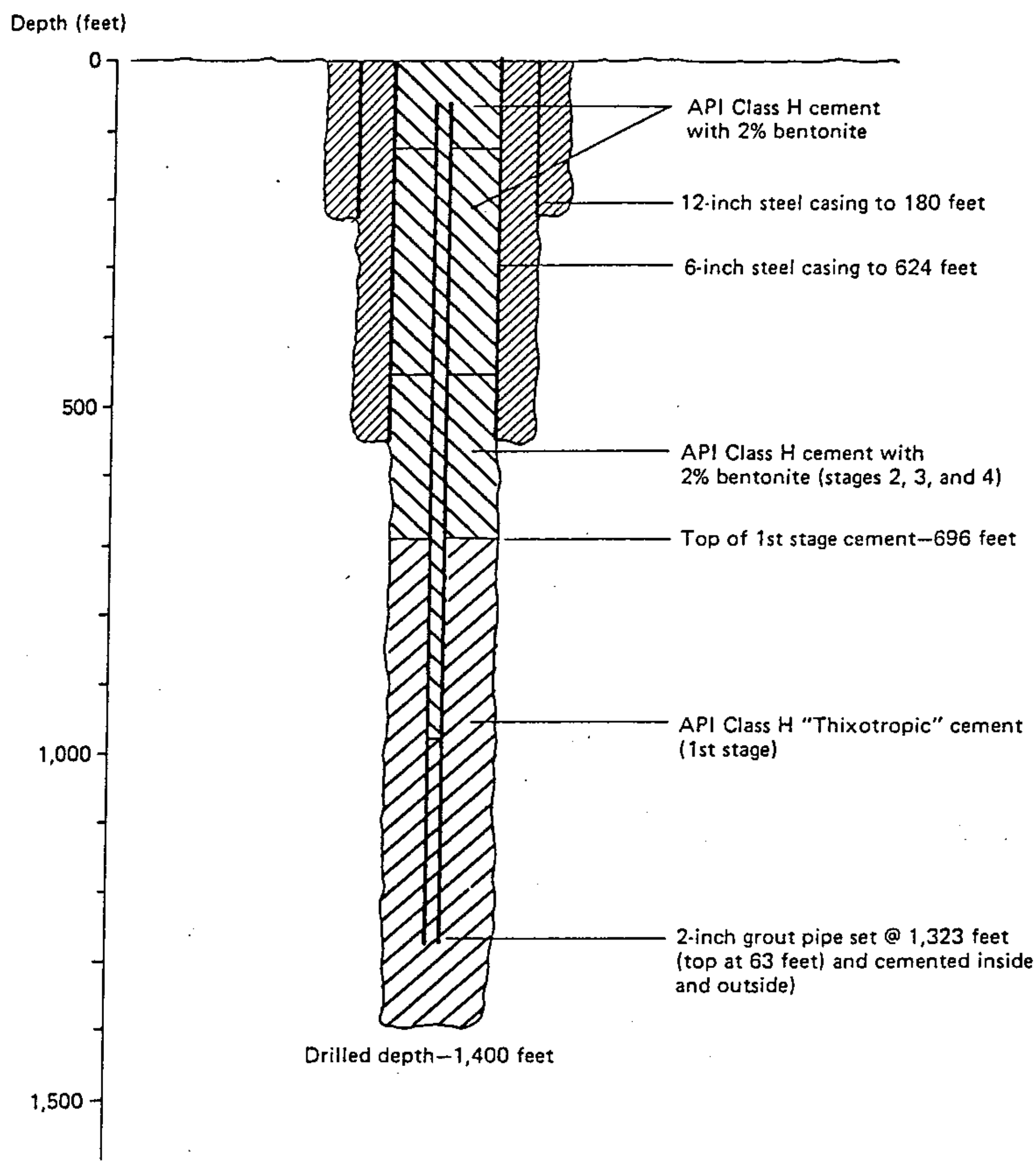


DRAWING NO. 1A. DETAIL OF CASING AND LINER CONNECTIONS.

FC43202.A2



DRAWING NO. 2. WELL PLUGGING DIAGRAM—IW-2.



DRAWING NO. 3. WELL PLUGGING DIAGRAM—SMW-1.

Appendix E
LABORATORY PROCEDURES AND METHODOLOGY

Standard Methods
For the Examination of Water and Wastewater

FOURTEENTH EDITION

Prepared and published jointly by:
American Public Health Association
American Water Works Association
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508 OXYGEN DEMAND (CHEMICAL)

The chemical oxygen demand (COD) determination is a measure of the oxygen equivalent of that portion of the organic matter in a sample that is susceptible to oxidation by a strong chemical oxidant. It is an important, rapidly measured parameter for stream and industrial waste studies and control of waste treatment plants. However, in the absence of a catalyst the method fails to include some organic compounds (such as acetic acid) that are biologically available to the stream organisms, while including some biological compounds (such as cellulose) that are not a part of the immediate biochemical load on the oxygen assets of the receiving water. The carbonaceous portion of nitrogenous compounds can be determined, but there is no reduction of the dichromate by ammonia in a waste or by ammonia liberated from the proteinaceous matter. With certain wastes containing toxic substances, this test or a total organic carbon determination may be the only method for determining the organic load. Where wastes contain only readily available organic bacterial food and no toxic matter, the results can be used to approximate the ultimate carbonaceous BOD values.

The use of exactly the same technic each time is important because only a part of the organic matter is included, the proportion depending on the chemical oxidant used, the structure of the organic compounds, and the manipulative procedure.

The dichromate reflux method has been selected for the COD determination because it has advantages over other oxidants in oxidizability, applicability to a wide variety of samples, and ease of manipulation. The test will find its major usefulness for waste control purposes after many values have been obtained and correlated with some other important parameter or parameters.

1. General Discussion

a. Principle: Most types of organic matter are destroyed by a boiling mixture of chromic and sulfuric acids. A sample is refluxed with known amounts of potassium dichromate and sulfuric acid and the excess dichromate is titrated with ferrous ammonium sulfate. The amount of oxidizable organic matter, measured as oxygen equivalent, is proportional to the potassium dichromate consumed.

b. Interference and inadequacies: Straight-chain aliphatic compounds, aromatic hydrocarbons, and pyridine are not oxidized to any appreciable extent, although this method gives more nearly complete oxidation than the permanganate method. The straight-chain compounds are oxidized more effectively when silver sulfate is added as a catalyst; however, silver sulfate reacts with chloride, bromide, or iodide to produce precipitates that are oxidized only partially by the procedure. There is no advantage in using the catalyst in the oxidation of aromatic hydrocarbons, but it is essential to the oxidation of straight-chain alcohols and acids.

The oxidation and other difficulties caused by the presence of chloride may be overcome by using a complexing technic for the elimination of chloride. This is accomplished by adding mercuric sulfate to the samples before refluxing. This ties up the chloride ion as a soluble mercuric chloride complex and greatly reduces its ability to react further.

Nitrite exerts a COD of 1.1 mg/mg N. Since concentrations of nitrite in polluted waters rarely exceed 1 or 2 mg/l the interference is considered insignificant and usually is ignored. To eliminate a significant interference due to nitrite, add 10 mg sulfamic acid/mg nitrite N in the refluxing flask. Add the sulfamic acid to the standard dichromate solution, since it must be included in the distilled water blank.

c. Application: The method can be used to determine COD values of 50 mg/l or more with the concentrated dichromate. With the dilute dichromate, values below 10 mg/l are less accurate but indicate the order of magnitude.

d. Sampling and storage: Test unstable samples without delay. Homogenize samples containing settleable solids in a blender to permit representative sampling. If there is to be a delay before analysis, preserve the sample by acidification with sulfuric acid. Make initial dilutions in volumetric flasks for wastes containing a high COD in order to reduce the error inherent in measuring small volumes.

2. Apparatus

a. Reflux apparatus, consisting of 500-ml or 250-ml erlenmeyer flasks with ground-glass 24/40 neck* and 300-mm jacket Liebig, West, or equivalent condensers† with 24/40 ground-glass joint, and a hot plate having suf-

*Corning 5000 or equivalent.
†Corning 2360, 91548, or equivalent.

ficient power to produce at least 1.4 W/cm² (9 W/in.²) of heating surface, or equivalent, to insure adequate boiling of the contents of the refluxing flask.

3. Reagents

a. Standard potassium dichromate solution, 0.250*N:* Dissolve 12.259 g $K_2Cr_2O_7$, primary standard grade, previously dried at 103 C for 2 hr, in distilled water and dilute to 1,000 ml.

b. Sulfuric acid reagent: conc H_2SO_4 containing 22 g silver sulfate, Ag_2SO_4, per 4 kg (9-lb) bottle (1 to 2 days required for dissolution).

c. Standard ferrous ammonium sulfate titrant, 0.01*N:* Dissolve 39 g $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ in distilled water. Add 20 ml conc H_2SO_4, cool, and dilute to 1,000 ml. Standardize this solution daily against the standard $K_2Cr_2O_7$ solution.

Standardization—Dilute 10.0 ml standard $K_2Cr_2O_7$ solution to about 100 ml. Add 30 ml conc H_2SO_4 and cool. Titrate with the ferrous ammonium sulfate titrant, using 2 to 3 drops (0.10 to 0.15 ml) ferroin indicator.

$$\text{Normality} = \frac{\text{ml } K_2Cr_2O_7 \times 0.25}{\text{ml } Fe(NH_4)_2(SO_4)_2}$$

d. Ferroin indicator solution: Dissolve 1.485 g 1,10-phenanthroline monohydrate, together with 695 mg $FeSO_4 \cdot 7H_2O$ in water and dilute to 100 ml. This indicator solution may be purchased already prepared.‡

e. Mercuric sulfate, $HgSO_4$, crystals.

f. Sulfamic acid: Required only if the interference of nitrites is to be eliminated (see ¶ 1*b* above).

‡G.F. Smith Chemical Company, Columbus, Ohio.

4. Procedure

a. Treatment of samples with COD values over 50 mg/l:

Place 50.0 ml sample or a smaller sample portion diluted to 50.0 ml in the 500-ml refluxing flask. Add 1 g $HgSO_4$,§ several boiling chips, and 5.0 ml H_2SO_4. Add the H_2SO_4 very slowly, with mixing to dissolve the $HgSO_4$. Cool while mixing to avoid possible loss of volatile materials in the sample. Add 25.0 ml 0.250 *N* $K_2Cr_2O_7$ solution and again mix. Attach the flask to the condenser and start the cooling water. Add the remaining H_2SO_4 (70 ml) through the open end of the condenser. Continue swirling and mixing while the acid is being added. Mix the reflux mixture thoroughly before heat is applied; if this is not done, local heating occurs in the bottom of the flask and the mixture may be blown out of the condenser.

Alternatively, use sample volumes from 10.0 ml to 50.0 ml and adjust volumes, weights, and normalities accordingly. Consult Table 508:I below for examples of applicable ratios. Maintain these ratios and follow the complete procedure as outlined above.

Use 1 g $HgSO_4$ with a 50.0-ml sample to complex 100 mg chloride (2,000 mg/l). For smaller volume samples use less $HgSO_4$, according to the chloride concentration; maintain a 10:1 ratio of $HgSO_4$:Cl. A slight precipitate does not affect the determination adversely. As a general rule, COD cannot be measured accurately in samples containing more than 2,000 mg/l chloride.

§$HgSO_4$ may be measured conveniently by volume, using a reagent spoon (e.g., Hach Company No. 638 or equivalent).

TABLE 508:I. REAGENT QUANTITIES AND NORMALITIES FOR VARIOUS SAMPLE SIZES

Sample Size *ml*	0.25*N* Standard Dichromate *ml*	Conc H_2SO_4 with Ag_2SO_4 *ml*	$HgSO_4$ *g*	Normality of $Fe(NH_4)_2(SO_4)_2$	Final Volume Before Titration *ml*
10.0	5.0	15	0.2	0.05	70
20.0	10.0	30	0.4	0.10	140
30.0	15.0	45	0.6	0.15	210
40.0	20.0	60	0.8	0.20	280
50.0	25.0	75	1.0	0.25	350

Reflux the mixture for 2 hr or use a shorter period for particular wastes if it has been found to give maximum COD. Cover the open end of the condenser with a small beaker to prevent foreign material from entering the refluxing mixture. Cool and wash down the condenser with distilled water.

Dilute the mixture to about twice its volume with distilled water, cool to room temperature, and titrate the excess dichromate with standard ferrous ammonium sulfate, using ferroin indicator. Generally, use 2 to 3 drops (0.10 to 0.15 ml) indicator. Although the quantity of ferroin is not critical, use a constant volume. Take as the end point the sharp color change from blue-green to reddish brown, even though the blue-green may reappear within minutes.

Reflux in the same manner a blank consisting of distilled water, equal in volume to that of the sample, together with the reagents.

b. Alternate procedure for low-COD samples:

Follow the standard procedure, ¶ 4*a*, with two exceptions: (i) Use 0.025*N* standard $K_2Cr_2O_7$, and (ii) back-titrate with 0.10*N* ferrous ammonium sulfate. Exercise extreme care with this procedure because even a trace of organic matter in the glassware or the atmosphere may cause a gross error. If a further increase in sensitivity is required, reduce a larger sample to 20 ml (final total volume 60 ml) by boiling in the refluxing flask on a hot plate in the presence of all reagents. Carry a blank through the same procedure. This technic has the advantage of concentrating the sample without significant loss of easily digested volatile materials. Hard-to-digest volatile materials such as volatile acids are lost, but an improvement is gained over ordinary evaporative concentration methods. As sample volume increases, chloride concentration also increases and more $HgSO_4$ is required.

c. Determination of standard solution: Evaluate the technic and quality of reagents with a standard solution of either glucose or potassium acid phthalate. See Precision and Accuracy, below, for reference to phthalate. Because glucose has a theoretical COD of 1.067 g/g, dissolve 468.6 mg glucose in distilled water and dilute to 1,000 ml for a 500-mg/l COD solution. Potassium acid phthalate has a theoretical COD of 1.176 g/g; therefore, dissolve 425.1 mg potassium acid phthalate in distilled water and dilute to 1,000 ml for a 500-mg/l COD solution. A 98 to 100% recovery of the theoretical oxygen demand can be expected with potassium acid phthalate. This reagent has an advantage over glucose in that it can be standardized chemically. It is also stable over a period of time, whereas glucose may be decomposed biologically quite rapidly.

5. Calculation

$$\text{mg/l COD} = \frac{(a-b)N \times 8{,}000}{\text{ml sample}}$$

where COD = chemical oxygen demand from dichromate, a = ml $Fe(NH_4)_2(SO_4)_2$ used for blank, b = ml $Fe(NH_4)_2(SO_4)_2$ used for sample, and N = normality of $Fe(NH_4)_2(SO_4)_2$.

6. Precision and Accuracy

A set of synthetic unknown samples containing potassium acid phthalate and sodium chloride was tested by 74 laboratories. At 200 mg/l COD in the absence of chloride, the standard deviation was ±13 mg/l (coefficient of variation, 6.5%). At 160 mg/l COD and 100 mg/l chloride, the standard deviation was ±14 mg/l (10.8%).

The accuracy of this method has been determined by Moore and associates. For most organic compounds the oxidation is 95 to 100% of the theoretical value. Benzene, toluene, and pyridine are not oxidized.

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424 pH VALUE

The pH of most natural waters falls within the range of 4 to 9. The majority of waters are slightly basic because of the presence of carbonates and bicarbonates. A departure from a normal pH for a given water could be caused by the influx of acidic or alkaline industrial wastes. Neutralization of spent acids or bases is an important waste treatment practice, and measurement and control of pH in industrial effluents is often required for water pollution control. It is also relatively common to practice pH adjustment of water treatment plant effluents to control corrosion in distribution systems.

The pH of a solution refers to its hydrogen ion activity and is expressed as the logarithm of the reciprocal of the hydrogen ion activity in moles per liter at a given temperature. It is used in the calculation of carbonate, bicarbonate, and carbon dioxide, corrosion and stability index, and other acid-base equilibria of importance to water and wastewater analysis and treatment control. The practical pH scale extends from 0, very acidic, to 14, very alkaline, with 7 corresponding to exact neutrality at 25 C. Whereas "alkalinity" and "acidity" are measures of the total resistance to pH change or buffering capacity of a sample, pH represents the free hydrogen ion activity not bound by carbonate or other bases.

