RECOMMENDATIONS ON TESTING PROCEDURES AT THE GLADYS MCCALL AND PLEASANT BAYOU GEOPRESSURED TEST WELLS

By

M. P. R. Light

Bureau of Economic Geology
W. L. Fisher, Director
The University of Texas at Austin
University Station, Box X
Austin, Texas 78713

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CONTENTS

Figures

Tables

ABSTRACT

Nine possible testing procedures for the Gladys McCall and Pleasant Bayou geopressured fields are listed. Evidence is presented that shows that reduction in salinity due to shale water addition to Gladys McCall formation waters can be measured over a 2-year period, but water analyses will need to be done under strictly controlled laboratory conditions. Sidetrack coring of geopressured reservoirs after production appears to be the most effective way of estimating total volumes of compaction and shale water recharge of geopressured formations. Sidetrack coring of the Andrau ('C') sandstone in the Pleasant Bayou No. 2 well will give the maximum amount of information on post-production changes in shales and sandstones.

Three preferred testing procedures are suggested in order of decreasing scientific payback and cost. The best testing procedure is to continue testing the Gladys McCall well for 2 years, then to cut a sidetrack core and plug and abandon the well. At the same time, a sidetrack core must be cut in the Pleasant Bayou well and this well plugged and abandoned. Total cost of these tests will be several million dollars. The next best testing procedure that will give a large scientific payback is to cut sidetrack cores and then plug and abandon both the Gladys McCall and Pleasant Bayou wells at a cost of about $1.1 million. The last testing procedure, which will also give a large scientific payback, is to cut a sidetrack core and plug and abandon Pleasant Bayou, and plug and abandon Gladys McCall at a cost of about $600,000.

INTRODUCTION

The purpose of the geopressured-geothermal program is to develop a set of parameters that will enable private industry to determine the economic viability of a geopressured field using production data from a single test well. However, application of standard reservoir engineering techniques to data gathered from the Gladys McCall geopressured reservoir results in reservoir size estimates several times larger than geological estimates (Pritchett and Riney, 1985). Though simulation models based on the reservoir limits test were found to be in good agreement with bottomhole pressures during the first 6 months of production testing at Gladys McCall, the reservoir volume had to be increased by a factor of three to adequately match the production history through September 1984 (Pritchett and Riney, 1985).

Many sources for this excess water have been suggested, but shale-water recharge of permeable sandstones during production-induced pressure drawdown (Fowler, 1970; Riney and Garg, 1985), rock compaction (Hamilton and Stanley, 1984), or leaking faults (Fowler, 1970) are the most likely sources of the waters.

ESTIMATION OF SOURCES OF GEOPRESSURED WATERS

At the present time there is no accurate way of estimating the volume of water added to a geopressured reservoir by shale dewatering, rock compaction, and leaking faults. The geological estimate of the size of geopressured reservoir using standard reservoir engineering parameters can be represented by a block (fig. 1-1) consisting of sand grains, pore water, compaction water, and water that will be mobilized (M) during production. For a production period from time $T = 0$ to $T = t$, a volume of water equal to (a) should theoretically be produced (fig. 1-1).

In geopressured reservoirs, additional water is added because of the reduction of reservoir volume owing to compaction (C), shale water recharge (S), and the introduction of deep waters via faults (B) (fig. 1-2). As a result of these additions, the amount of water produced during a production period ($T = 0$ to $T = t$) will be

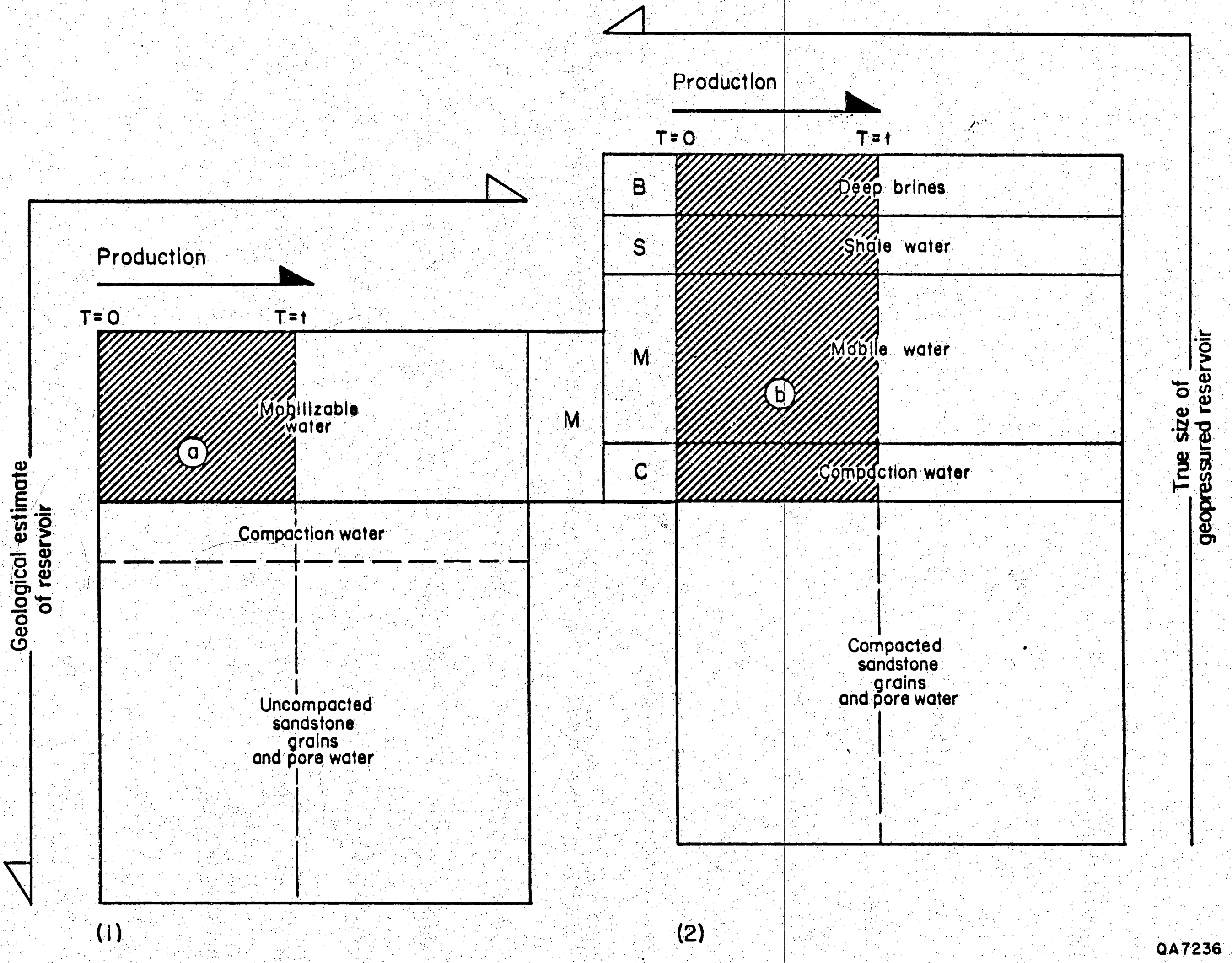


Figure 1. Geological estimate of geopressured reservoir size (1-1) using standard reservoir engineering parameters compared to the true size of a geopressured reservoir (1-2) by considering the addition of deep brines, compaction, and shale waters.