The pH can be measured either colorimetrically or electrometrically. The colorimetric method is less expensive but suffers from interferences due to color, turbidity, salinity, colloidal matter, and various oxidants and reductants. The indicators are subject to deterioration as are the color standards with which they are compared. Moreover, no single indicator encompasses the pH range of interest in waters and wastewaters. In poorly buffered liquids, the indicators themselves may alter the pH of the sample unless preadjusted to nearly the same pH as the sample. For these reasons, the colorimetric method is suitable only for rough estimation and is not described herein. (For details on the colorimetric method, see Clark,[1] Kolthoff,[2] and AWWA.[3]) The glass electrode method is the standard technic.

1. General Discussion

a. Principle: Although the hydrogen electrode is recognized as the primary standard, the glass electrode is less subject to interferences and is used in combination with a calomel reference electrode. The glass-reference electrode pair produces a change of 59.1 mV/pH unit at 25 C.

b. Interferences: The glass electrode is relatively free from interference from color, turbidity, colloidal matter, oxidants, reductants, or high salinity, except for a sodium error at high pH. This error at a pH above 10 may be reduced by using special "low sodium error" electrodes. When using ordinary glass electrodes, make approximate corrections for the sodium error in accordance with information supplied by the manufacturer. Temperature exerts two significant effects on pH measurement: the pH potential, i.e., the change in potential per pH unit, varies with temperature; and ionization in the sample also varies.* The first effect can be overcome by a temperature compensation adjustment provided on the better commercial instruments. The second effect is inherent in the sample and is taken into consideration by recording both temperature and pH of each sample.

2. Apparatus

a. Electronic pH meter with temperature compensation adjustment.

b. Glass electrode: Glass electrodes are available for measurement over the entire pH range with minimum-sodium-ion-error types for high pH-high sodium samples.

c. Reference electrode: Use a calomel, silver-silver chloride, or other constant-potential electrode.

d. Magnetic stirrer, with teflon-coated stirring bar or a mechanical stirrer with inert plastic-coated or glass impeller.

e. Flow chamber for measurement of continuously flowing or unbuffered solutions.

3. Standard Solutions

a. General preparation: Calibrate the electrode system against standard buffer solutions of known pH. Because buffer solutions may deteriorate as a result of mold growth or contamination, prepare fresh as needed for accurate work by weighing the amounts of chemicals specified in Table 424:I, dissolving in dis-

* This ionization, dependent on values of the ionization constants for the various weak acids and bases in the sample at a particular temperature, is to a significant extent related to the alkalinity. Increasing alkalinity reduces the effect of temperature change on the pH. This effect of alkalinity is not a direct relationship but it can be quite pronounced even at very low concentrations of alkalinity.

The temperature dial on pH meters is designed only to correct for the temperature characteristics of the electrodes. Instruments without a temperature dial are often provided with data from which this correction for the characteristics of the electrodes may be calculated.

Data for calculating, by interpolation, the pH of natural waters at temperatures other than that of the measurement have been provided by Langelier.[4]

TABLE 424:I. PREPARATION OF pH STANDARD SOLUTIONS

Standard Solution (molality)	pH at 25 C	Weight of Chemicals Needed/1,000 ml Aqueous Solution at 25 C
Primary standards:		
Potassium hydrogen tartrate (saturated at 25 C)	3.557	6.4 g $KHC_4H_4O_6$*
0.05 potassium dihydrogen citrate	3.776	11.41 g $KH_2C_6H_5O_7$
0.05 potassium hydrogen phthalate	4.008	10.12 g $KHC_8H_4O_4$
0.025 potassium dihydrogen phosphate+0.025 disodium hydrogen phosphate	6.865	3.388 g KH_2PO_4†+3.533 g Na_2HPO_4†‡
0.008695 potassium dihydrogen phosphate+0.03043 disodium hydrogen phosphate	7.413	1.179 g KH_2PO_4†+4.302 g Na_2HPO_4†‡
0.01 sodium borate decahydrate (borax)	9.180	3.80 g $Na_2B_4O_7 \cdot 10H_2O$‡
0.025 sodium bicarbonate+0.025 sodium carbonate	10.012	2.092 g $NaHCO_3$+2.640 g Na_2CO_3
Secondary standards:		
0.05 potassium tetroxalate dihydrate	1.679	12.61 g $KH_3C_4O_8 \cdot 2H_2O$
Calcium hydroxide (saturated at 25 C)	12.454	1.5 g $Ca(OH)_2$*

* Approximate solubility.
† Dry chemical at 110 to 130 C for 2 hr.
‡ Prepare with freshly boiled and cooled distilled water (carbon-dioxide-free).

tilled water at 25 C, and diluting to 1,000 ml. This procedure is particularly important for the borate and carbonate buffers.

Use distilled water having a conductivity of less than 2 μsiemens at 25 C and a pH 5.6 to 6.0 for the preparation of all standard solutions. Freshly boil and cool this distilled water to expel the carbon dioxide to produce a pH of 6.7 to 7.3 for the preparation of the borate and phosphate solutions. Dry the potassium dihydrogen phosphate at 110 C to 130 C for 2 hr before weighing. Do not heat the unstable hydrated potassium tetroxalate above 60 C nor dry the other specified buffer salts.

Although ACS-grade chemicals are generally satisfactory for the preparation of buffer solutions, use certified materials available as NBS standard samples from the National Bureau of Standards where the greatest accuracy is required. For routine analysis, commercially available buffer tablets, powders, or solutions of tested quality also are permissible. In preparing buffer solutions from solid salts, dissolve all the material; otherwise, the pH calibration will be incorrect. Prepare and calibrate the electrode system with buffer solutions with pH approximating that of the sample to minimize error resulting from nonlinear response of the electrode.

As a rule, select and prepare the buffer solutions classed as primary standards in Table 424:I; reserve the secondary standards for extreme situations encountered in wastewater measurements. Consult Table 424:II for the accepted pH of the standard buffer solutions at temperatures other than 25 C. Where the intent is to apply them for routine control, store the buffer solutions and samples preferably in polyethylene bottles or, at least, pyrex glassware. Even in such circumstances, replace buffer solutions every 4 wk.

b. Saturated potassium hydrogen tartrate solution: Shake vigorously an excess (5 to 10 g) of finely crystalline $KHC_4H_4O_6$ with 100 to 300 ml distilled water at 25 C in a glass-stoppered bottle. Separate the clear solution from the undissolved material by decantation or filtration. If this solution is to be used for routine control, preserve for 2 months or more by adding a thymol crystal (8-mm diam) for each 200 ml solution.

c. Saturated calcium hydroxide solution: Place the well-washed, low-alkali-grade calcium carbonate, $CaCO_3$, in a platinum dish and ignite for 1 hr at 1,000 C. After cooling the calcium oxide, hydrate by slowly adding distilled water with stirring and heating to boiling. Cool and filter the suspension and collect the solid calcium hydroxide on a fritted glass filter of medium porosity. Dry the calcium hydroxide in an oven at 110 C, cool, and pulverize to uniformly fine granules. Vigorously shake an excess of fine granules with distilled water in a stoppered polyethylene bottle, allowing the temperature to come to 25 C after mixing. Filter the supernatant under suction through a sintered glass filter of medium porosity and use the filtrate as the buffer solution. Discard the buffer solution when atmospheric carbon dioxide causes turbidity to appear.

4. Procedure

Because of the differences between the many makes and models of commercially available pH meters, it is impossible to provide detailed instructions for the proper operation of every instrument. In each case, follow the manufacturer's instructions. Thoroughly wet the glass and reference electrodes by immersing the tips in water overnight or in accordance with instructions. Thereafter, when the meter is not in use for pH measurement, keep the tips of the electrodes immersed in water.

Before use, remove the electrodes from the water and rinse with distilled or demineralized water. Dry the electrodes by gentle wiping with a soft tissue. Standardize the instrument with the electrodes immersed in a buffer solution with a pH approaching that of the sample and note the temperature of the buffer and the pH at the measured temperature. Remove the electrodes from the buffer, rinse thoroughly, and dry. Immerse in a second buffer approximately 4 pH units different from the first and note the pH reading; the reading should be within 0.1 unit of the pH for the second buffer. Rinse electrodes thoroughly, dry, and immerse in the sample. Agitate the sample sufficiently to provide homogeneity and keep solids in suspension. If the sample temperature is different from that of the buffers, let the electrodes equilibrate with the sample. Measure the sample temperature and set the temperature compensator on the pH meter to the measured temperature. Note and record the pH and temperature. Rinse electrodes and immerse in water until the next measurement.

When only occasional pH measurements are made, standardize the instrument before each measurement. Where frequent measurements are made, less frequent standardization (every 1 or 2 hr) is satisfactory. However, if sample pH values vary widely, standardize more frequently with a buffer having a pH within 1 to 2 pH units of that of the sample. Measure with two or more buffers of different pH at least once daily and more frequently if samples contain abrasive solids or dissolved fluorides, in order to check the linearity of response. When electrode response to two buffers 4 pH units different shows differences greater than 0.1 pH unit, replace the glass electrode.

pH measurements in high-purity waters such as condensate or demineralizer effluents are subject to atmospheric contamination and require special procedures for accurate pH measurement.

5. Precision and Accuracy

The precision and accuracy attainable with a given pH meter will depend on the type and condition of the instrument and the care used in standardization and operation. Guard against possible erratic results arising from mechanical or electrical failures—weak batteries, damaged electrodes, plugged liquid junctions, and fouling of the electrodes with oily or precipitated materials. With the proper care, a precision of ±0.02 pH unit and an accuracy of ±0.05 pH unit can be achieved with many of the new models. However, ±0.1 pH unit represents the limit of accuracy under normal conditions. For this reason, report pH values to the nearest 0.1 pH unit. A synthetic sample consisting of a Clark and Lubs buffer solution of pH 7.3 was analyzed electrometrically by 30 laboratories, with a standard deviation of ±0.13 pH unit.

6. References

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SULFATE

Catalog No. 16300

METHOD: Turbidimetric
WORKING RANGE: 0-300 mg/1
COLOR CODE: Green

PROCEDURE:

1. Turn instrument on. Allow 5 minutes warm up.

2. Insert meter scale (16300) into the meter.

3. Select one of the empty unmarked vials and fill about 3/4 full with the sample to be tested. Wipe clean with a dry tissue and insert vial into the cuvette holder.

4. Select the No. 2 filter and adjust to zero adjust.

5. Transfer 5ml of sample to be tested to the green capped vial, recap and shake to dissolve the chemical. Wipe clean as in step 3 and insert the vial into the cuvette holder.

6. Read mg/1 sulfate directly from the meter scale.

7. If the reading should be off the scale, use the approximate dilution.

CAUTION: Mercurous mercury, silica (over 500 mg/1), and silver interfere.

REFERENCE: Standard Methods, 14th Edition., pg. 496: 427C
ASTM, D516-59T

427 SULFATE

Sulfate is widely distributed in nature and may be present in natural waters in concentrations ranging from a few to several thousand milligrams per liter. Mine drainage wastes may contribute high sulfate by virtue of pyrite oxidation. Sodium and magnesium sulfate exert a cathartic action and should not be present in excess in drinking water.

1. Selection of Method

The choice of method will depend on the concentration range of sulfate and the degree of accuracy required. Dilution or concentration of the sample will bring most waters into the desired range for any of the methods. Method A is the preferred standard method and is the most accurate for sulfate concentrations above 10 mg/l. It should be used for obtaining theoretical ion balances and whenever results of the greatest accuracy are required. Method B is similar but substitutes drying of the filter and residue for the more rigorous heat treatment by ignition at 800 C that is required to expel occluded water. This method is acceptable in routine work where the greatest attainable accuracy is not required. Method C is more rapid and may be either more or less accurate than Methods A or B for sulfate concentrations less than 10 mg/l, depending on a number of factors, including the skill of the analyst. Although usually less accurate than Methods A or B above 10 mg/l, Method C may be applied to concentrations up to 60 mg/l. Sulfate also may be determined by the automated method described in Section 607.

2. Sampling and Storage

In the presence of organic matter certain bacteria may reduce sulfate to sulfide. To avoid this, store heavily polluted or contaminated samples at low temperatures or treat with formaldehyde. Sulfite may be oxidized to sulfate by dissolved oxygen above pH 8.0. If samples contain sulfite, adjust the pH below this level.

427 C. Turbidimetric Method

1. General Discussion

a. Principle: Sulfate ion is precipitated in a hydrochloric acid medium with barium chloride in such a manner as to form barium sulfate crystals of uniform size. The absorbance of the barium sulfate suspension is measured by a nephelometer or transmission photometer and the sulfate ion concentration is determined by comparison of the reading with a standard curve.

b. Interference: Color or suspended matter in large amounts will interfere with this method. Some suspended matter may be removed by filtration. If both are small in comparison with the sulfate ion concentration, interference is corrected for as indicated in ¶4*d* below. Silica in excess of 500 mg/l will interfere, and in waters containing large quantities of organic material it may not be possible to precipitate barium sulfate satisfactorily.

There are no ions other than sulfate in normal waters that will form insoluble compounds with barium under strongly acid conditions. Make determinations at room temperature, which may vary over a range of 10 C without causing appreciable error.

c. Minimum detectable concentration: Approximately 1 mg/l sulfate.

2. Apparatus

a. Magnetic stirrer: It is convenient to incorporate a timing device to permit the magnetic stirrer to operate for exactly 1 min. Use a constant stirring speed. It is also convenient to incorporate a fixed resistance in series with the motor operating the magnetic stirrer to regulate the speed of stirring. Use magnets of identical shape and size. The exact speed of stirring is not critical, but it should be constant for each run of samples and standards and should be adjusted to about the maximum at which no splashing occurs.

b. Photometer: One of the following is required, with preference in the order given:

1) *Nephelometer.*

2) *Spectrophotometer,* for use at 420 nm, providing a light path of 4 to 5 cm.

3) *Filter photometer,* equipped with a violet filter having maximum transmittance near 420 nm and providing a light path of 4 to 5 cm.

c. Stopwatch, if the magnetic stirrer is not equipped with an accurate timer.

d. Measuring spoon, capacity 0.2 to 0.3 ml.

3. Reagents

a. Conditioning reagent: Mix 50 ml glycerol with a solution containing 30 ml conc HCl, 300 ml distilled water, 100 ml 95% ethyl or isopropyl alcohol, and 75 g NaCl.

b. Barium chloride, $BaCl_2$, crystals, 20 to 30 mesh.

c. Standard sulfate solution: Prepare a standard sulfate solution as described in 1) or 2); 1.00 ml = 100 μg SO_4.

1) Dilute 10.41 ml standard 0.0200*N* H_2SO_4 titrant specified in Alkalinity, Section 403.3*c*, to 100 ml with distilled water.

2) Dissolve 147.9 mg anhydrous Na_2SO_4 in distilled water and dilute to 1,000 ml.

4. Procedure

a. Formation of barium sulfate turbidity: Measure 100 ml sample, or a suitable portion made up to 100 ml, into a 250-ml erlenmeyer flask. Add exactly 5.00 ml conditioning reagent and mix in the stirring apparatus. While the solution is being stirred, add a spoonful of $BaCl_2$ crystals and begin timing immediately. Stir for exactly 1 min at a constant speed.

b. Measurement of barium sulfate turbidity: Immediately after the stirring period has ended, pour some of the solution into the absorption cell of the photometer and measure the turbidity at 30-sec intervals for 4 min. Because maximum turbidity usually occurs within 2 min and the readings remain constant thereafter for 3 to 10 min, consider the turbidity to be the maximum reading obtained in the 4-min interval.

c. Preparation of calibration curve: Estimate the sulfate concentration in the sample by comparing the turbidity reading with a calibration curve prepared by carrying sulfate standards through the entire procedure. Space the standards at 5 mg/l increments in the 0- to 40-mg/l sulfate range. Above 40 mg/l the accuracy of the method decreases and the suspensions of barium sulfate lose stability. Check reliability of the calibration curve by running a standard with every three or four unknown samples.

d. Correction for sample color and turbidity: Correct for the color and turbidity present in the original sample by running blanks from which the $BaCl_2$ is withheld.