increased to (G) (fig. 1-2). If the volume of compaction water and shale water recharge can be measured during a production period (T = 0 to T = t), then the volume of deep brine that has invaded the reservoir along leaking faults can be estimated:

Let Wt = total formation water production at time T = t

$$Wt = Mt + Ct + St + Bt$$

Where

Mt = produced mobile water estimate at time T = t using standard reservoir engineering methods with known reservoir porosity, size, and pressure drawdown

Ct = Produced compaction water at time T = t estimated from measured compaction in sidetrack core

St = Produced shale water at time T = t estimated from pyrolysis and compaction studies of shales, salinity studies of waters in shales, and amounts of decrease in formation water salinities during production

Bt = Produced deep brines that have invaded the reservoir along leaking faults.

Then:

$$Bt = Wt - (Mt + Ct + St)$$

All unknowns on the right side of the latter equation can be estimated so that the value of Bt can be calculated. Hence, all parameters should now be available to calculate the true production capacity of a geopressured reservoir.

METHODS OF DETECTING DIFFERENT FORMATION WATERS

Leaking Faults

Saline brines leaking into reservoirs along fault planes from adjacent fault blocks can be detected only by slight increases in the salinity of formation waters (Fowler, 1970). These effects will not be visible in the relatively short production tests conducted at geopressured wells.

Rock Compaction

Rock compaction during production helps to maintain reservoir pressure by mobilizing pore water during pore-space reduction in overpressured reservoirs. The degree of rock compaction that has occurred in a reservoir during production can be directly estimated only by comparing the change in sandstone thickness and porosity before and after production. Thickness changes can best be measured by cutting a sidetrack core through the entire geopressured reservoir unit at a distance from the cased hole. Near the hole, compaction has been resisted by the casing reinforcing the strata. This is also a region having large changes in pressures and hence variable degrees of compaction during production.

Electric logs run in the sidetrack hole and direct thickness measurements of the sandstone unit will give the percentage of compaction the reservoir has undergone. Very accurate directional surveys will need to be run in the sidetrack hole so that hole orientation can be corrected for in the estimate of cored thickness. Porosities and permeabilities of the sandstone in the sidetrack core can be compared to those of cores cut before production and the percentage of compaction can be estimated. Porosity reductions of 7 to 10 percent were found in experimentally compacted sandstones from the Hitchcock N. E. field (Light, in press). Experimentally compacted sandstones from the pre-production core can be directly compared to those in the sidetrack core to accurately estimate the type and degree of compaction. Measurement of the sandstone thickness and porosity reduction will allow an estimate to be made of the volume of water added to the reservoir by compaction.

Shear fractures caused by the increased lithostatic stress during production induced pressure drawdown (Light, in press) should be searched for in the sidetrack core (fig. 2). These shear fractures may act as conduits guiding fluids to the wellbore and could explain the relatively high permeability of geopressured sandstones after long periods of production.

Shale Dewatering

Shale water recharge of permeable sandstones during production (Riney and Garg, 1985) helps to maintain reservoir pressure during production by adding more water to overpressured reservoirs from adjacent shales. Decreases in the salinity of formation waters during production result from the dilution of original formation waters by waters squeezed out of the shales (Fowler, 1970). Accurate measurement of the

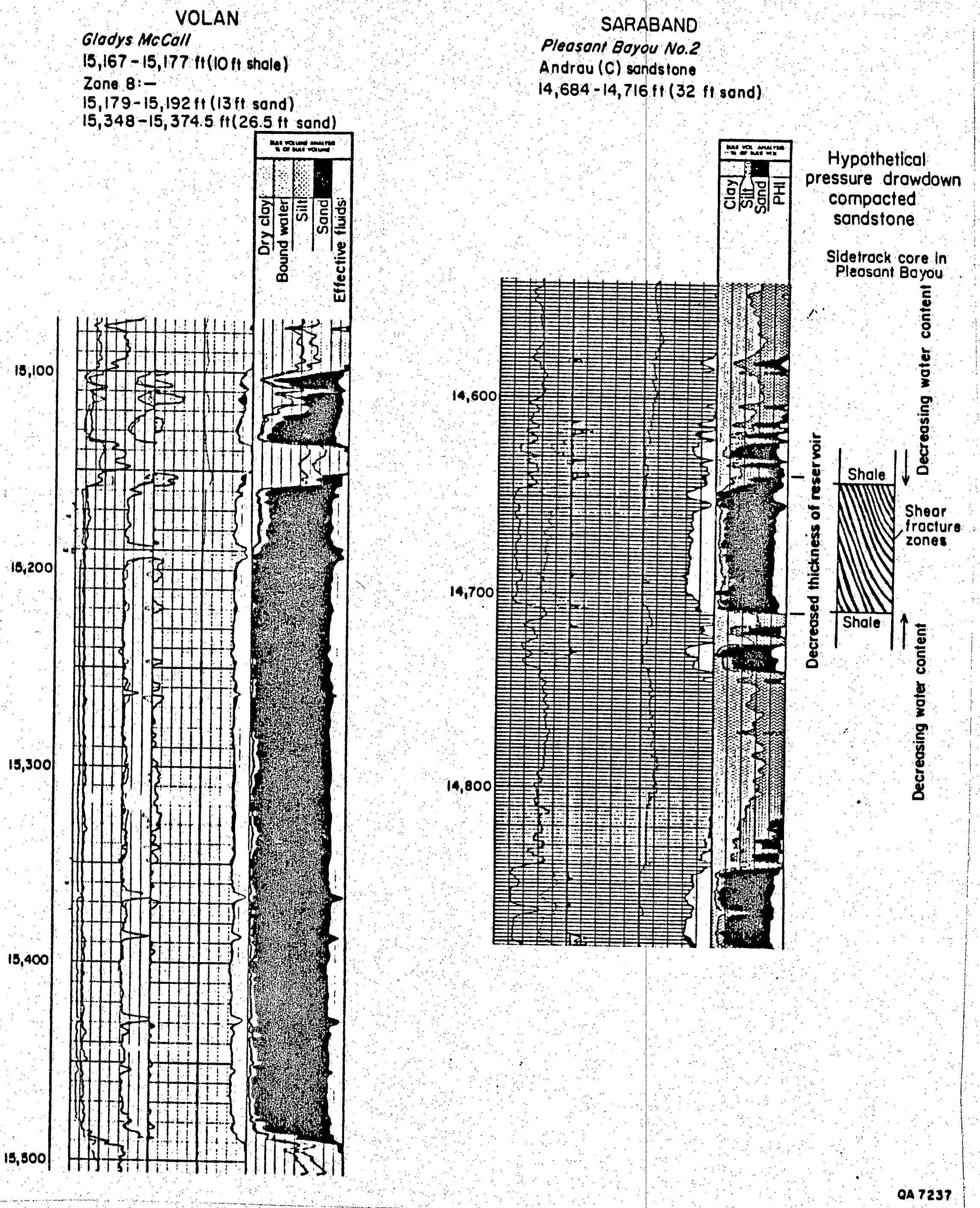


Figure 2. Computer processed electric logs of the geopressured reservoir intervals at the Gladys McCall No. 1 and Pleasant Bayou No. 2 wells compared to a hypothetical 100-ft (30.5-m) sidetrack core. Uncompacted and experimentally compacted sandstones from the Frio 'A' reservoir, Hitchcock N. E. field are shown with porosity reduction data and probable trends of pressure-drawdown-induced shear fracture systems (Light, in press).

chloride content of formation waters during long periods of production should allow an estimate to be made of the volume of shale water being added to the formation water. Additional confirmatory evidence can be obtained by cutting a sidetrack core through the sandstone reservoir and its bounding shale units (fig. 2). Water content of the shale adjacent to and at various distances from the sandstone can be measured by a pyrolysis method, and a compaction gradient can be constructed for the shales adjacent to the reservoir. A decreasing water content toward the reservoir will indicate the total amount of shale water loss (fig. 2). In addition, the salinity of the shale waters can be measured and used to compute the volume of shale water that had to be added to the formation waters to cause the salinity decline. The salinity of shale water can be obtained by perforating and testing shale horizons during cross-flow perforation tests and accurately analyzing the composition of produced waters.

The most effective method of estimating the volume of compaction and shale waters added to formation waters during production is to measure the salinity decline in a reservoir over time, perforate and produce shale waters from an overpressured shale horizon, and cut a 100-ft (30.5-m) sidetrack core through an entire geopressured reservoir sequence and its adjacent shales.

HISTORICAL ESTIMATES OF SALINITY VARIATIONS

Fowler (1970) has estimated the percentage change in chloride concentration over a 28-year period using 94 water analyses from Frio sandstones in the Chocolate Bayou field, Brazoria County, Texas (table 1). The percentage change in chloride ion concentration over this period has been converted to a percent change per year (table 1).

Table 1. Historical estimates of salinity variation in the Chocolate Bayou field, Brazoria County, Texas (after Fowler, 1970).

East Chocolate Bayou

Reservoir	Sampling Dates From	Sampling Dates To	Percent Cl Change	Production Period in Years	Percent Cl Change Per Year
Frio A	5-1-46	12-16-64	-12.4	18.63	-0.67
Alibel	12-18-56	3-27-68	-33.0	11.27	-2.93
U. Hou. Fms.	6-23-42	4-11-68	+2.3	26.37	+0.087
L. Hou. Fms.	12-18-56	11-24-64	-31.8	7.93	-4.01
Rycade	10-26-56	12-16-64	-28.0	8.14	-3.44
Banfield	4-16-52	12-16-64	-16.6	12.59	-1.32
U. Weiting	12-16-64	4-11-68	-6.3	3.89	-1.62
L. Weiting	12-16-64	3-27-68	-8.5	3.28	-2.59
"S"	12-18-56	4-11-68	+0.8	11.32	+0.07

West Chocolate Bayou

Reservoir	Sampling Dates From	Sampling Dates To	Percent Cl Change	Production Period in Years	Percent Cl Change Per Year
Frio A	9-1-46	4-11-68	-6.0	21.61	-0.28
Frio B	6-15-46	4-11-68	-0.5	21.83	-0.02
Frio C	7-16-47	4-11-68	+0.7	20.74	+0.03
Andrau	5-7-40	12-18-56	-42.3	16.45	-2.57

The most common pattern is decreasing salinity with time, which results from dilution of the original formation waters by fresher waters squeezed out of the shales adjacent to the aquifers (Fowler, 1970). The Lower Houston Farms sandstone in the East Chocolate Bayou field shows the largest decline in chloride concentration of -4.01 percent/year, whereas the chloride concentration fell by some 2.57 percent/year in the Andrau ('C') geopressured sandstone in the West Chocolate Bayou field (table 1, fig. 3). The mean rate of chloride concentration decline estimated from all the data is -1.48 percent/year.

Some sandstone reservoirs (Upper Houston Farms, 'S' and Frio C) showed slight increases in chloride content ranging from +0.087 to +0.03 percent/year, which results from water encroachment across faults from more saline aquifers in adjacent fault blocks (Fowler, 1970).

Standard laboratory methods of estimating the chloride content of formation waters have relative standard deviations (coefficient of variation) of 1.7 percent (S. W. Tweedy, personal communication, 1986). For chloride concentrations of 58,000 mg/L (Gladys McCall), chloride estimates will be within 1,000 mg/L, whereas for higher values (79,000 mg/L, Pleasant Bayou) estimates will be within 1,350 mg/L of the actual value. Analyses of chloride contents of brines using the new kit designed by researchers at Rice University have a precision of some 2 to 5 percent (M. B. Tomson, personal communication, 1986). At the 5 percent level, chloride concentration estimates for the Gladys McCall well will be within 2,900 mg/L, whereas for Pleasant Bayou waters they will be within 4,000 mg/L.

The mean rate of chloride concentration decline from historic data (Fowler, 1970) is -1.48 percent/year, in contrast to -2.57 percent/year for the Andrau ('C') geopressured sandstone (table 1, fig. 3). We can therefore expect a rate of decline in the chloride content of formation waters at the Gladys McCall well of 1.5 to