5. Calculation

$$mg/l\ SO_4 = \frac{mg\ SO_4 \times 1{,}000}{ml\ sample}$$

6. Precision and Accuracy

A synthetic unknown sample containing 259 mg/l sulfate, 108 mg/l Ca, 82 mg/l Mg, 3.1 mg/l K, 19.9 mg/l Na, 241 mg/l chloride, 0.250 mg/l nitrite N, 1.1 mg/l nitrate N, and 42.5 mg/l total alkalinity (contributed by $NaHCO_3$) was analyzed in 19 laboratories by the turbidimetric method, with a relative standard deviation of 9.1% and a relative error of 1.2%.

427 D. Bibliography

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DETERMINATION OF SULFIDE

METHOD: METHYLENE BLUE
WORKING RANGE: 0.1 - 1.8 mg/l
COLOR CODE: WHITE DOT

SAMPLE PREPARATION AND INTERFERENCES: Sampling and testing should be carried out with all possible speed. Aeration of the sample should be avoided. Some strong reducing agents prevent the formation of color or diminish its intensity. High sulfide concentrations may completely inhibit the reaction. Concentrations of Sulfide and Thiosulfate up to 10 mg/l have no effect, although high concentrations retard the reaction. Dithionite causes high results. Nitrite and Sulfide are not likely to be found together.

PROCEDURE:

1. Turn the instrument on. Allow 5 minutes warm-up.
2. Insert the meter scale into the meter.
3. Fill the uncapped empty vial about 3/4 full with the sample to be tested. Wipe the vial clean with a dry tissue and insert the vial into the cuvette holder.
4. Select the #3 filter and adjust the meter needle to zero adjust.
5. To the White-Dot Capped Vial add 5 ml of the sample to be tested with a pipette. Add 1 drop of reagent #2 to the vial, cap and shake to mix. Wait 1-3 minutes.
6. After waiting add 3 drops Reagent #3. Recap and shake to mix. Wipe clean with a dry tissue and insert into the cuvette holder.
7. Read mg/l Sulfide directly from the meter scale.
8. Discard the White-Dot Capped Vial.

REFERENCE: Standard Methods, 14th Edition, Page 503.

428 SULFIDE

1. General Discussion

Sulfide is often present in groundwater, especially in hot springs, and it is common in wastewaters, coming in part from the decomposition of organic matter, sometimes from industrial wastes, but mostly from the bacterial reduction of sulfate. Hydrogen sulfide escaping into the air from sulfide-containing wastewater causes odor nuisances. The threshold odor concentration of H_2S in clean water is between 0.01 and 0.1 μg/l. H_2S is very toxic and has claimed the lives of numerous workmen in sewers. It attacks metals directly, and indirectly has caused serious corrosion of concrete sewers, because it is oxidized biologically to sulfuric acid on the pipe wall.

From an analytical standpoint, three categories of sulfide in water and wastewater are distinguished:

a. Total sulfide includes dissolved H_2S and HS^-, as well as *acid-soluble* metallic sulfides present in the suspended matter. The S^{2-} is negligible, amounting to less than 0.5% of the dissolved sulfide at pH 12, less than 0.05% at pH 11, etc. Copper and silver sulfides are so insoluble that they do not respond in the ordinary sulfide determinations; they can be ignored for practical purposes.

b. Dissolved sulfide is that remaining after the suspended solids have been removed by flocculation and settling.

c. Un-ionized hydrogen sulfide may be calculated from the concentration of dissolved sulfide, the pH of the sample, and the practical ionization constant of hydrogen sulfide.

2. Sampling and Storage

Take samples with a minimum of aeration. Preserve a sample for a total sulfide determination by putting 4 drops of 2*N* zinc acetate into a 100-ml bottle, filling completely with the sample, and stoppering.

3. Qualitative Tests

A qualitative test for sulfide is often useful and is advisable in the examination of certain industrial wastes containing interfering substances that may give a false negative result in the methylene blue procedure.

a. Antimony test: Add 0.5 ml saturated solution of potassium antimony tartrate to about 200 ml sample in a bottle, and follow with 0.5 ml 6*N* HCl in excess of phenolphthalein alkalinity. The yellow Sb_2S_3 is discernible at a sulfide concentration of 0.5 mg/l. Comparisons with samples of known sulfide concentrations make the technic roughly quantitative. The only known interferences are metallic ions such as lead, which hold the sulfide so firmly that it does not produce antimony sulfide, and dithonite, which decomposes in acid solution to produce sulfide.

b. Silver sulfide-silver electrode test: The potential of a silver sulfide-silver electrode assembly relative to a reference electrode varies with the activity of the sulfide ion in solution. By correcting for the ion activity coefficient and pH, this potential allows an estimate of the sulfide concentration. Standardize the electrode frequently against a sulfide solution of known strength. An electrode of

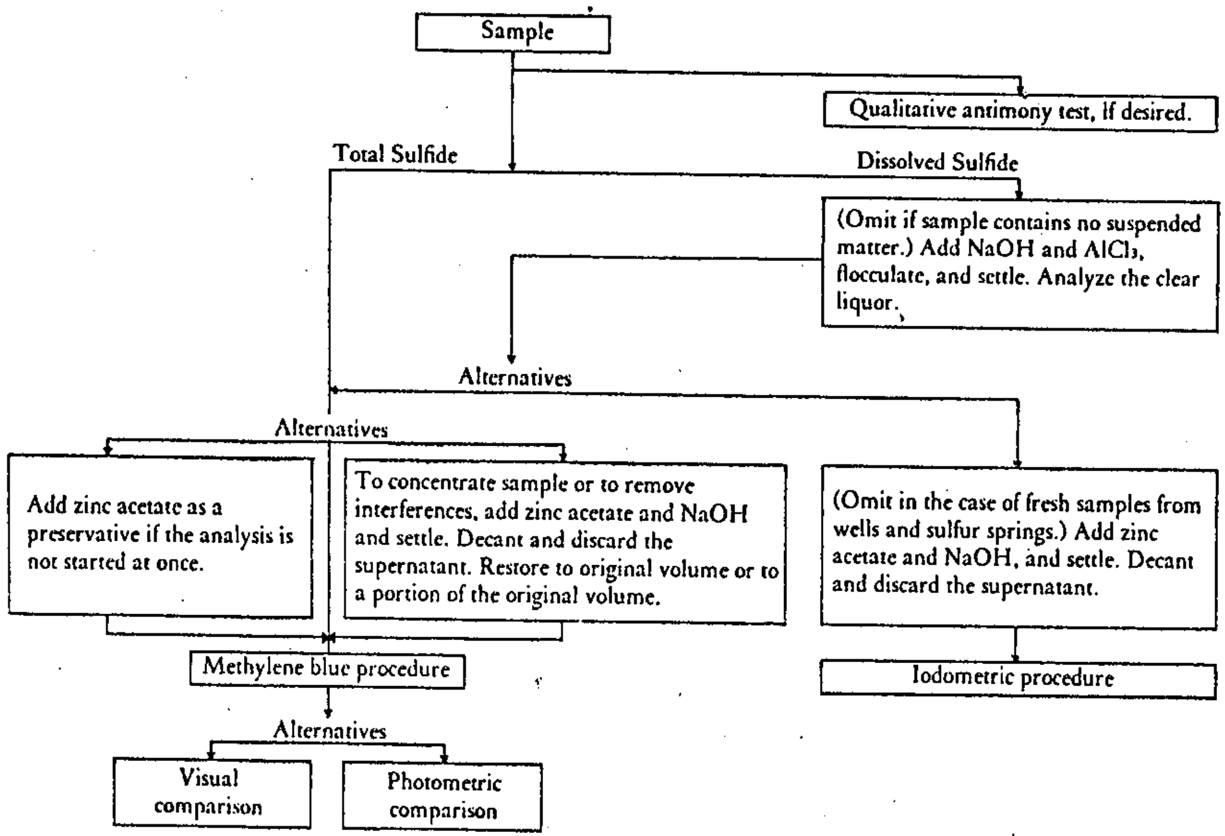


Figure 428:1. Analytical flow paths for sulfide determinations.

this type can be used as an endpoint indicator for titration of dissolved sulfide with a standard solution of a silver or lead salt, but slow response is always a problem.

c. Lead acetate paper and silver foil tests: Confirm odors attributed to H_2S with lead acetate paper. On exposure to the vapor of a slightly acidified sample, the paper becomes blackened by the formation of PbS. A strip of silver foil is more sensitive than lead acetate paper. Clean the silver by dipping in a sodium cyanide solution, and rinse. Silver is particularly suitable for long-time exposure in the vicinity of possible H_2S sources because the black Ag_2S is permanent, whereas PbS slowly oxidizes.

4. Selection of Quantitative Methods

Iodine reacts with sulfide in acid solution, oxidizing it to sulfur. A titration based on this reaction is an accurate method for determining sulfide at concentrations above 1 mg/l if interferences are absent and if loss of H_2S is avoided. The unmodified iodine method (D) is useful for standardizing the colorimetric method and is suitable for analyzing samples freshly taken from wells or springs. The method can be used for wastewater and partly oxidized water from sulfur springs if interfering substances are separated first.

The colorimetric method (C) is based on the reaction of sulfide, ferric chloride, and dimethyl-p-phenylenediamine (p-aminodimethylaniline) under conditions that produce methylene blue. Ammonium phosphate is added after color development to remove the ferric chloride color. The procedure is applicable at sulfide concentrations only up to 20 mg/l.

Figure 428:1 shows analytical flow paths for sulfide determinations under various conditions and options.

428 A. Separation of Soluble and Insoluble Sulfides

Unless the sample is entirely free from suspended solids (dissolved sulfide equals total sulfide), to measure dissolved sulfide first remove insoluble matter. Accomplish the separation by producing an aluminum hydroxide floc that is settled, leaving a clear supernatant for analysis.

1. Apparatus

Glass bottles with stoppers. Use 100 ml if sulfide will be determined by the methylene method, and 500 to 1,000 ml if by the titrimetric method.

2. Reagents

a. Sodium hydroxide solution, NaOH, 6*N*.

b. Aluminum chloride solution, 6N: Because of the hygroscopic and caking tendencies of this chemical, purchase 100-g (or 1/4-lb) bottles of the hexahydrate, $AlCl_3 \cdot 6H_2O$. Dissolve the contents of a previously unopened 100-g

428 C. Methylene Blue Method

1. Apparatus

a. Matched test tubes, approximately 125 mm long and 15 mm OD.

b. Droppers, delivering 20 drops/ml methylene blue solution. To obtain uniform drops it is essential to hold the dropper in a vertical position and to allow the drops to form slowly.

c. If photometric rather than visual color determination will be used, either:

1) *Spectrophotometer,* for use at a wavelength of 625 nm with cells providing light paths of 1 cm and 1 mm, or

2) *Filter photometer,* with a filter providing maximum transmittance near 600 nm.

2. Reagents

a. Amine-sulfuric acid stock solution: Dissolve 27 g N,N-dimethyl-*p*-phenylenediamine oxalate* (also called *p*-aminodimethylaniline oxalate) in a cold mixture of 50 ml conc H_2SO_4 and 20 ml distilled water. Cool and dilute to 100 ml with distilled water. The amine oxalate should be fresh; an old supply may be oxidized and discolored to a degree that results in interfering colors in the test. Store in a dark glass bottle. When this stock is diluted and used in

* Eastman catalog No. 5672 has been found satisfactory for this purpose.

the procedure with a sulfide-free sample, it must yield a colorless solution.

b. Amine-sulfuric acid reagent: Dilute 25 ml amine-sulfuric acid stock solution with 975 ml 1+1 H_2SO_4. Store in a dark glass bottle.

c. Ferric chloride solution: Dissolve 100 g $FeCl_3 \cdot 6H_2O$ in 40 ml water.

d. Sulfuric acid solution, H_2SO_4, 1+1.

e. Diammonium hydrogen phosphate solution: Dissolve 400 g $(NH_4)_2HPO_4$ in 800 ml distilled water.

f. Methylene blue solution I: Use USP grade dye or one certified by the Biological Stain Commission. The dye content should be reported on the label and should be 84% or more. Dissolve 1.0 g in distilled water and make up to 1 l. This solution will be approximately the correct strength, but because of variation between different lots of dye, standardize against sulfide solutions of known strength and adjust its concentration so that 0.05 ml (1 drop)=1.0 mg/l sulfide.

Standardization—Put several grams of clean, washed crystals of sodium sulfide, $Na_2S \cdot 9H_2O$, into a small beaker. Add somewhat less than enough water to cover the crystals. Stir occasionally for a few minutes, then pour the solution into another vessel. This solution reacts slowly with oxygen, but the change is unimportant in a period of a few hours. Make the solution daily. To 1 l distilled water add 1 drop of solution and mix. Immediately determine the sulfide concentration by the methylene blue procedure and by the titrimetric procedure. Repeat the procedures, using more than 1 drop of Na_2S solution or smaller volumes of water, until at least five tests have been made, with a range of sulfide concentrations between 1 and 8 mg/l. Calculate the average percent error of the methylene blue result as compared to the titrimetric result. If the average error is negative, that is, the methylene blue results are lower than the titrimetric results, dilute the methylene blue solution by the same percentage, so that a greater volume will be used in matching colors. If the methylene blue results are high, increase the strength of the solution by adding more dye.

g. Methylene blue solution II: Dilute 10.00 ml of the adjusted methylene blue solution I to 100 ml.

3. Procedure

a. Color development: Transfer 7.5 ml sample to each of two matched test tubes, using a special wide-tip pipet or filling to the marks on the test tubes. Add to Tube A 0.5 ml amine-sulfuric acid reagent and 0.15 ml (3 drops) $FeCl_3$ solution. Mix immediately by inverting the tube slowly, only once. To Tube B add 0.5 ml 1+1 H_2SO_4 and 0.15 ml (3 drops) $FeCl_3$ solution and mix. The presence of sulfide ion will be indicated by the appearance of blue color in Tube A. Color development is usually complete in about 1 min, but a longer time is often required for the fading out of the initial pink color. Wait 3 to 5 min, then add 1.6 ml $(NH_4)_2HPO_4$ solution to each tube. Wait 3 to 15 min and make color comparisons. If zinc acetate was used wait at least 10 min before making a visual color comparison.

b. Color determination:

1) Visual color estimation—Add methylene blue solution I or II, depending on the sulfide concentration and the

desired accuracy of the test, dropwise, to the second tube, until the color matches that developed in the first tube. If the concentration exceeds 20 mg/l, repeat the test with a portion of the sample diluted to one tenth.

With methylene blue solution I, adjusted so that 0.05 ml (1 drop) = 1.0 mg/l sulfide when 7.5 ml of sample are used:

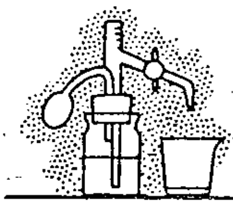
mg/l sulfide
= No. drops solution I + 0.1 (No. drops solution II)

2) Photometric color measurement—A cell with a light path of 1 cm is suitable for measuring sulfide concentrations from 0.1 to 2.0 mg/l. Use shorter or longer light paths for higher or lower concentrations. The upper limit of the method is 20 mg/l. Zero the instrument with a portion of the treated sample from Tube B. Prepare calibration curves on the basis of the colorimetric tests made on Na_2S solutions simultaneously analyzed by the titrimetric method, plotting concentration vs. absorbance. A straight-line relationship between concentration and absorbance can be assumed from 0 to 1.0 mg/l.

Read the sulfide concentration from the calibration curve

4. Precision and Accuracy

The accuracy is about ±10%. The standard deviation has not been determined.



NALCO ANALYTICAL PROCEDURE

6 CHLORIDE

RANGE: Unlimited

SENSITIVITY: 2 ppm as NaCl/0.1 ml of titrant

PROCEDURE:

1. Measure 50 ml of clear supernatant or filtered sample into a casserole.
2. Add 2 drops of "P" indicator (Solution 222). If a pink color develops, add N/50 H_2SO_4 (Solution 226) until the solution just turns colorless. If the solution does not turn pink, proceed directly with Step 3. (See Note 1)
3. Add 5 drops of K_2CrO_4 indicator (Solution 224). Mix.
4. Titrate with $AgNO_3$ (Solution 229) until one drop gives the yellow solution its first indication of brick-red cast.