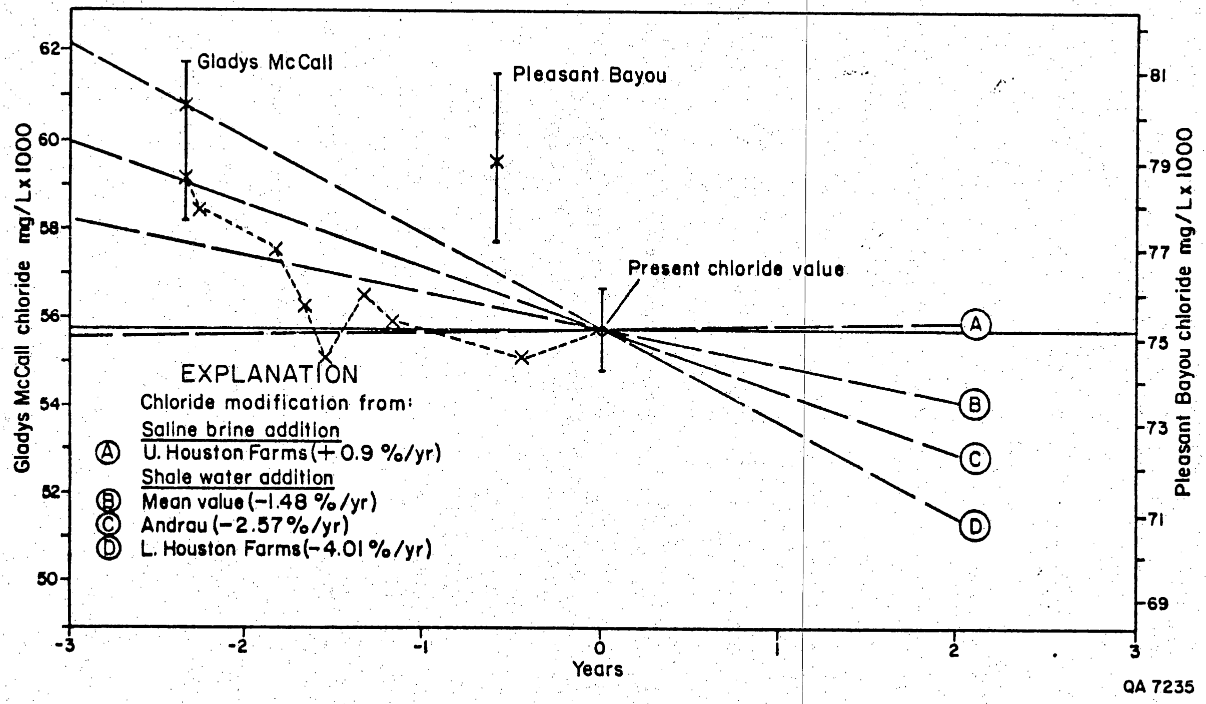


Figure 3. Diagram showing known range of variation of chloride content of formation waters with time for both saline brine and shale water addition (after Fowler, 1970). Measured chloride values for the Gladys McCall and Pleasant Bayou geopressured wells are compared to present chloride values (Goldsberry, 1981; Rodgers, 1983; Sloan, 1983; Tomson and Matson, 1985).

2.5 percent/year (fig. 3). If the Gladys McCall well is produced for 2 years, the chloride content of the formation waters should decline by 3 to 5 percent (1,740 to 2,900 mg/L) (fig. 3). This reduction in the chloride concentration in the formation waters will be visible only if the samples are analyzed in one laboratory under accurately reproducible conditions where the coefficient of variation (1.7 percent) is less than the total variation (3 to 5 percent). The precision of field measured salinities will probably mask any true chloride concentration variations.

The slight increases in chloride content (+0.03 to +0.09 percent/year) due to water encroachment from more saline aquifers in adjacent fault blocks (Fowler, 1970) will not be visible during the proposed 2-year production test at the Gladys McCall well (fig. 3). This well must be produced for 19 years before the salinity increase (0.09 percent/year) will exceed the coefficient of variation (1.7 percent) of the most accurately reproducible laboratory estimates.

GEOPRESSURED FORMATION WATER SALINITY ESTIMATES

The Andrau ('C') geopressured sandstone has produced in excess of 3.5 million barrels of brine in 0.53 years production between September 1982 and April 1983 (Blumhardt, 1983). Chloride concentrations of formation waters at the beginning of production averaged around 79,000 mg/L (Kharaka and others, 1979; Goldsberry, 1981; Rodgers, 1983). More recent analyses give the formation waters a salinity of 75,200 (Tomson and Matson, 1985). This is a larger salinity decrease than was reported by Fowler (1970) over a 16.5-year production period for the Andrau sandstone in the West Chocolate Bayou field, and it may result largely from different analytical techniques that masked the actual salinity decline.

The Zone 8 sand has been tested for more than 1.5 years, during which time the chloride content has apparently fallen from 59,290 mg/L (January 1984) to 57,700 (September, 1986) (Sloan, 1983; Tomson and Matson, 1985; Randolph, 1986), a 1.8 percent/year decline. However, the reduction in chloride content in the Gladys McCall waters is similar to the trend estimated by Fowler (1970) for the Andrau ('C') (2.57 percent/year) and Lower Houston Farms (4.01 percent/year) reservoirs (fig. 3). Furthermore, the trend of chloride reduction for the Gladys McCall well (dotted line on fig. 3) mimics the pressure drawdown curves between the fourth quarter of 1983 and the fourth quarter of 1985, during which time the gas/water ratio remained fairly constant. This indicates that this salinity decline is a result of shale dewatering, a conclusion that will be discussed in more detail in a forthcoming report. Two formation water samples from the Zone 8 sand collected in October 1983 and December 1986 have been reanalyzed at Rice University (M. B. Tomson, personal communication, 1987). The October 1983 sample contains 2.4 percent more chloride than does the original analysis, which probably results from water loss or evaporation during storage. The December 1986 sample contains 0.6 percent less chloride than does a sample analyzed in September 1986 (Randolph, 1986) and represents a 1.9 percent/year decline in chloride content.

A solution to this real problem is to reanalyze all formation water samples from the Gladys McCall well for chloride at one laboratory under strictly controlled conditions so that any slight decline in the salinity will become visible. The error in reanalyzing waters stored for 3 years (2.4 percent) is less than the probable reduction in chloride content at the Gladys McCall well over a 2-year testing period (4 percent). Formation water samples from the Gladys McCall well are currently stored at Rice University (M. B. Tomson, personal communication, 1987). The current cost of reanalyzing samples for chloride is $8 per sample (see appendix).

ALTERNATIVE CORING PROCEDURES

Cost limitations (tables 2 and 3) (C. R. Featherstone, personal communication, 1986) limit the maximum length of the sidetrack core that could be cut at the Pleasant Bayou or Gladys McCall wells to 100 ft (30.5 m). A core of this length in the Pleasant Bayou test well cut from 14,620 ft to 14,720 ft (4,456 m to 4,487 m) would sample at least 10 ft of shale above the reservoir, the entire Andrau reservoir sandstone, and 10 ft of shale below the reservoir (fig. 2, table 4). Two separate cores (stored at the Bureau of Economic Geology) have already been cut in the Andrau sandstone at the Pleasant Bayou No. 1 and No. 2 wells prior to production; they are 17 ft and 32 ft (5 and 10 m) long (fig. 2, table 4). Detailed porosity and permeability measurements are available on the cores (Morton and others, 1983), and direct comparison with post-compaction sidetrack cores is possible. Pressure coring is not required, as it is the rock fabric and not the fluid content of the reservoirs that needs to be investigated.