CALCULATION:

PPM Chloride as NaCl = (20) (ml $AgNO_3$ used)

NOTES:

1. The pH of the sample must be between 7 and 10. H-6 (Solution 279) can be used to adjust acidic samples.
2. The ppm as NaCl figure can be converted to ppm as Cl using the following formula:

$$\text{ppm as Cl} = \text{ppm as NaCl} \times 0.607$$

APPARATUS	PART NO.
10-ml Automatic Buret with Amber Bottle	.0402
No. 3 Casserole	.0701
Stirring Rods	.2302
1-oz Dropper Bottle (Labeled as Requested)	.0351
50-ml Graduated Cylinder	.1201

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Titrimetric Method

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408 CHLORIDE

Chloride, in the form of Cl^- ion, is one of the major inorganic anions in water and wastewater. In potable water, the salty taste produced by chloride concentrations is variable and dependent on the chemical composition of the water. Some waters containing 250 mg/l chloride may have a detectable salty taste if the cation is sodium. On the other hand, the typical salty taste may be absent in waters containing as much as 1,000 mg/l when the predominant cations are calcium and magnesium.

The chloride concentration is higher in wastewater than in raw water because sodium chloride is a common article of diet and passes unchanged through the digestive system. Along the sea coast, chloride may be present in high concentrations because of leakage of salt water into the sewerage system. It may also be increased by industrial processes.

A high chloride content harms metallic pipes and structures, as well as agricultural plants.

Selection of method: Four methods are presented for the determination of chlorides. Since the first two are similar in most respects, selection is largely a matter of preference. The argentometric method (A) is suitable for use in relatively clear waters when 0.15 to 10 mg Cl are present in the portion of sample titrated. The mercuric nitrate method (B) has an easier end point. The potentiometric method (C) is suitable for colored or turbid samples in which color-indicated end points might be difficult to observe. The potentiometric method can be used without a pretreatment step for samples containing ferric ions (if not present in an amount greater than the chloride concentration), chromic phosphate, and ferrous and other heavy metal ions. The ferricyanide method, given in Part 602, is an automated modification which, although used routinely by many laboratories, is listed for the first time as a tentative method.

408 A. Argentometric Method

1. General Discussion

a. Principle: In a neutral or slightly alkaline solution, potassium chromate can indicate the end point of the silver nitrate titration of chloride. Silver chloride is precipitated quantitatively before red silver chromate is formed.

b. Interference: Substances in amounts normally found in potable waters will not interfere. Bromide, iodide, and cyanide register as equivalent chloride concentrations. Sulfide, thiosulfate, and sulfite ions interfere but can be removed by treatment with hydrogen peroxide. Orthophosphate in excess of 25 mg/l interferes by precipitation as silver phosphate. Iron in excess of 10 mg/l interferes by masking the end point.

2. Reagents

a. Chloride-free water: If necessary, use redistilled or deionized distilled water.

b. Potassium chromate indicator solution: Dissolve 50 g K_2CrO_4 in a little distilled water. Add silver nitrate solution until a definite red precipitate is formed. Let stand 12 hr, filter, and dilute to 1 l with distilled water.

c. Standard silver nitrate titrant, 0.0141*N:* dissolve 2.395 g $AgNO_3$ in distilled water and dilute to 1,000 ml. Standardize against 0.0141*N* NaCl by the procedure described in ¶3*b* below. Store in a brown bottle. Standard silver nitrate solution 0.0141*N*=500 μg Cl/1.00 ml.

d. Standard sodium chloride, 0.0141*N:* Dissolve 824.1 mg NaCl (dried at 140 C) in chloride-free water and dilute to 1,000 ml; 1.00 ml=500 μg Cl.

e. Special reagents for removal of interference:

1) *Aluminum hydroxide suspension:* Dissolve 125 g aluminum potassium sulfate or aluminum ammonium sulfate, $AlK(SO_4)_2 \cdot 12H_2O$ or $AlNH_4(SO_4)_2 \cdot 12H_2O$, in 1 l distilled water. Warm to 60 C and add 55 ml conc NH_4OH slowly with stirring. Let stand about 1 hr, transfer the mixture to a large bottle, and wash the precipitate by successive additions, with thorough mixing and decantations of distilled water, until free from chloride. When freshly prepared, the suspension occupies a volume of approximately 1 l.

2) *Phenolphthalein indicator solution.*

3) *Sodium hydroxide,* NaOH, 1*N.*

4) *Sulfuric acid,* H_2SO_4, 1*N.*

5) *Hydrogen peroxide,* H_2O_2, 30%.

3. Procedure

a. Sample preparation: Use a 100-ml sample or a suitable portion diluted to 100 ml.

If the sample is highly colored, add 3 ml $Al(OH)_3$ suspension, mix, let settle, filter, wash, and combine filtrate and washing.

If sulfide, sulfite, or thiosulfate is present, add 1 ml H_2O_2 and stir for 1 min.

b. Titration: Titrate samples in the pH range 7 to 10 directly. Adjust samples not in this range with H_2SO_4 or NaOH solution. Add 1.0 ml K_2CrO_4 indicator solution. Titrate with standard silver nitrate titrant to a pinkish yellow end point. Be consistent in end-point recognition.

Standardize the silver nitrate titrant and establish the reagent blank value by the titration method outlined above. A blank of 0.2 to 0.3 ml is usual for the method.

4. Calculation

$$\text{mg/l Cl} = \frac{(A-B) \times N \times 35{,}450}{\text{ml sample}}$$

where A = ml titration for sample, B = ml titration for blank, and N = normality of $AgNO_3$.

$$\text{mg/l NaCl} = \text{mg/l Cl} \times 1.65$$

5. Precision and Accuracy

A synthetic unknown sample containing 241 mg/l chloride, 108 mg/l Ca, 82 mg/l Mg, 3.1 mg/l K, 19.9 mg/l Na, 1.1 mg/l nitrate N, 0.25 mg/l nitrite N, 259 mg/l sulfate, and 42.5 mg/l total alkalinity (contributed by $NaHCO_3$) in distilled water was analyzed in 41 laboratories by the argentometric method, with a relative standard deviation of 4.2% and a relative error of 1.7%.

NALCO ANALYTICAL PROCEDURE

3 ALKALINITY (P & M)

(OVER)

RANGE: Unlimited

SENSITIVITY: 2 ppm as $CaCO_3$/0.1 ml of titrant

PROCEDURE:

1. Measure 50 ml of clear supernatant or filtered sample into a casserole.

2. Add 2 drops of P indicator (Soln. No. 222). If no pink color appears P alkalinity equals zero.

3. If a pink color appears, titrate with N/50 H_2SO_4 (Soln. No. 226) stirring gently until one drop turns the entire solution colorless. Record the number of ml used.

4. Add 5 drops of Special Indicator (Soln. No. 260).

5. Do not refill buret, but continue titrating with the N/50 H_2SO_4 (Soln. No. 226) until one drop of the acid turns the entire solution salmon pink. Record the total ml of acid used.

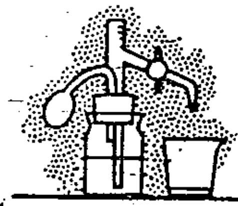
CALCULATION:

PPM P as $CaCO_3$ = (20) (ml of H_2SO_4 recorded in Step 3)

PPM M as $CaCO_3$ = (20) (ml of H_2SO_4 recorded in Step 5)

NOTES:

1. Three drops of methyl orange can be substituted for special indicator if desired. Color change will be from faint orange to salmon pink.



NALCO ANALYTICAL PROCEDURE

* 4 ALKALINITY (O) *

(-OH ALKALINITY) 150-200 PPM

RANGE: Unlimited

SENSITIVITY: 2 ppm as $CaCO_3$/0.1 ml of titrant

PROCEDURE:

1. Measure 50 ml of clear supernatant or filtered sample into a casserole.
2. Add 1 scoop (0.5g) of $BaCl_2$ crystals (Solution 209) or 10 ml of 10% $BaCl_2$ (Solution 232). Mix. TO REMOVE CARBONATE
3. Wait 5 minutes, then add 2 drops of P indicator (Solution 222). Titrate with N/50 H_2SO_4 (Solution 226) until one drop turns the solution colorless. Note the number of ml used.

CALCULATION:

PPM O as $CaCO_3$ = (20) (ml H_2SO_4 used in Step 3)

NOTES:

1. The equation relating P, M, and O alkalinity is 2P — M = O.
2. Use the "O" alkalinity procedure when interferences affect the "M" alkalinity (PO_4, Some Organics).

APPARATUS	PART NO.
10 ml Buret	0401
50 ml Graduated Cylinder	1201
Casserole	0701
Stirring Rod	2302
1-oz Round Solids Bottle with 0.5g Scoop in Cap	0350
1-oz Round Dropper Bottle (labeled as desired)	0351

SOLUTION	SHELF LIFE	SOLUTION NO.
N/50 Sulfuric Acid	1 Yr	226
— Phenolphthalein	6 Mo	222 —
Special Indicator	6 Mo	260
10% $BaCl_2$	1 Yr	232
$BaCl_2$ Crystals	1 Yr	209

403 ALKALINITY

The alkalinity of a water is its quantitative capacity to neutralize a strong acid to a designated pH. The measured value may vary significantly with the end point pH used in the determination. Alkalinity is a measure of a gross property of water and can be interpreted in terms of specific substances only when the chemical composition of the sample is known.

Alkalinity is significant in many uses and treatments of natural and wastewaters. Because the alkalinity of many surface waters is primarily a function of carbonate, bicarbonate, and hydroxide content, the alkalinity is taken as an indication of the concentration of these constitutents. The measured values may include contributions from borates, phosphates, or silicates if these are present. The alkalinity in excess of alkaline earth concentrations is significant in determining the suitability of a water for irrigation. Alkalinity measurements are used in the interpretation and control of water and wastewater treatment processes. Raw domestic wastewater has an alkalinity only slightly greater than that of the water supply. Properly operating anaerobic digesters typically have supernatant alkalinities in the range of 2,000 to 4,000 mg/l as $CaCO_3$.[1] For industrial wastes, the measurement can indicate change in quality if the source of the sample is known to have generally stable levels of alkalinity.

1. General Discussion

a. Principle: Hydroxyl ions present in a sample as a result of dissociation or hydrolysis of solutes are neutralized by titration with standard acid. The alkalinity thus depends on the end point pH used. For methods of determining inflection points from titration curves and the rationale for titrating to fixed pH end points, see Section 402.1*a*.

For samples of low alkalinity (less than 20 mg/l $CaCO_3$) use an extrapolation technic based on the near proportionality of the concentration of hydrogen ions to the excess of titrant beyond the equivalence point. The amount of standard acid required to lower the pH exactly 0.30 pH unit is carefully measured. Because this change in pH corresponds to an exact doubling of the hydrogen ion concentration, a simple extrapolation can be made to the equivalence point.[2, 3]

b. End points: When the alkalinity of a water is due entirely to hydroxide, carbonate, or bicarbonate content, the pH at the equivalence point of the titration is determined by the concentration of CO_2 present at that stage. The CO_2 concentration depends in turn on the total carbonate species originally in the sample and any losses that may have occurred during the titration. The following pH values are suggested as the equivalence points for the corresponding alkalinity concentrations as calcium carbonate:

	End point pH Total	End point pH Phenolphthalein
Alkalinity, mg/l:		
30	5.1	8.3
150	4.8	8.3
500	4.5	8.3
Silicates, phosphates known or suspected	4.5	8.3
Industrial waste or complex system	3.7*	8.3

c. Interferences: Soaps, oily matter, suspended solids, or precipitates may

*METHYL ORANGE

coat the glass electrode and cause a sluggish response. Allow additional time between titrant additions to let the electrode come to equilibrium. Do not filter, dilute, concentrate, or alter the sample in any way.

d. Selection of method: Determine the alkalinity of the sample from the volume of standard acid required to titrate a portion of the sample to a designated pH taken from the table of ¶1*b*. Titrate at room temperature with a properly calibrated pH meter or electrically operated titrator, or color indicators.

Report an alkalinity less than 20 mg/l $CaCO_3$ only if it has been determined by the low alkalinity method of ¶4*c*.

Construct a titration curve for the standardization of reagents.

Color indicators may be used for routine and control titrations in the absence of interfering color and turbidity and for preliminary titrations to select the sample size and strength of titrant (see below).

e. Sample size: See Section 402.1*e* for the selection of the sample size to be titrated and the normality of titrant, substituting 0.02 *N* or 0.1 *N* H_2SO_4 (or HCl) for the standard alkali of that method. For the low alkalinity method, titrate a 200-ml sample with 0.02 *N* H_2SO_4 from a 10-ml buret.

f. Sampling and storage: See Section 402.1*f*.

2. Apparatus

See Section 402.2.

3. Reagents

a. Sodium carbonate solution, approximately 0.05 *N*: Dry 3 to 5 g primary standard Na_2CO_3 at 250 C for 4 hr and cool in a desiccator. Weigh 2.5±0.2 g (to the nearest mg), transfer to a 1-l volumetric flask, and fill to the mark with distilled water.

b. Standard sulfuric acid or hydrochloric acid, 0.1 *N*: Dilute 3.0 ml conc H_2SO_4 or 8.3 ml conc HCl to 1 l with distilled or deionized water. Standardize against 40.00 ml 0.05 *N* Na_2CO_3 solution, with about 60 ml water, in a beaker by titrating potentiometrically to pH of about 5. Lift out electrodes, rinse into the same beaker, and boil gently for 3 to 5 min under a watch glass cover. Cool to room temperature, rinse the cover glass into the beaker, and finish the titration to the pH inflection point. Calculate the normality according to

$$\text{Normality, } N = \frac{A \times B}{53.00 \times C}$$

where A = g Na_2CO_3 weighed into 1 l, B = ml Na_2CO_3 solution taken for titration, and C = ml acid used. Use measured normality in calculations or adjust to exactly 0.1000 *N*. A 0.1000 *N* solution = 5.00 mg $CaCO_3$/ml.

c. Standard sulfuric acid or hydrochloric acid, 0.02 *N*: Dilute 200.00 ml 0.1000 *N* standard acid to 1,000 ml with distilled or deionized water. Standardize by potentiometric titration of 15.00 ml 0.05 *N* Na_2CO_3 according to the procedure of ¶3*b*. 0.0200 *N* solution = 1.00 mg $CaCO_3$/ml.

d. Mixed bromcresol green-methyl red indicator solution: Use either the aqueous or the alcoholic solution:

1) Dissolve 20 mg methyl red sodium salt and 100 mg bromcresol green sodium salt in 100 ml distilled water.

2) Dissolve 20 mg methyl red and

100 mg bromocresol green in 100 ml 95% ethyl alcohol or isopropyl alcohol.

e. Methyl orange solution.

f. Phenolphthalein solution.

g. Sodium thiosulfate, 0.1 *N:* See Section 402.3*b*.

4. Procedure

a. Color change: See Section 402.4*a*. The color response of the mixed bromcresol green-methyl red indicator is approximately as follows: above pH 5.2, greenish blue; pH 5.0, light blue with lavender gray; pH 4.8, light pink-gray with bluish cast; and pH 4.6, light pink. Check the color changes against the reading of a pH meter under the conditions of the titration.

b. Potentiometric titration curve: Follow the procedure for the determination of acidity (Section 402.4*b*), substituting the appropriate normality of standard acid solution for the standard NaOH, and continue the titration to pH 3.7 or lower. Do not filter, dilute, concentrate, or alter the sample in any way.

c. Potentiometric titration to preselected pH: Determine the appropriate end point pH according to ¶1*b*. Prepare the sample and titration assembly (Section 402.4*b*). Titrate to the end point pH without recording intermediate pH values and without undue delay. As the end point is approached make smaller additions of acid and be sure that pH equilibrium is reached before adding more titrant.

d. Potentiometric titration of low alkalinity: For alkalinities less than 20 mg/l titrate 100 to 200 ml according to the procedure of ¶4*c*, above, using a 10-ml microburet and 0.02 *N* standard acid solution. Stop the titration at a pH in the range 4.3 to 4.7 and record the volume and exact pH. Very carefully add additional titrant to lower the pH of the solution exactly 0.30 pH unit and again record the volume. Precise standardization of the pH meter is unnecessary for this determination.

5. Calculations

a. Potentiometric titration to end point pH:

$$\text{Alkalinity, mg/l } CaCO_3 = \frac{A \times N \times 50{,}000}{\text{ml sample}}$$

where A = ml standard acid used and N = normality of standard acid, or

$$\text{Alkalinity, mg/l } CaCO_3 = \frac{A \times T \times 1{,}000}{\text{ml sample}}$$

where T = titer of standard acid, mg $CaCO_3$/ml.

Report the pH of the end point used as follows: "The alkalinity to pH ______ = ______ mg/l $CaCO_3$" and indicate clearly if this pH corresponds to an inflection point of the titration curve.

b. Potentiometric titration of low alkalinity:

$$\text{Total alkalinity, mg/l } CaCO_3 = \frac{(2B-C) \times N \times 50{,}000}{\text{ml sample}}$$

where B = ml of titrant to first recorded pH, C = total ml of titrant to reach pH 0.3 unit lower, and N = normality of acid.

c. Calculation of alkalinity relationships: The results obtained from the phenolphthalein and total alkalinity determinations offer a means for the stoichiometric classification of the three principal forms of alkalinity present in many water supplies. The classification ascribes the entire alkalinity to bicarbonate, carbonate, and hydroxide, and assumes the absence of other (weak) acids of inorganic or organic composition, such as silicic, phosphoric, and boric acids. It further presupposes the incompatibility of hydroxide and bicarbonate alkalinities. Since the calculations are made on a stoichiometric basis, ion concentrations in the strictest sense are not represented in the results. According to this scheme:

1) Carbonate alkalinity is present when the phenolphthalein alkalinity is not zero but is less than the total alkalinity.

2) Hydroxide alkalinity is present if the phenolphthalein alkalinity is more than half the total alkalinity.

3) Bicarbonate alkalinity is present if the phenolphthalein alkalinity is less than half the total alkalinity. These relationships may be calculated by the following scheme, where *P* is the phenolphthalein alkalinity and *T* is the total alkalinity (¶1*b*):

Select the smaller value of *P* or (*T*-*P*). Then, carbonate alkalinity equals twice the smaller value. When the smaller value is *P*, the balance (*T*-2*P*) is bicarbonate. When the smaller value is (*T*-*P*), the balance (2*P*-*T*) is hydroxide. All results are expressed as $CaCO_3$. The mathematical conversion of the results is shown in Table 403:I.

Alkalinity relationships also may be computed nomographically (see Carbon Dioxide, Section 407). Accurately measure the pH of the water, calculate the OH^- concentration as milligrams per liter $CaCO_3$, and calculate the concentrations of CO_3^{2-} and HCO_3^- as milligrams per liter $CaCO_3$ from the OH^- concentration, and the phenolphthalein and total alkalinities by the following equations:

$$CO_3^{2-} = 2P - 2[OH^-]$$
$$HCO_3^- = T - 2P + [OH^-]$$

Similarly, if difficulty is experienced with the phenolphthalein end point, or if a check on the phenolphthalein titration is desired, calculate the phenolphthalein alkalinity as $CaCO_3$ from the results of the nomographic determinations of the carbonate (CO_3^{2-}) and hydroxide (OH^-) ion concentrations:

$$P = 1/2\,[CO_3^{2-}] + [OH^-]$$

TABLE 403:I. ALKALINITY RELATIONSHIPS*

Result of Titration	Hydroxide Alkalinity as $CaCO_3$	Carbonate Alkalinity as $CaCO_3$	Bicarbonate Alkalinity as $CaCO_3$
P=0	0	0	T
P<½T	0	2P	T−2P
P=½T	0	2P	0
P>½T	2P−T	2(T−P)	0
P=T	T	0	0

*Key: P—phenolphthalein alkalinity; T—total alkalinity.

6. Precision and Accuracy

No general statement can be made about precision because of the great variation in sample characteristics. The precision of the titration is likely to be much greater than the uncertainties involved in sampling and handling the sample before the analysis.

In the range of 10 to 500 mg/l, where the alkalinity is due entirely to carbonates or bicarbonates, a standard deviation of 1 mg/l can be achieved. Forty analysts in 17 laboratories analyzed synthetic water samples containing increments of bicarbonate equivalent to 120 mg/l $CaCO_3$. The titration procedure of ¶4*b* was used, with an end point pH of 4.5. The standard deviation was 5 mg/l and the average bias (lower than the true value) was 9 mg/l.[4]

7. References

1. Pohland, F.G. & D.E. Bloodgood. 1963. Laboratory studies on mesophilic and thermophilic anaerobic sludge digestion. *J. Water Pollut. Control Fed.* 35:11.
2. Larson, T.E. & L.M. Henley. 1955. Determination of low alkalinity or acidity in water. *Anal. Chem.* 27:851.
3. Thomas, J.F.J. & J.J. Lynch. 1960. Determination of carbonate alkalinity in natural waters. *J. Amer. Water Works Ass.* 52:259.
4. Winter, J.A. & M.R. Midgett. 1969. FWPCA Method Study 1. Mineral and Physical Analyses. FWPCA, Washington, D.C.

8. Bibliography

American Society for Testing & Materials. 1970. Standard Methods for Acidity or Alkalinity of Water. ASTM Publ. D1067-70, Philadelphia, Pa.

Brown, E., M.W. Skougstad & M.J. Fishman. 1970. Methods of collection and analysis of water sample for dissolved minerals and gases. Chapter A1 in Book 5, Techniques of Water-Resources Investigation of the United States Geological Survey. U.S. Geol. Surv., Washington, D.C.

APPENDIX F

IW-3 OPERATING DATA

Month	Total Flow (Gal.)	Avg. Flow/day (Gal./day)	Avg. Temp. (°F.)
3-77	3,413,000	853,000	116
4-77	4,505,000	282,000	88
5-77	792,000	46,000	82
6-77	302,000	18,000	87
7-77	88,000	6,000	88
8-77	639,000	34,000	89
9-77	245,000	12,000	88
10-77	369,000	18,000	85
11-77	17,272,000	617,000	98
12-77	32,991,000	1,100,000	114
	60,616,000		
1-78	35,917,000	1,159,000	113
2-78	34,144,000	1,219,000	113
3-78	37,626,000	1,214,000	114
4-78	12,393,000	443,000	89
5-78	436,000	21,000	85
6-78	223,000	12,000	90
7-78	---	---	--
8-78	---	---	--
9-78	---	---	--
10-78	11,000	4,000	84
11-78	27,860,000	961,000	112
12-78	39,228,000	1,353,000	117
	187,838,000		
1-79	43,566,000	1,405,000	116
2-79	37,341,000	1,334,000	115
3-79	43,656,000	1,408,000	118
4-79	4,951,000	236,000	83
5-79	191,000	11,000	83
6-79	131,000	33,000	87
7-79	51,000	13,000	90
8-79	---	---	--
9-79	---	---	--
10-79	44,167,000	1,425,000	115
11-79	48,896,000	1,630,000	116
12-79	49,195,000	1,587,000	115
	272,145,000		

Month	Total Flow (Gal.)	Avg. Flow/day (Gal./day)	Avg. Temp. (°F.)
1-80	42,719,000	1,378,000	113
2-80	44,107,000	1,521,000	113
3-80	45,352,000	1,463,000	112
4-80	49,210,000	1,640,000	114
5-80	63,365,000	2,044,000	113
6-80	38,698,000	1,290,000	104
7-80	395,000	99,000	87
8-80	---	---	--
9-80	---	---	--
10-80	2,929,000	418,000	108
11-80	39,258,000	1,309,000	111
12-80	42,568,000	1,373,000	114
	368,601,000		
1-81	42,308,000	1,365,000	114
2-81	40,754,000	1,456,000	116
3-81	42,094,000	1,358,000	113
4-81	59,141,000	1,971,000	116
5-81	53,704,000	1,732,000	115
6-81	43,929,000	1,464,000	107
7-81	1,074,000	63,000	85
8-81	410,000	51,000	87
9-81	233,000	116,000	90
10-81	3,132,000	149,000	82
11-81	34,044,000	1,135,000	109
12-81	37,616,000	1,213,000	107
	358,439,000		
1-82	37,571,000	1,212,000	105
2-82	30,725,000	1,097,000	105
3-82	39,652,000	1,279,000	107
4-82	38,888,000	1,296,000	106
5-82	1,698,000	74,000	80
6-82	794,000	32,000	86
7-82	120,000,000	24,000	84
8-82	691,000	36,000	84
9-82	834,000	40,000	83
10-82	1,512,000	94,000	80
11-82	16,660,000	926,000	106
12-82	32,146,000	1,037,000	111
	320,732,000		

Appendix G
MONITORING DATA

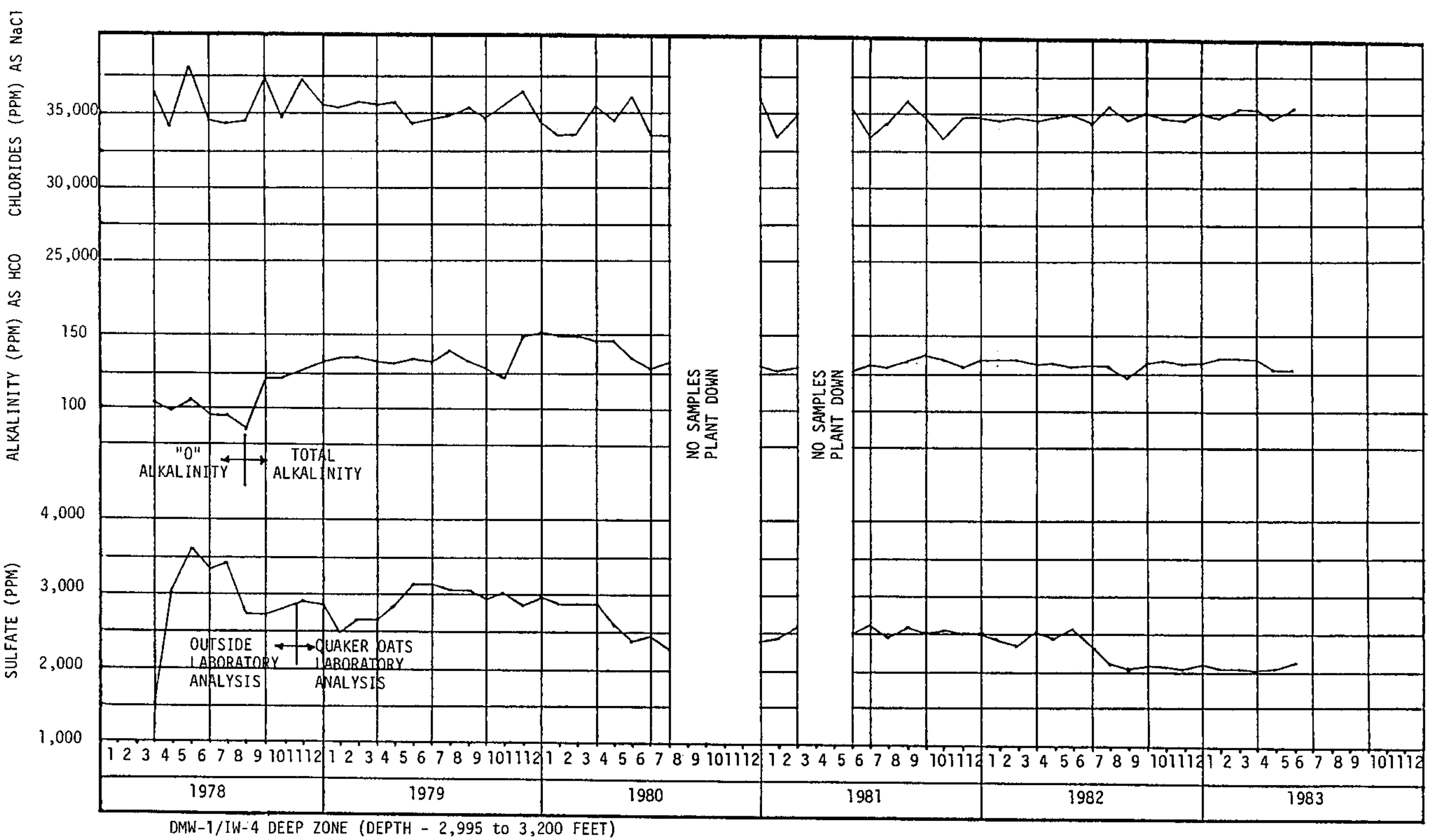


FIGURE G-1.
Monitoring Data.

CH2M HILL

FC43202.D0

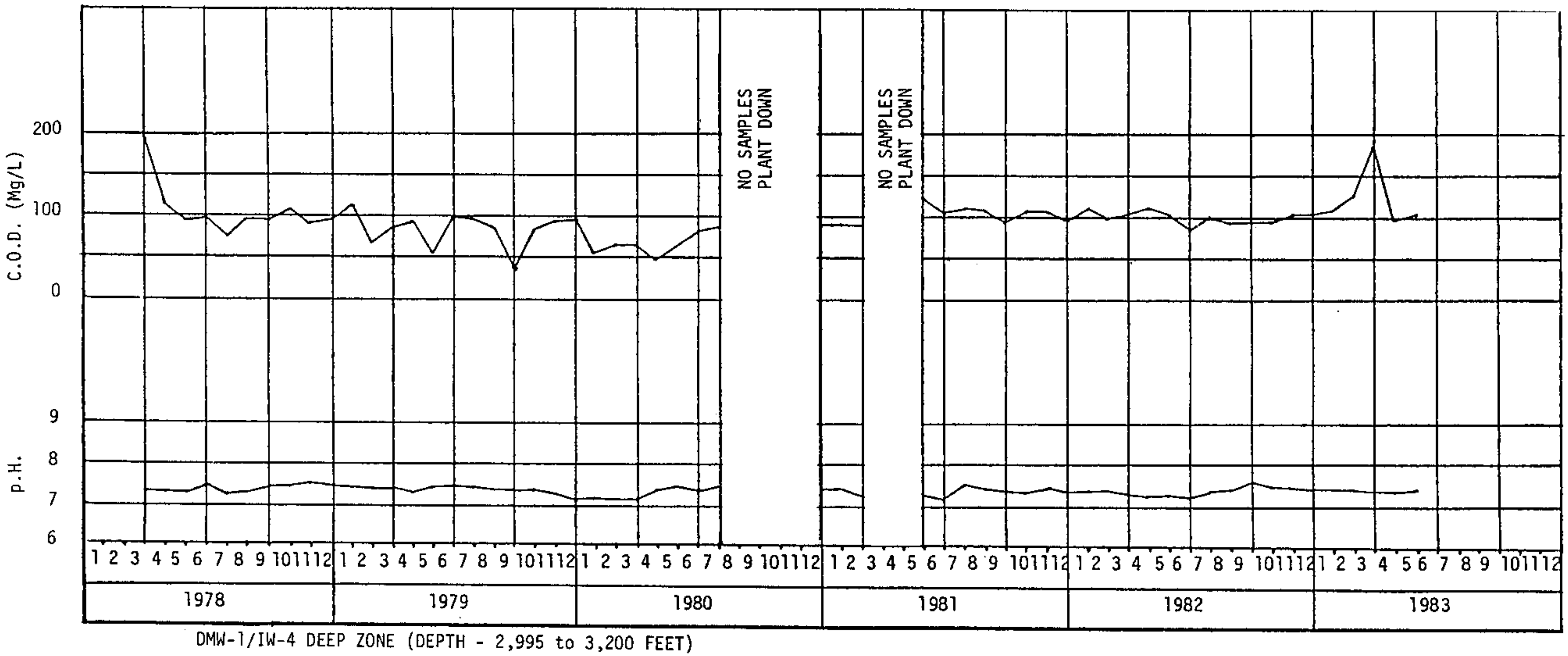


FIGURE G-2.
Monitoring Data.