One 100-ft sidetrack core could be cut in the Gladys McCall well through the sand-shale-sand sequence at the top of the Zone 8 sandstone between 15,180 ft and 15,280 ft (4,627 m to 4,657 m) (fig. 2, table 4). However, this core will examine only one bounding shale and about 27 percent of the Zone 8 sand, which is about 340 ft (104 m) thick. A 10-ft (3-m) shale core (15,167 ft to 15,177 ft; 4,623 m to 4,626 m) and a 13-ft (4-m) sandstone core (15,169 ft to 15,192 ft; 4,624 m to 4,631 m) cut at the Gladys McCall well prior to production are available in this interval (fig. 2, table 4). A 26.5-ft (8-m) sandstone core was also cut in the Zone 8 sandstone between 15,348 ft (4,678 m) and 15,375 ft (4,686 m) (fig. 2, table 4). An alternative coring scheme would be to cut two 50-ft cores through the top and bottom of the Zone 8 sandstone and adjacent shales, but this would require redrilling all 340 ft (104 m) of the Zone 8 sandstone.

Table 2. Budget estimate to cut a sidetrack core at the Pleasant Bayou test well.

Phase 1

Clean out well
Replace water with mud
Drill out packer
Set cement plug over perforations

Estimated cost: $180,500

Phase 2

Set packer and whipstock at 14,100 ft
Sidetrack
Cut core from 14,620 to 14,720 ft

Estimated cost: $235,000

Phase 3

Plug well and abandon

Estimated cost: $ 75,000

Contingencies: $ 19,500

<u>Total estimated cost:</u> <u>$510,000</u>

Table 3. Budget estimate to cut a sidetrack core at the Gladys McCall test well.

Phase 1

Clean out well
Replace water with mud
Set cement plug over perforations

Estimated cost: $273,000

Phase 2

Set packer and whipstock
Sidetrack
Cut core from 15,180 to 15,280 ft

Estimated cost: $235,000

Phase 3

Plug well and abandon

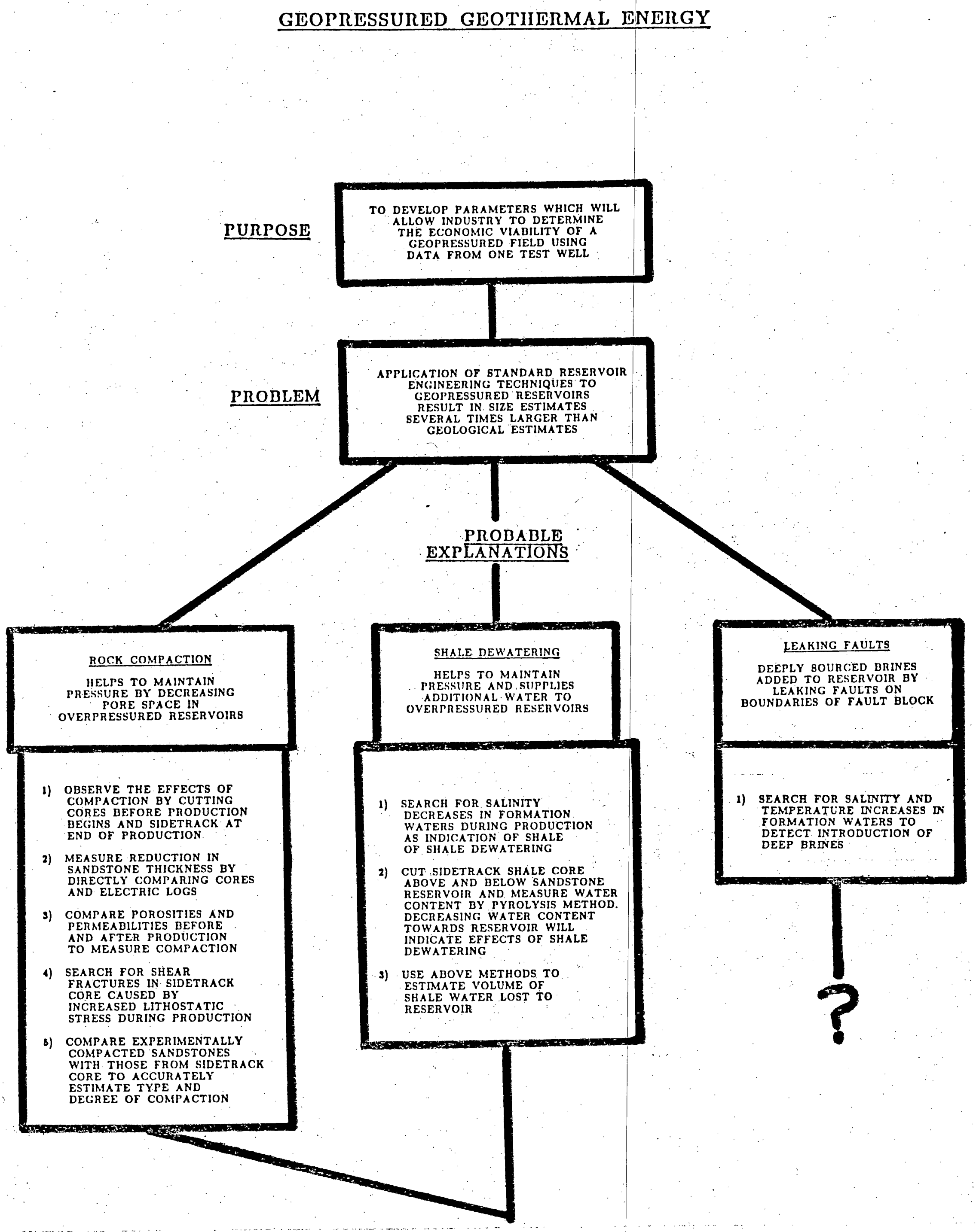
Estimated cost: $ 75,000

Contingencies: $ 19,500

Total estimated cost: $602,500

Note: Cost of cleaning out the well could be higher because of the state of the tubing and scale.

Table 4. Logic flow chart comparing coring procedures at the Gladys McCall and Pleasant Bayou test wells.