CH2M HILL

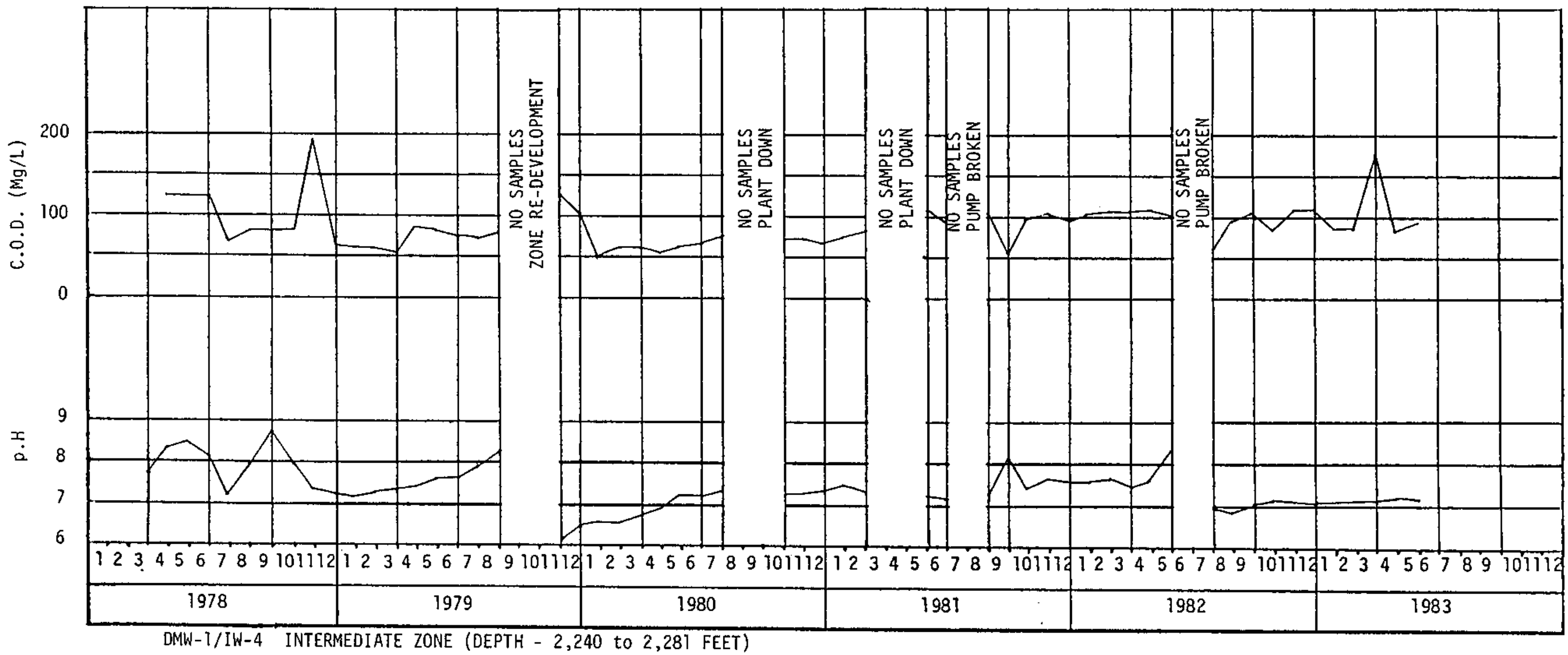


FIGURE G-4.
Monitoring Data.

CH2M HILL

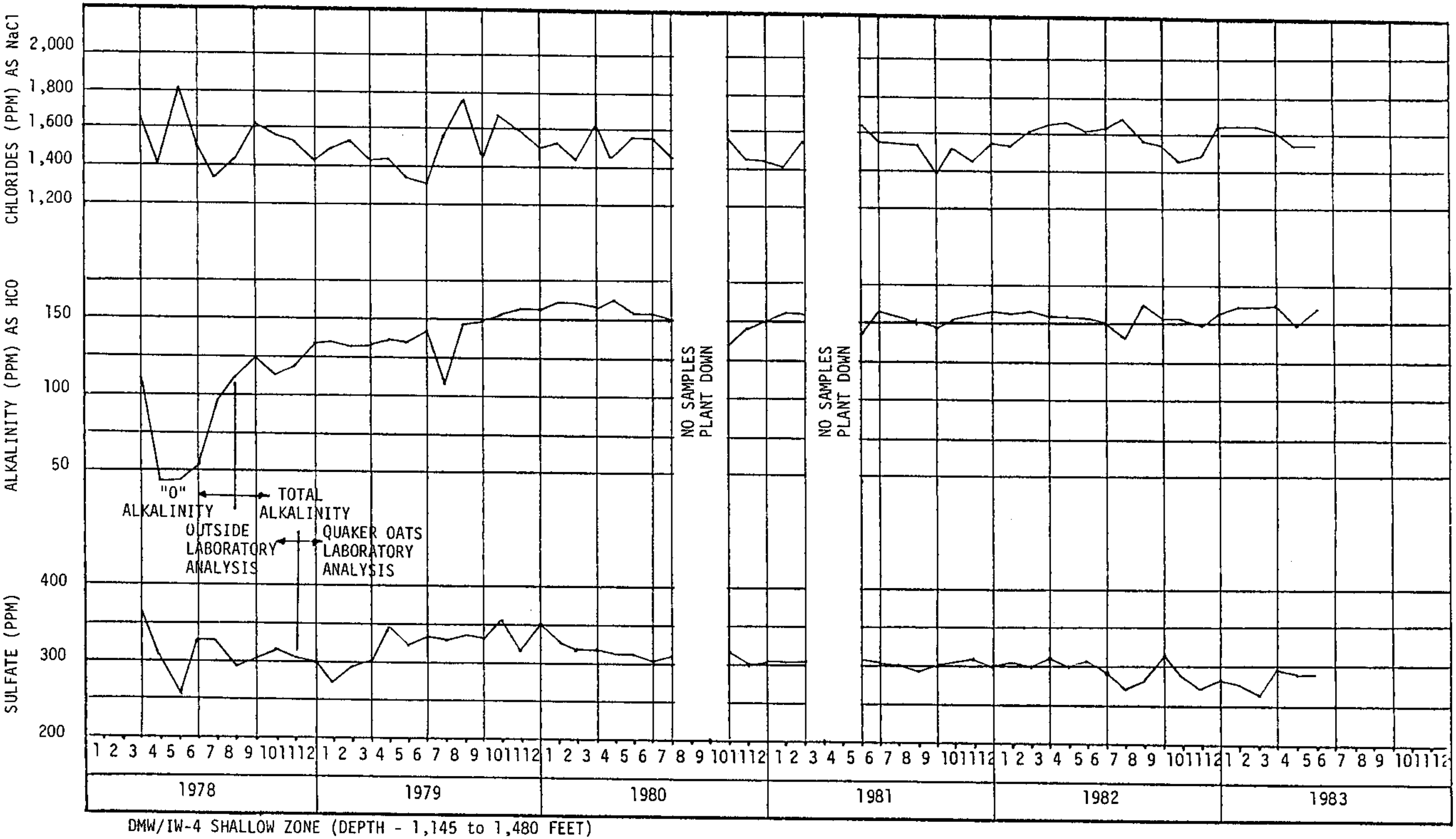


FIGURE G-5.
Monitoring Data.

CH2M HILL

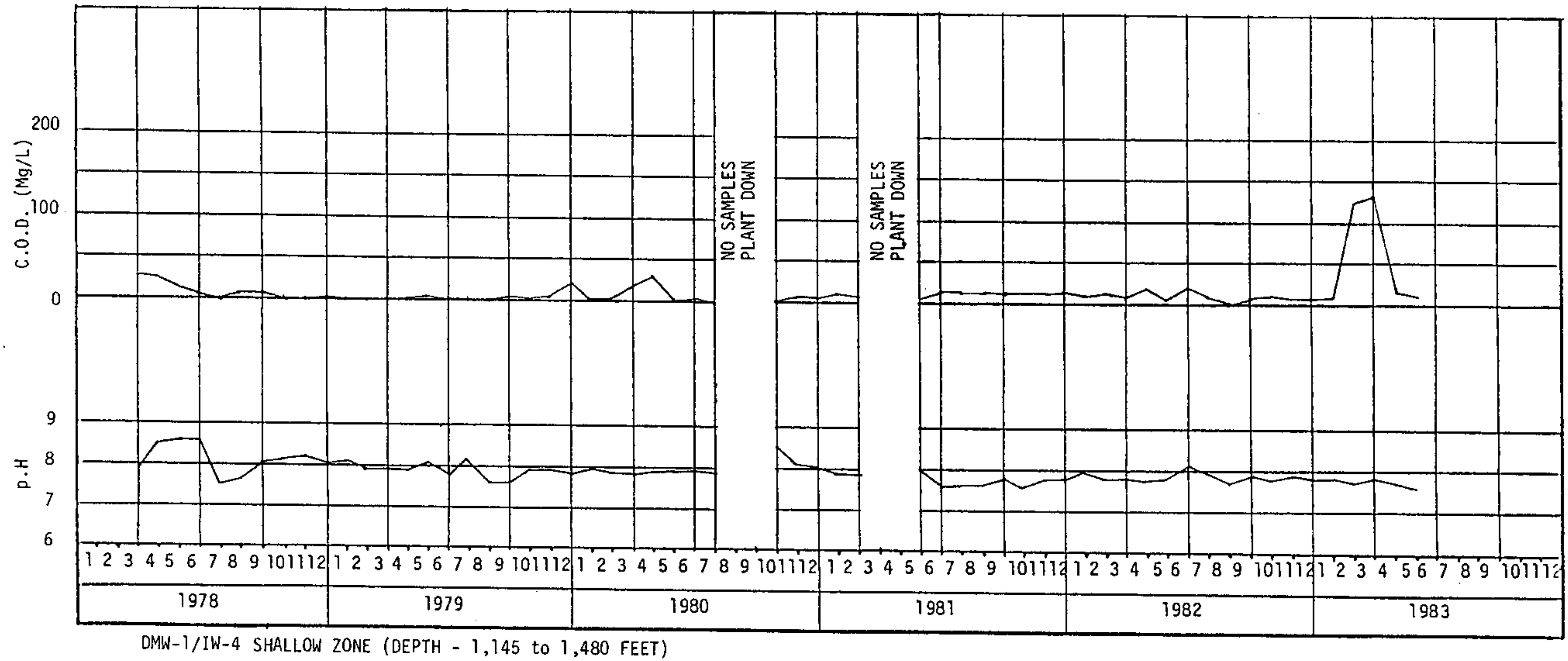


FIGURE G-6.
Monitoring Data.

CH2M HILL

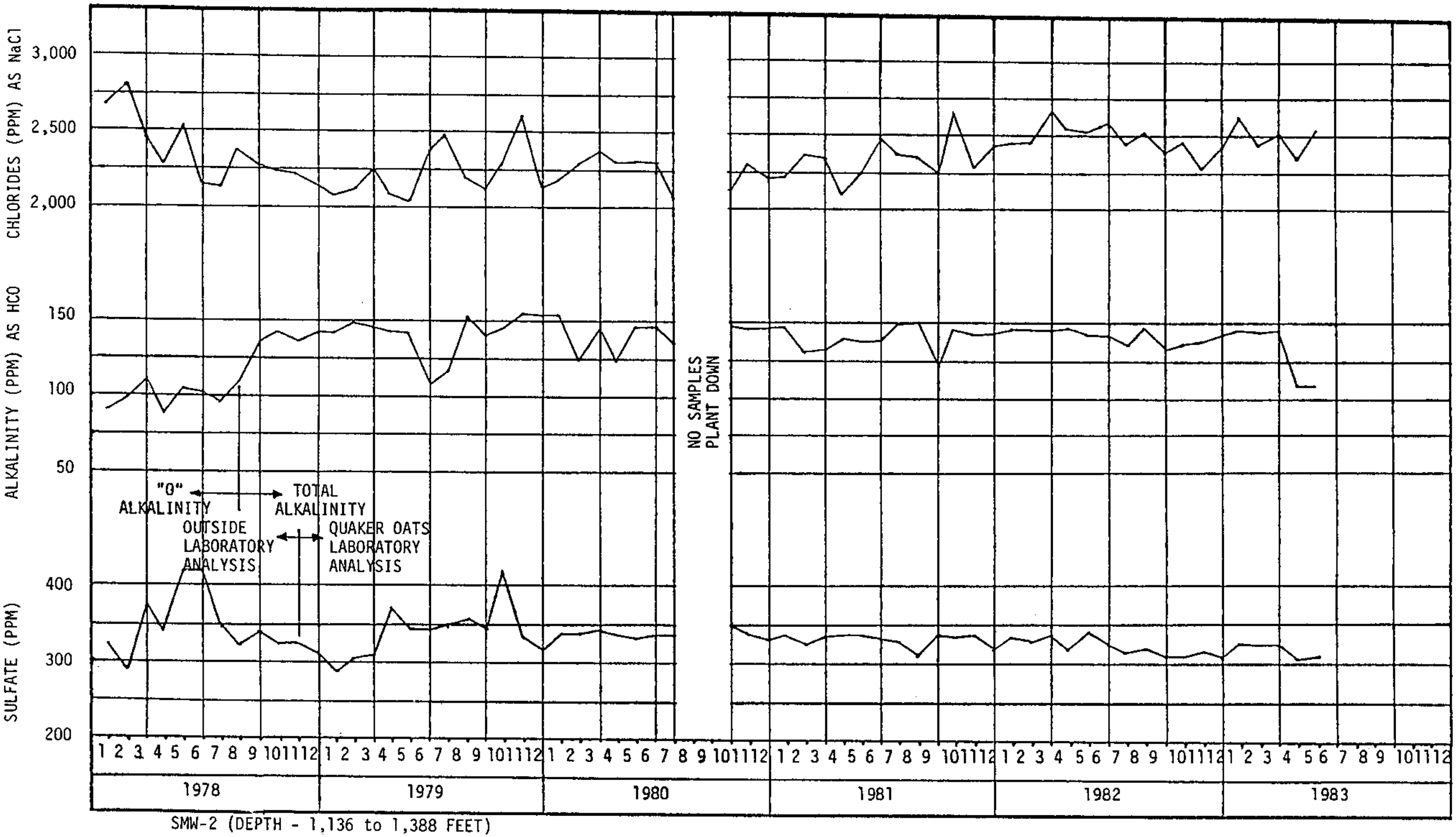


FIGURE G-7.
Monitoring Data.

CH2M HILL

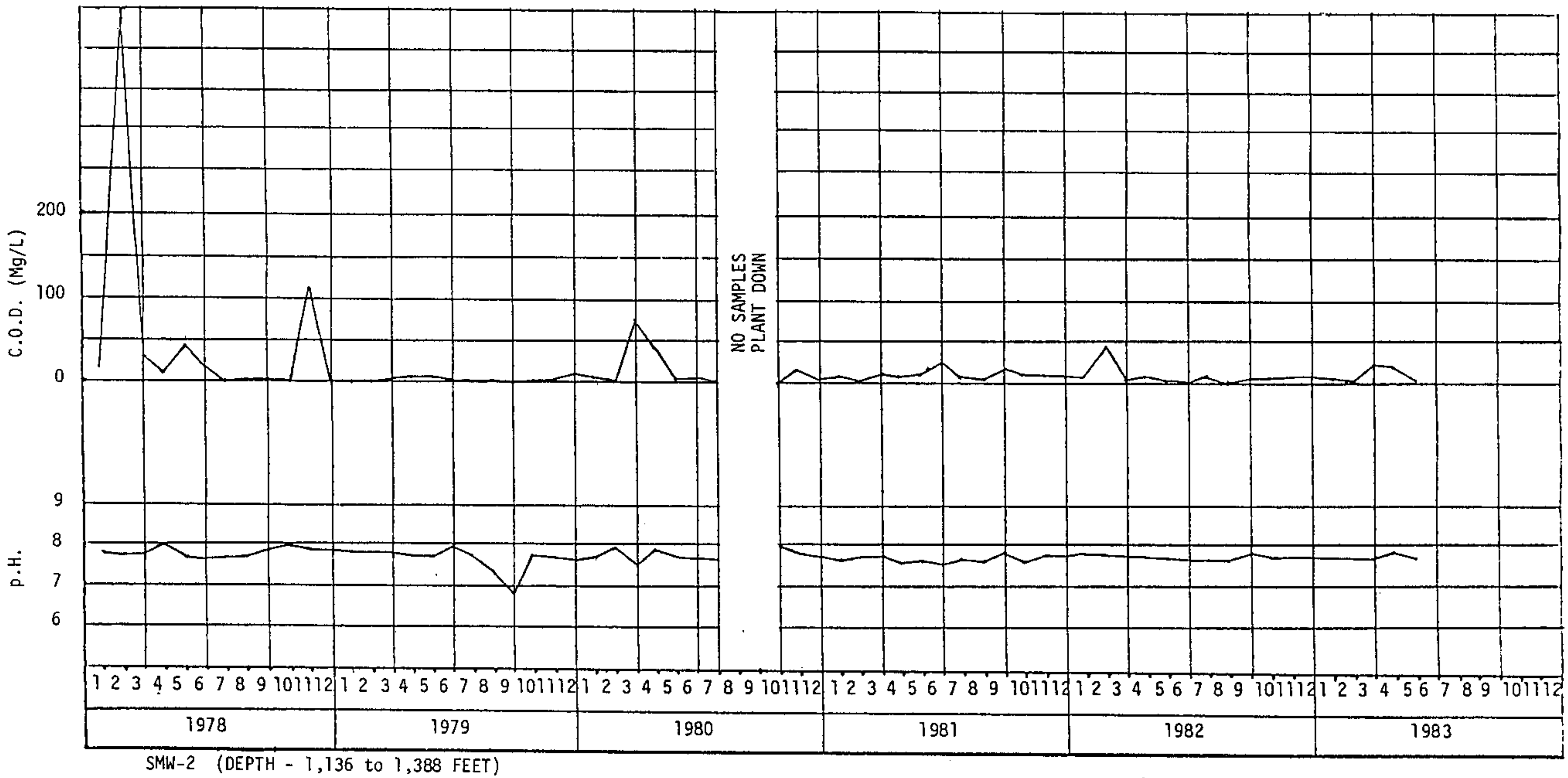


FIGURE G-8.
Monitoring Data.

CH2M HILL

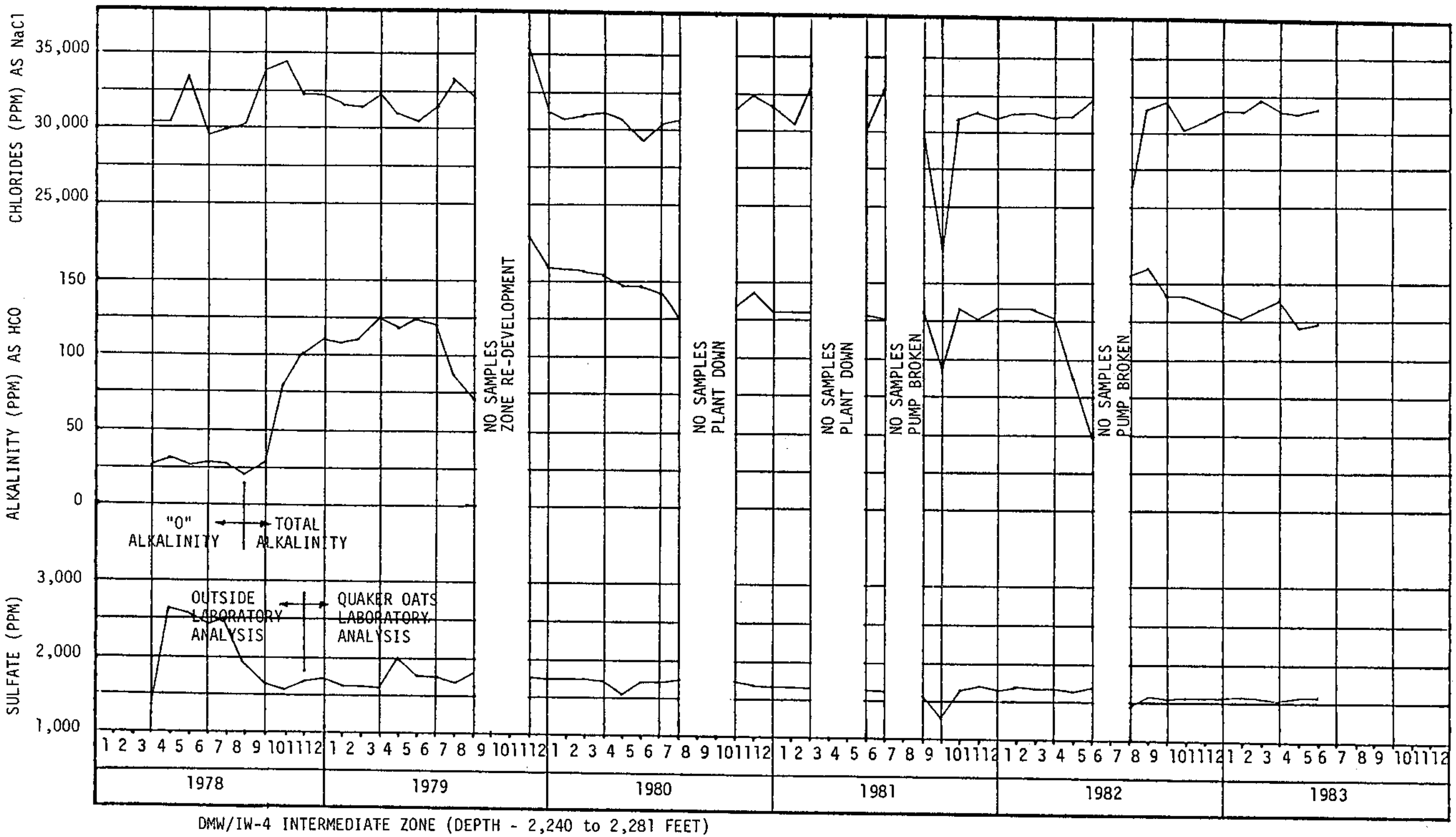


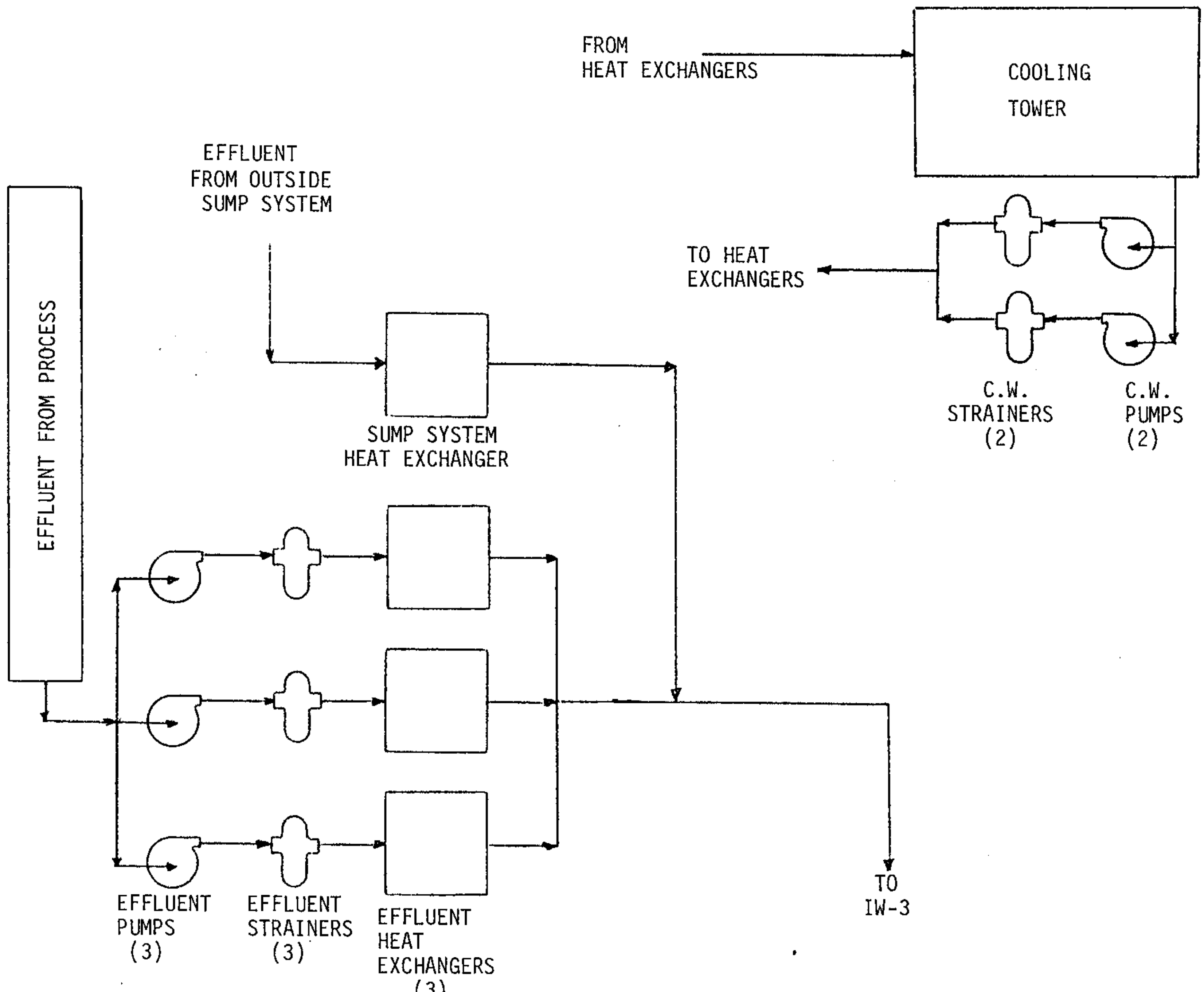
FIGURE G-3.
Monitoring Data.

APPENDIX H

DRAWINGS AND MAPS

DRAWINGS:

1. Disposal Well Cooling System Schematic Diagram (1)
2. IW-3 Wellhead (1)
3. DMW-1/IW-4 Wellhead and Monitoring Piping (2)
4. SMW-2 Wellhead (1)
5. Plat Plans Recorded with the Palm Beach County Property Records
6. Belle Glade Quadrangle

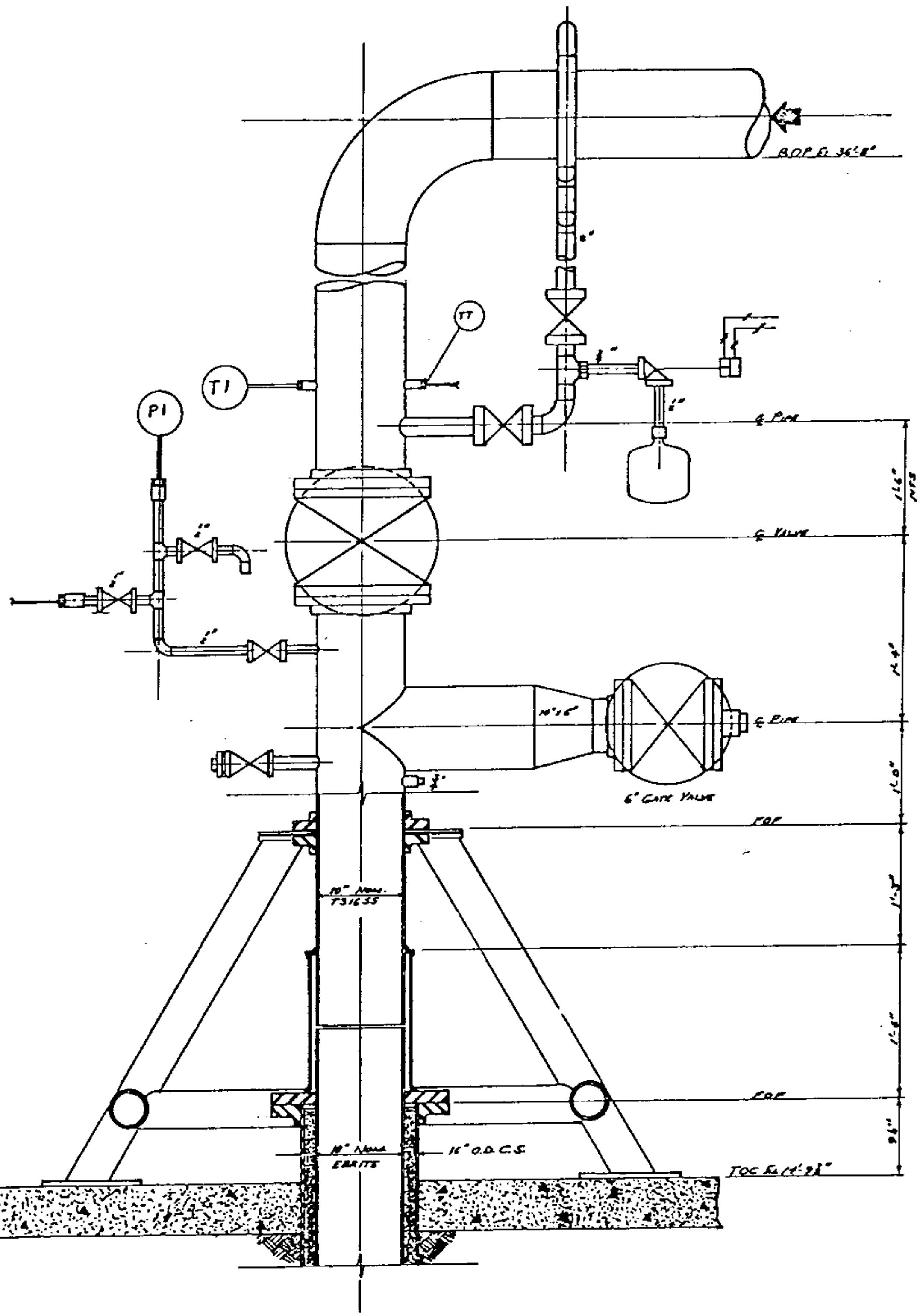


Issue	Date	By	Approved
0	8-2-83	JLC	

TITLE
DISPOSAL WELL COOLING SYSTEM
SCHEMATIC DIAGRAM

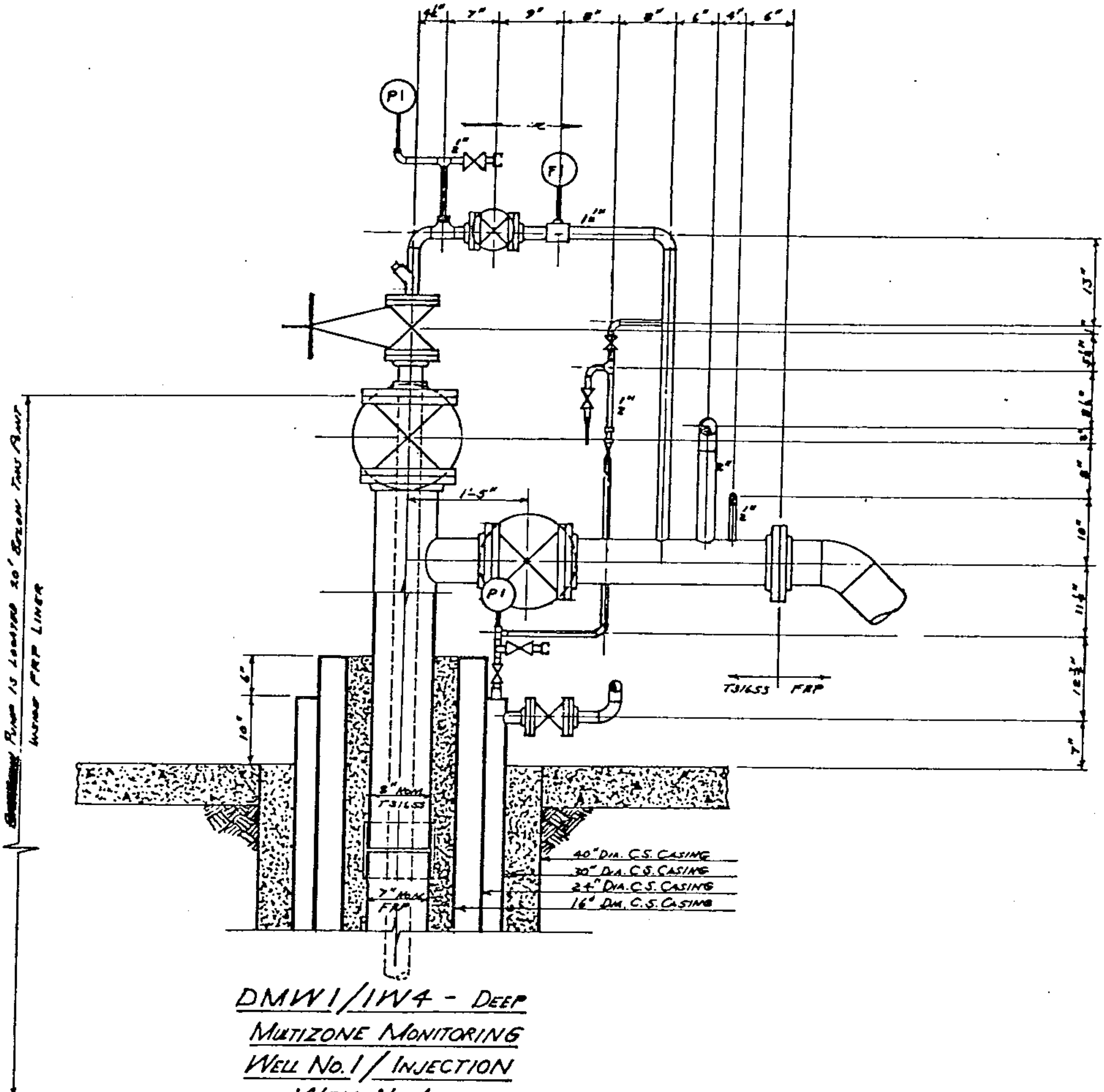
THE QUAKER OATS COMPANY
CHICAGO, ILL.