TO DEVELOP PARAMETERS WHICH WILL ALLOW INDUSTRY TO DETERMINE THE ECONOMIC VIABILITY OF A GEOPRESSURED FIELD USING DATA FROM ONE TEST WELL

APPLICATION OF STANDARD RESERVOIR ENGINEERING TECHNIQUES TO GEOPRESSURED RESERVOIRS RESULT IN SIZE ESTIMATES SEVERAL TIMES LARGER THAN GEOLOGICAL ESTIMATES

ROCK COMPACTION

HELPS TO MAINTAIN PRESSURE BY DECREASING PORE SPACE IN OVERPRESSURED RESERVOIRS

1) OBSERVE THE EFFECTS OF COMPACTION BY CUTTING CORES BEFORE PRODUCTION BEGINS AND SIDETRACK AT END OF PRODUCTION
2) MEASURE REDUCTION IN SANDSTONE THICKNESS BY DIRECTLY COMPARING CORES AND ELECTRIC LOGS
3) COMPARE POROSITIES AND PERMEABILITIES BEFORE AND AFTER PRODUCTION TO MEASURE COMPACTION
4) SEARCH FOR SHEAR FRACTURES IN SIDETRACK CORE CAUSED BY INCREASED LITHOSTATIC STRESS DURING PRODUCTION
5) COMPARE EXPERIMENTALLY COMPACTED SANDSTONES WITH THOSE FROM SIDETRACK CORE TO ACCURATELY ESTIMATE TYPE AND DEGREE OF COMPACTION

SHALE DEWATERING

HELPS TO MAINTAIN PRESSURE AND SUPPLIES ADDITIONAL WATER TO OVERPRESSURED RESERVOIRS

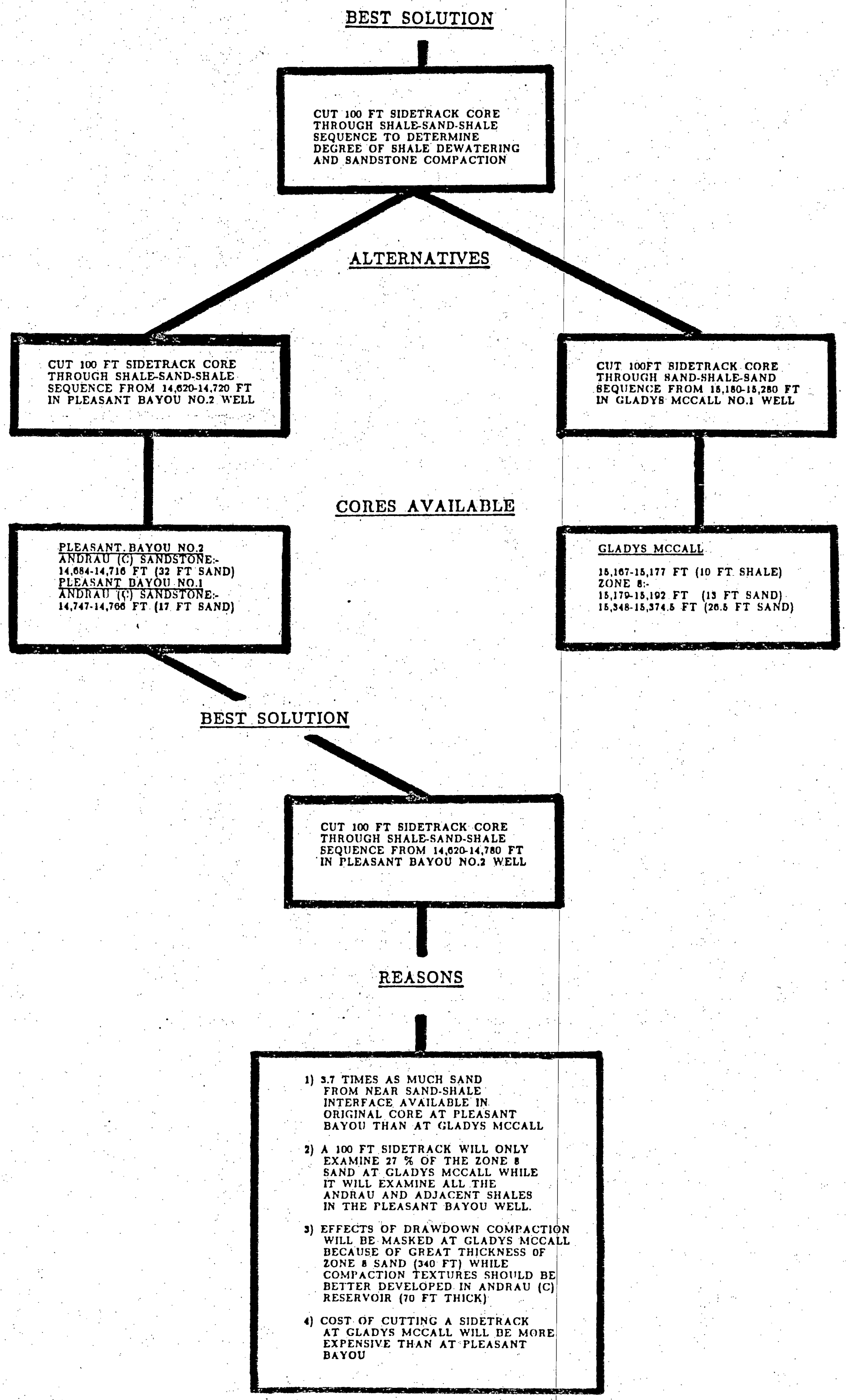
1) SEARCH FOR SALINITY DECREASES IN FORMATION WATERS DURING PRODUCTION AS INDICATION OF SHALE OF SHALE DEWATERING
2) CUT SIDETRACK SHALE CORE ABOVE AND BELOW SANDSTONE RESERVOIR AND MEASURE WATER CONTENT BY PYROLYSIS METHOD. DECREASING WATER CONTENT TOWARDS RESERVOIR WILL INDICATE EFFECTS OF SHALE DEWATERING
3) USE ABOVE METHODS TO ESTIMATE VOLUME OF SHALE WATER LOST TO RESERVOIR

LEAKING FAULTS

DEEPLY SOURCED BRINES ADDED TO RESERVOIR BY LEAKING FAULTS ON BOUNDARIES OF FAULT BLOCK

1) SEARCH FOR SALINITY AND TEMPERATURE INCREASES IN FORMATION WATERS TO DETECT INTRODUCTION OF DEEP BRINES

Table 4 (continued)



BEST SOLUTION

CUT 100 FT SIDETRACK CORE
THROUGH SHALE-SAND-SHALE
SEQUENCE TO DETERMINE
DEGREE OF SHALE DEWATERING
AND SANDSTONE COMPACTION

ALTERNATIVES

CUT 100 FT SIDETRACK CORE
THROUGH SHALE-SAND-SHALE
SEQUENCE FROM 14,620-14,720 FT
IN PLEASANT BAYOU NO.2 WELL

CUT 100FT SIDETRACK CORE
THROUGH SAND-SHALE-SAND
SEQUENCE FROM 15,180-15,280 FT
IN GLADYS MCCALL NO.1 WELL

CORES AVAILABLE

PLEASANT BAYOU NO.2
ANDRAU (C) SANDSTONE:-
14,684-14,716 FT (32 FT SAND)
PLEASANT BAYOU NO.1
ANDRAU (C) SANDSTONE:-
14,747-14,766 FT (17 FT SAND)

GLADYS MCCALL

15,167-15,177 FT (10 FT SHALE)
ZONE 8:-
15,179-15,192 FT (13 FT SAND)
15,348-15,374.5 FT (26.5 FT SAND)

BEST SOLUTION

CUT 100 FT SIDETRACK CORE
THROUGH SHALE-SAND-SHALE
SEQUENCE FROM 14,620-14,780 FT
IN PLEASANT BAYOU NO.2 WELL

REASONS

1) 3.7 TIMES AS MUCH SAND FROM NEAR SAND-SHALE INTERFACE AVAILABLE IN ORIGINAL CORE AT PLEASANT BAYOU THAN AT GLADYS MCCALL

2) A 100 FT SIDETRACK WILL ONLY EXAMINE 27 % OF THE ZONE 8 SAND AT GLADYS MCCALL WHILE IT WILL EXAMINE ALL THE ANDRAU AND ADJACENT SHALES IN THE PLEASANT BAYOU WELL.

3) EFFECTS OF DRAWDOWN COMPACTION WILL BE MASKED AT GLADYS MCCALL BECAUSE OF GREAT THICKNESS OF ZONE 8 SAND (340 FT) WHILE COMPACTION TEXTURES SHOULD BE BETTER DEVELOPED IN ANDRAU (C) RESERVOIR (70 FT THICK)

4) COST OF CUTTING A SIDETRACK AT GLADYS MCCALL WILL BE MORE EXPENSIVE THAN AT PLEASANT BAYOU

CONCLUSIONS

Several testing procedures that could be undertaken at the Gladys McCall and Pleasant Bayou wells have been compared (table 5). Of these, the preferred choice that will give the maximum scientific payback will be to produce the Gladys McCall well for an additional 2 years to measure the rate of chloride decline and then sidetrack core, perforate and test shale horizons, and plug and abandon both the Gladys McCall and the Pleasant Bayou test wells (No. 8, table 5). In this scenario, formation water samples must be analyzed by a single laboratory under strictly reproducible conditions where a low coefficient of variation is to be expected (1.7 percent). Samples need to be collected only on weekly intervals to obtain a good set of data (100 points). The salinity of formation waters in adjacent shales should also be measured in sidetrack cores so that the volume of shale water added to the produced formation waters can be estimated.

If the Gladys McCall well cannot be kept open, it is recommended that sidetrack cores be cut in both the Pleasant Bayou and Gladys McCall wells (No. 9, table 5) and that both wells be plugged and abandoned at a cost of $1.1 million (tables 2 and 3). In this scenario, formation waters collected during previous production at the Gladys McCall well and stored at Rice University (M. B. Tomson, personal communication, 1987) could be reanalyzed for chloride by one laboratory under strictly controlled conditions to measure the salinity decline (1.5 to 2.5 percent/year) over the production period. Salinity of formation waters in adjacent shales should also be measured in the sidetrack core so that the volume of shale water added to the produced formation waters can be estimated.

If only one sidetrack core can be cut, it is recommended that the Gladys McCall well be plugged and abandoned (No. 7, table 5). A 100-ft (30.5-m) sidetrack core

Table 5. Comparison of test procedures at the Gladys McCall and Pleasant Bayou test wells.

Number	Gladys McCall	Pleasant Bayou	Comment
(1)	Leave GM open continue prod.	Reopen PB.	Too expensive. No scientific payback.
(2)	Leave GM open continue prod.	Plug and abandon PB.	Less expensive. No scientific payback.
(3)	Plug and abandon GM.	Reopen PB.	Less expensive. No scientific payback.
(4)	Leave GM open continue prod.	Cut sidetrack core. Plug and abandon.	Expensive but large scientific payback.
(5)	Cut sidetrack core. Plug and abandon GM.	Plug and abandon PB.	Less expensive but less scientific payback.
(6)	Plug and abandon GM.	Reopen PB. Cut sidetrack core. Plug and abandon PB.	Too expensive. Less scientific payback.
(7)	Plug and abandon GM.	Cut sidetrack core. Plug and abandon PB.	Less expensive. Large scientific payback.
(8)	Leave GM open. Cut sidetrack core. Plug and abandon GM.	Cut sidetrack core. Plug and abandon PB.	Expensive but maximum scientific payback.
(9)	Cut sidetrack core. Plug and abandon GM.	Cut sidetrack core. Plug and abandon PB.	Less expensive. Large scientific payback.

<u>Preferred priority of actions</u>

1st choice (No. 8)	Maximum scientific payback
2nd choice (No. 9)	Large scientific payback Cost: $1.1 million
3rd choice (No. 7)	Large scientific payback Cost: $600,000

should be cut through the shale-Andrau reservoir-shale sequence from 14,620 ft to 14,720 ft (4,456 m to 4,487 m) in the Pleasant Bayou No. 2 well (fig. 2, table 4). The reasons for this choice are:

(1) The sidetrack core will sample shales both above and below the Andrau ('C') sandstone in the Pleasant Bayou well, whereas it will sample only one shale in the Gladys McCall well unless two cores are cut at Gladys McCall at the top and base of the Zone 8 sand.

(2) A 100-ft (30.5-m) sidetrack core will examine only 27 percent of the Zone 8 sandstone in the Gladys McCall well, whereas it will penetrate the entire Andrau ('C') sandstone and adjacent shales.

(3) The effects of pressure drawdown compaction at Gladys McCall will be masked because of the great thickness of the Zone 8 sandstone (340 ft, 104 m), but compaction textures should be better developed in the Andrau ('C') sandstone, which is about 70 ft (21 m) thick at Pleasant Bayou.

(4) The cost of cutting a sidetrack core at Pleasant Bayou ($510,000) may be considerably less than that at the Gladys McCall well (C. R. Featherstone, personal communication, 1986).

Formation waters collected during previous tests at the Gladys McCall well could also be reanalyzed by a single laboratory.

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BUREAU OF ECONOMIC GEOLOGY
THE UNIVERSITY OF TEXAS AT AUSTIN

SPECIFIC WORK INSTRUCTION

TITLE MINERAL STUDIES LABORATORY ANALYTICAL PROCEDURE CHLORIDE BY TITRATION (MOHR METHOD) **SWI 1.1**	**REVISION:** 0 **DATE:** 10-31-86 **PAGE:** 1 OF 5
APPLICABILITY BUREAU-WIDE	**SUPERSEDES** THIS IS THE ORIGINAL ISSUANCE
APPROVAL 12/8/96 DIRECTOR DATE	**CONCURRENCE** Not applicable PROGRAM COORDINATOR DATE 12-8-86 QUALITY ASSURANCE OFFICER DATE

1. SCOPE

1.1 This method covers the determination of chloride ions in water, wastewater, brines, and extract media. The method is best applied to clear, colorless solutions, as the endpoint can be obscured in cloudy or colored samples. Chloride concentrations in solid samples can also be determined provided appropriate sample dissolution can be effected.

1.2 Solution chloride concentrations ranging from 5 ppm to saturation can be determined.

2. SUMMARY OF METHOD

2.1 Near-neutral solution is titrated with silver nitrate in the presence of a potassium chromate indicator. Chloride quantitatively precipitates as silver chloride until, at the equivalence point, all chloride in solution is consumed. Thereafter, silver will precipitate as the more soluble orange-colored silver chromate, the first occurrence of which is used to mark the endpoint of the titration.