File No.
Sheet 1 of 1



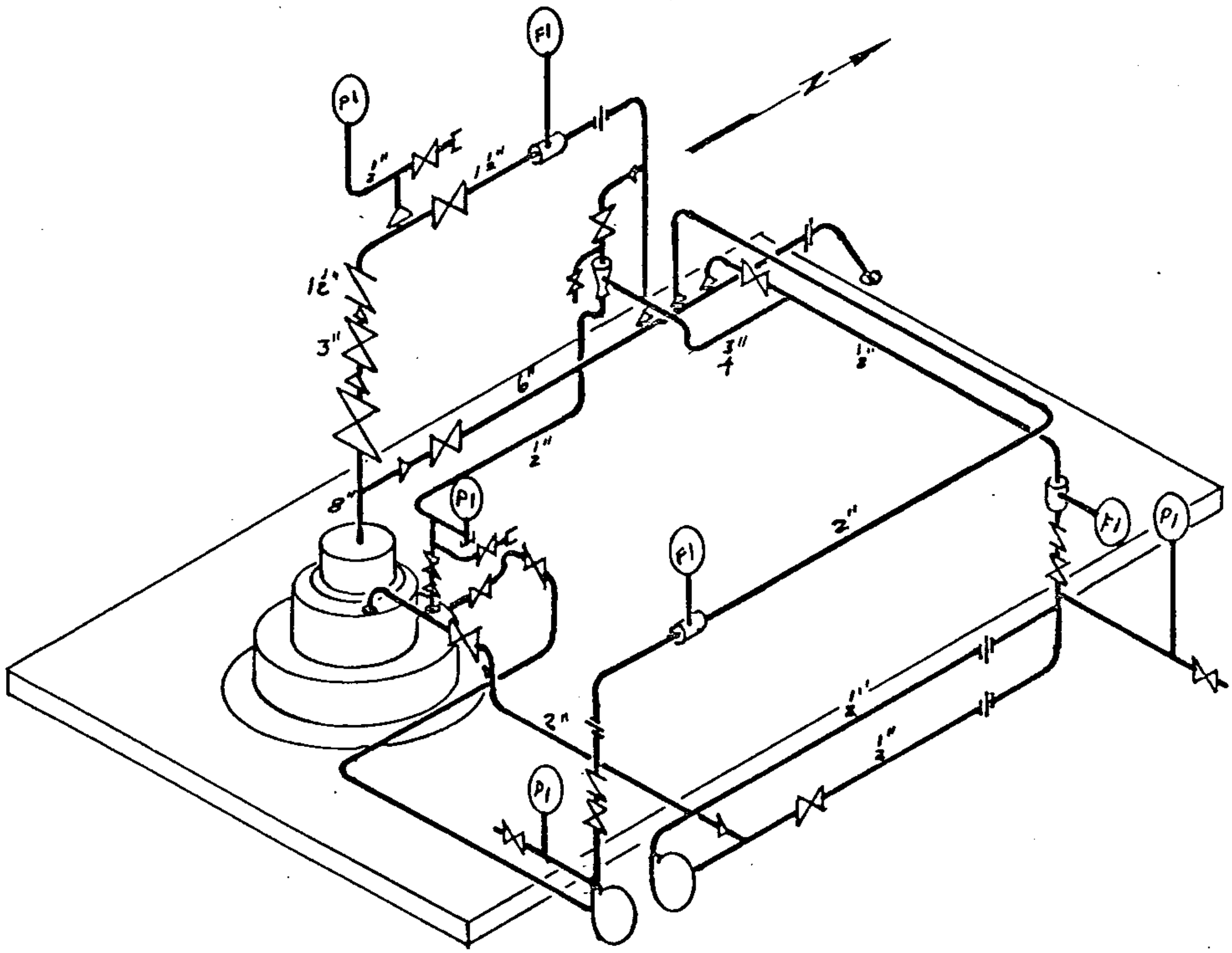
I/W 3 - Injection Well No. 3

SHEET 1 OF 1



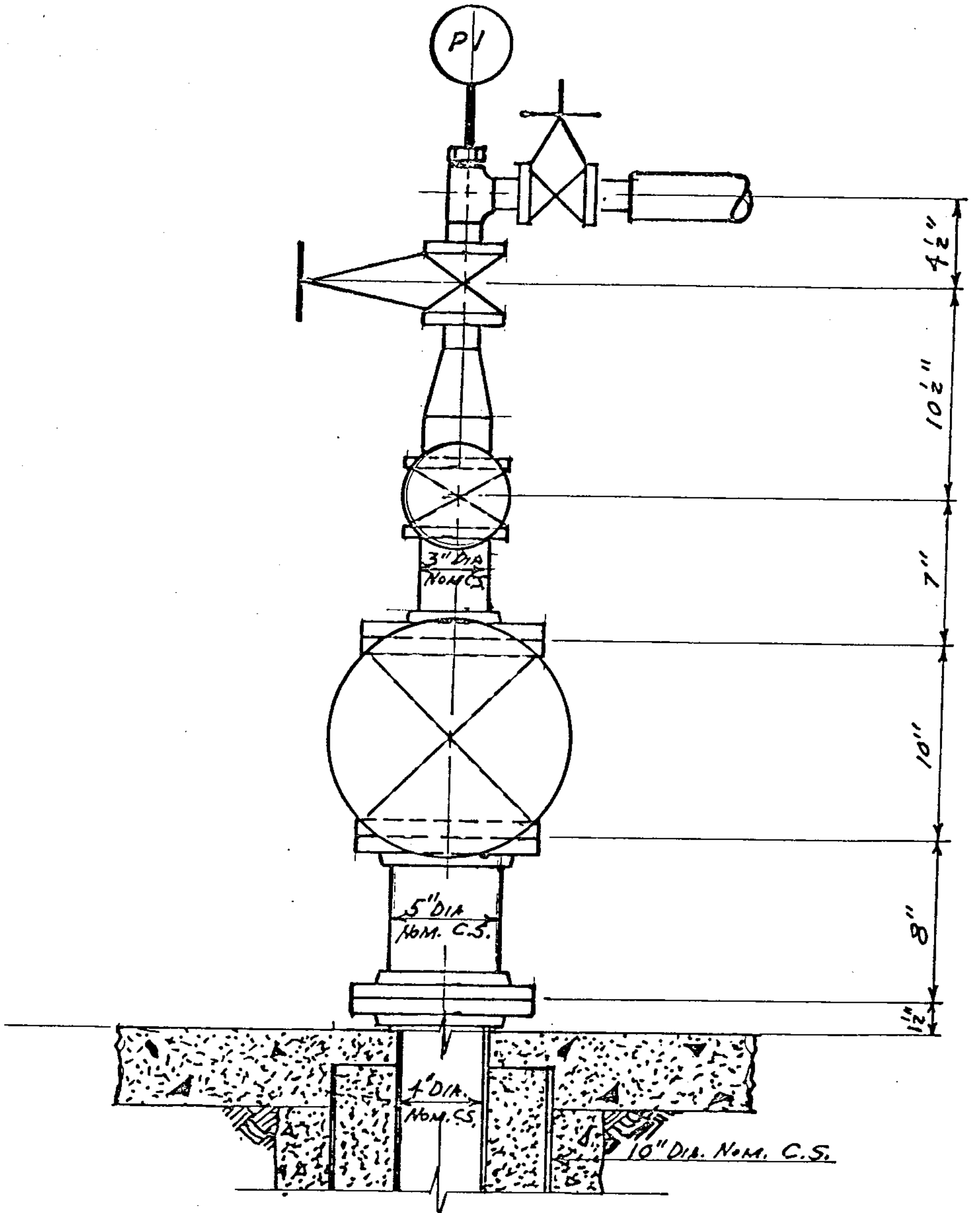
DMW1/IW4 - DEEP MULTIZONE MONITORING WELL No.1/ INJECTION WELL No. 4

SHEET 1 OF 2



DMW-1 / IW-4 Isometric View

SHEET 2 OF 2



SM/2 - SHALLOW
MONITORING WELL NO. 2

SHEET 1 OF 1

83 137185

1983 JUL 18 AM 9:25

AFFIDAVIT

STATE OF FLORIDA

COUNTY OF PALM PEACH

Personally appearing before me, FRANKLIN A. SHUTTS of HUTCHEON ENGINEERS, certifies that the information shown on the attached documents identified as Hutcheon Engineers Drawing No. 83-1-5200-00-041, was obtained under his direction and the information is true and correct to the best of his knowledge and belief.

This affidavit is being prepared in order to present the attached document in recordable form so it can be recorded in the County Courthouse property records.

Franklin A. Shutts
Reg. Land Surveyor
Fla. Cert. No. 2780

7/14/83 (SEAL)

STATE OF FLORIDA

COUNTY OF PALM BEACH

Sworn to and subscribed before me this 14th day of July, A.D. 1983

13.60

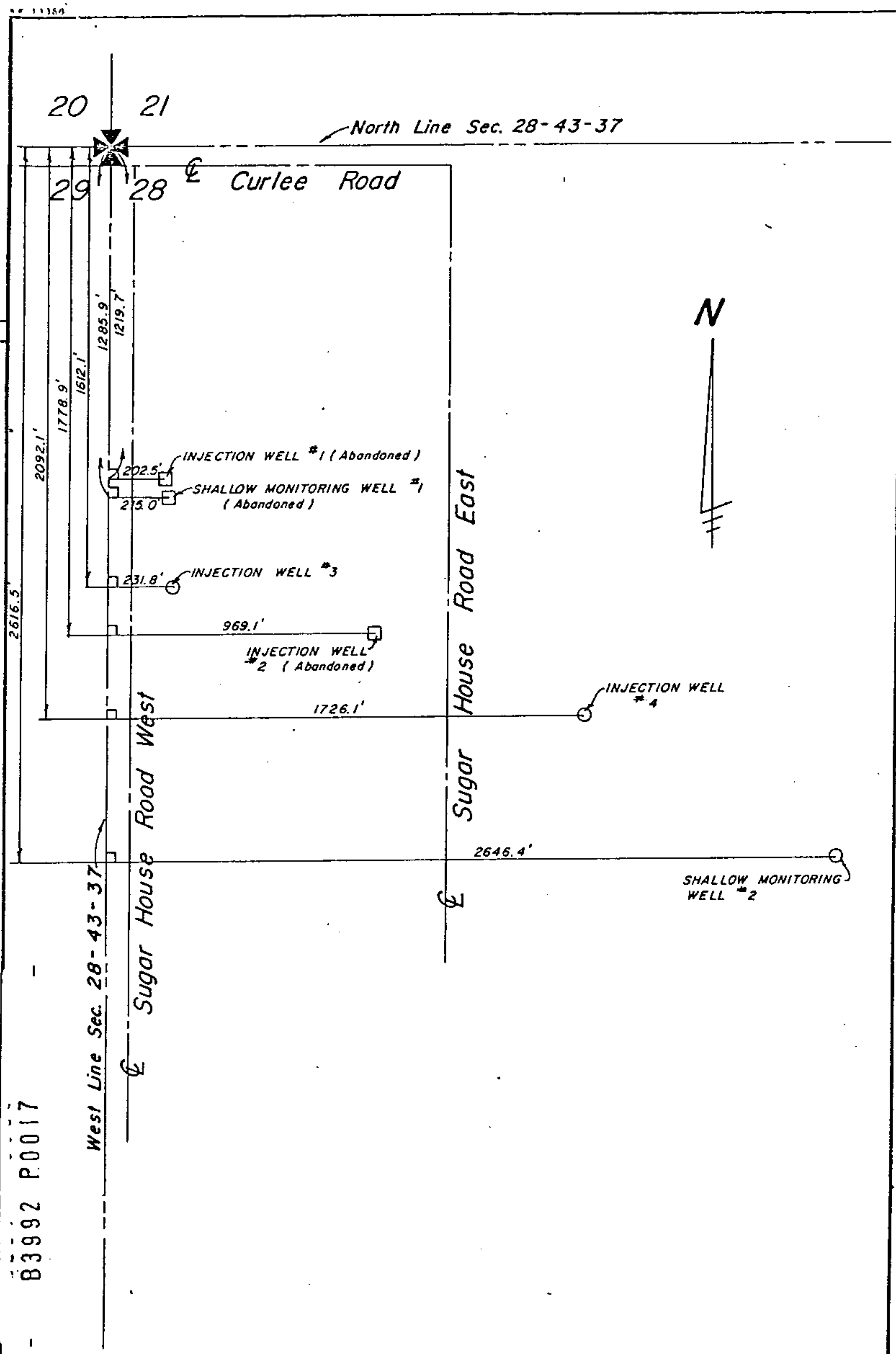
Notary Expires NOTARY PUBLIC STATE OF FLORIDA
MY COMMISSION EXPIRES NOV 16 1986
BONDED THRU GENERAL INSURANCE UND

Sandra E. Ferguson 7/14/83

(SEAL)

Jose Calais w/c

B3992 P0016



DSGN.	SCALE 1" = 40'	HUTCHEON ENGINEERS INCORPORATED	DATE 6-30-83	SHEET
DRW.	NOTEBOOK NO. PG.	CIVIL ENGINEERS & SURVEYORS	FILE & DRW. No. 83-1-5200-00-041	1 OF 2
		STUART WEST PALM BEACH BELLE GLADE		

DESCRIPTION FOR
QUAKER OATS

Being a description of the location of existing wells lying within Section 28, Township 43 South, Range 37 East, Palm Beach County, Florida, said existing well locations being more particularly described as follows:

INJECTION WELL NO. 1
Begin at the Northwest corner of said Section 28, thence run Southerly along the West line of said Section 28 a distance of 219.7 feet, thence at right angles to the preceding course run Easterly a distance of 202.5 feet to the centerline of the existing well.

SHALLOW MONITORING WELL NO. 1
Begin at the Northwest corner of said Section 28, thence run Southerly along the West line of said Section 28 a distance of 285.9 feet; thence at right angles to the preceding course run Easterly a distance of 215.0 feet to the centerline of the existing well.

INJECTION WELL NO. 3
Begin at the Northwest corner of said Section 28, thence run Southerly along the West line of said Section 28 a distance of 1612.1 feet; thence at right angles to the preceding course run Easterly a distance of 231.8 feet to the centerline of the existing well.

INJECTION WELL NO. 2
Begin at the Northwest corner of said Section 28, thence run Southerly along the West line of said Section 28 a distance of 1778.9 feet; thence at right angles to the preceding course run Easterly a distance of 969.1 feet to the centerline of the existing well.

INJECTION WELL NO. 4
Begin at the Northwest corner of said Section 28, thence run Southerly along the West line of said Section 28 a distance of 2092.1 feet; thence at right angles to the preceding course run Easterly a distance of 1726.1 feet to the centerline of the existing well.

SHALLOW MONITORING WELL NO. 2
Begin at the Northwest corner of said Section 28, thence run Southerly along the West line of said Section 28 a distance of 2616.5 feet; thence at right angles to the preceding course run Easterly a distance of 2646.4 feet to the centerline of the existing well.

I HEREBY CERTIFY that the information shown and described hereon was obtained under my direction on June 27, 1983.

I FURTHER CERTIFY that all measurements are true and correct to the best of my knowledge and belief.

Franklin A. Shutts 6/30/83
Franklin A. Shutts
Reg. Land Surveyor
Fla. Cert. No. 2780

RECORD VERIFIED
PALM BEACH COUNTY, FLA
JOHN B. DUNKLE
CLERK CIRCUIT COURT

DSGN.	SCALE	HUTCHEON ENGINEERS INCORPORATED	DATE 6/30/83	SHEET
DRW.	NOTEBOOK NO. PG.	CIVIL ENGINEERS & SURVEYORS	FILE & DRW. No. 83-1 5200-00 041	2 OF 2
CK.		STUART WEST PALM BEACH BELLE GLADE		