2.2 Relevant reactions:

$Cl^- + Ag^+$ ----> $AgCl$ (white ppt.)
$2\ Ag^+ + CrO_4^{2-}$ ----> Ag_2CrO_4 (orange ppt.)

3. SIGNIFICANCE

3.1 The classical Mohr method provides a convenient, simple, yet accurate procedure for chloride analysis, utilizing readily available equipment and reagents.

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4. INTERFERENCES

4.1 Bromide, iodide, and cyanide register as equivalent chloride concentrations but are normally present at low levels relative to chloride. If the orthophosphate concentration is greater than 25 mg/L, Ag_3PO_4 will precipitate, thus interfering.

4.2 Sulfide, thiosulfate, and sulfite interfere but can be removed by treatment with hydrogen peroxide or oxidizing acid.

4.3 The potentiometric mercuric nitrate or ion chromatographic method may be more suitable for colored or turbid samples in which the endpoint is difficult to observe and for samples whose constituents may form precipitates with the indicator, such as iron and other heavy metal ions.

4.4 It is the responsibility of the analyst to ensure the validity of the method for untested matrices. This can be ascertained by quantitative recovery of a known amount of chloride added to the sample.

5. APPARATUS

5.1 Erlenmeyer flask, 250 mL

5.2 Burette, 50 mL, class A, calibrated in 0.1 mL increments

6. REAGENTS/MATERIALS

6.1 Potassium chromate indicator --

6.1.1 (0.25 M), dissolve 50 grams potassium chromate (K_2CrO_4) in 100 mL of water and add silver nitrate ($AgNO_3$) until a slight red precipitate is produced. Let the solution stand in the dark overnight. Filter solution and dilute to 1 liter with water.

6.2 Silver nitrate solution --

6.2.1 (0.0141 N), for sample chloride concentrations <5000 ppm -- Dissolve 2.395 g $AgNO_3$ in distilled water and dilute to 1 liter. Prepare fresh, store in amber bottle, do not use without frequent restandardization.

6.2.2 (0.20 N), for sample chloride concentrations >5000 ppm --Dissolve 33.971 g $AgNO_3$ in distilled water and dilute to 1 liter. Prepare fresh, store in amber bottle, do not use without frequent restandardization.

6.3 Standard chloride solution, 2,000 ppm --

6.3.1 Dissolve 3.2969 g oven-dried reagent grade NaCl in distilled water and dilute to 1 liter.

6.4 pH adjusting solutions --

6.4.1 Basic solution -- Make about 1 liter of solution by adding NaOH to 1 liter of distilled water until pH is 8.5.

6.4.2 Acidic solution -- Prepare an acidic solution by adding HNO_3 to 1 liter of distilled water until the pH is 5.5 (distilled water [pH typically 6] is usually sufficient for slightly basic samples).

7. PREPARATION OF APPARATUS

7.1 Prepare and set up titration equipment in the conventional manner. Check burette tip and stopcock for accurate delivery of titrant.

8. CALIBRATION

8.1 This procedure does not require instrument or apparatus calibration. Reagent standardization is required and is described in Section 9.

9. PROCEDURE

9.1 Standardization of $AgNO_3$ -- Perform daily.

9.1.1 Take a 5 mL aliquot of the stock chloride (step 6.2.1 or 6.2.2) solution. Dilute with pH adjusting solution to a consistent volume (25 mL). The pH should be between 7 and 9. Add 1 mL K_2CrO_4 indicator solution and titrate with silver nitrate solution to a light orange endpoint. The endpoint can be better detected against a white background. Be consistent in endpoint recognition. Repeat using 10 mL stock chloride (step 6.2.1 or 6.2.2) solution.

9.1.2 Repeat the above procedure for a blank.

9.1.3 Calculate normality of $AgNO_3$ using the equation:

$$\underline{N}\ AgNO_3 = [(C*V) / (A-B)] / 35{,}450$$

where:

C = Cl standard concentration, in ppm
V = volume, in mL, of chloride standard
A = $AgNO_3$ titrant volume for standard used
B = $AgNO_3$ titrant volume for blank

9.2 Sample Analysis --

9.2.1 Take an appropriate aliquot of sample, depending on suspected chloride concentration (see Note 1), dilute to approximately 100 mL with deionized water, and adjust pH with pH-adjusting solution to pH 7 to 9 and titrate as described in Section 9.1.1.

9.2.2 Titrant volumes should be greater than 5 mL and less than 40 mL; if not, use a different aliquot of sample or adjust titrant strength.

9.2.3 If the presence of sulfide, sulfite, or thiosulfate is suspected in the sample, add 1 mL H_2O_2 (30%) prior to titration.

Note 1. Guide to sample aliquots and titrant concentration:

Sample Type	Sample Volume, mL	Titrant Concentration
Brines	0.1 -- 1	0.2 N
Seawater, Brackish Water	1 -- 5	0.2 N
Fresh, Natural Water	10 -- 50	0.014 N

9.3 Blank Analysis:

9.3.1 Repeat titration as in step 9.2 with several reagent blanks.

9.3.2 Average the resultant blank titration volumes for use in equation given in section 10.2.

10. DATA HANDLING

10.1 Keep detailed records of the analysis and record the pertinent information in the procedure log book.

10.2 Chloride Concentration Calculation --

$$C = (A - B) * N * 35{,}450 / V$$

where:

C = chloride concentration, in solution, in ppm
A = volume, in mL, of $AgNO_3$ used for sample
B = volume, in mL, of $AgNO_3$ used for blank
N = normality of $AgNO_3$
V = sample volume, in mL

10.3 If the solution analyzed is a result of a solid sample dissolution or extraction procedure, appropriate calculations must be carried out to express the chloride concentration on the basis of the solid sample.

10.4 Salinity--
The dissolved salts in seawater may be expressed as salinity, S:

$\% S = 1.80655 * C'$ (see references 12.1 or 12.4)

where C' is the chloride concentration expressed in parts per thousand, by weight.

11. QUALITY ASSURANCE/CONTROL

11.1 Acceptable recoveries for reference standards must accompany any sample analysis. The determination of acceptable recovery criteria will depend on

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the level of analysis required, amount of sample available, chloride concentration, and so on.

11.2 A standard seawater sample is available from the Institute of Oceanographic Sciences for which a certified chloride concentration value of 1.937% Cl is given. Use this standard for procedure validation when titrating samples with high chloride content. The error should not exceed 1.0% relative.

11.3 Round-robin performance evaluation samples, distributed by the Environmental Protection Agency, are also available and may be useful for validation of this method at lower chloride concentrations. The error should not exceed 5.0% relative.

11.4 Precision and accuracy estimates on typical samples will be available in future revisions.

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