A HYPOTHETICAL COMBINATION METHOD TO PROVIDE DATA FOR FORMATION WATER COMPATIBILITY

by

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ABTRACT

Industrial Water Technology, information concerning formation water, is required primarily in water injection projects to define the possibility of injection well plugging.

Water Injection, the most widespread secondary methods of oil recovery, is a pattern flooding when the water is injected over the entire oil bearing area of the reservoir. The main reason why this method is so widely used, is the high recovery achieved when water is the displacing agent, both in the case of a natural water drive and the water injected into reservoir artificially. However, if the flooding operation is carried out carelessly, the result may be entirely negative operation.

This paper describes a general discussion of industrial water technology including laboratory work, field work, interpretation data, field design and some calculation method of hypothetical mixing formation brine for the laboratory use and the generation of the valid data for selecting injection water in the prevention of occurency near wellbore damage.

I. INTRODUCTION

Formation waters are associated with all reservoir rock and many complicated problems of oil production.

A knowledge about their composition often helps in solving these problems. Water analysis is, therefore, an important tool which provides chemical and physical data for the interpretation of electric logs, for the reservoir studies and, by correlation with the analyses of known waters, may determine the source of water entering the bore hole.

Petroleum reservoirs contain water and oil in the capillary pore spaces; the exact nature of the relationship, however, is a complex and depends upon such factors as the geometry of the rock pores and the physical and chemical properties of the fluids. In general oil field terms, however, water are classified according to their position relative to the producing zones, and bottom water below.

Bottom water, in the restricted sense, underlies an accumulation, which is the case when the reservoir bed is thicker than the petroleum accumulation. Edge water occurs in the producing layer around the border of the accumulation in layers that are thinner than the vertical interval of the accumulation (oil and gas column).

In the complex oil zone, made up of several porous units, intermediate water may be found within the productive section as bottom or edge water in the individual members or as an entire water-bearing stratigraphic layer.

Oil field waters are usually saline except at shallow depth.

The dissolved salts present are primary chloride, sulphates, carbonate and bicarbonate of sodium, magnesium, and calcium, but minor amounts of other elements are usually also present. Normally, few of these other elements are determined by chemical analysis.

Water ranges from essentially fresh with less than one thousand milligrams per liter of dissolved solids to brines with more than two hundred fifty thousand milligrams per liter. The characteristics of water encountered in various porous zones of an oil field may differ sharply in chemical constituents, ion concentration, or both. These variations may occur laterally, that is , between different reservoirs in the same stratigraphic interval, or vertically, between different producing zones lying over the other.

In order to make the best use of the variation in water composition, the production engineer must have available a file or references of waters analyses from a wide variety of sources. The more completes the file, the more useful it becomes.

Laboratory studies of waters or solids such as scale may be performed independently of the field work or interpretation of the laboratory results. Individual analyses of formation, injection, or drill stem test waters are often made. Problem that exists in the operating systems can best be defined, remedied and even better, prevented by regular periodic studies of the system. The comparison of previous to present analysis can show trends and allows an evaluation of the previous recommendations.

II. LABORATORY WORK

A. *Laboratory Work Done Independently, consists of*

- Comprehensive analysis of water samples (dissolved ions, resistivity, undissolved solids and specific gravity)
- Plugging solids analysis (analysis of millipore filter residues follow the basic principles of "wet" chemical analysis)
- Scale analysis ("wet" chemical analysis techniques are used for a quantitative analysis of scale components)
- Differentiation between limestone and dolomite (a versenate analysis can be used, this analysis requires acid digestion of the rock)
- Qualitative compatibility studies of injection and formation waters (results of analysis can be used to indicate scaling as such carbonate deposition, gypsum precipitation or corrosion tendencies)
- etc.

The application of water analysis is to provide data for formation water compatibility, is not a new science but research activity has been continuing over a long stages between the reservoir and the final measurements and interpretation.

B. *Order of Hypothetical Combination*

In the laboratory, a synthetic formation brine can be reconstructed based on the chemical compositions of water analysis data, using "Order of Hypothetical Combination", as follows:

1. Combine all Ca^{++} as $CaCl_2$
2. Combine all Mg^{++} as $MgCl_2$
3. Combine all HCO_3^- as $NaHCO_3$
4. Combine Iron with sulfate as $FeSO_4$, if Sulfate is present otherwise with chloride as $FeCl_3$
5. If Sulfate is present combine with Na^+ as Na_2SO_4
6. Combine Ba^{++} with Cl^- as $BaCl_2$
7. Combine all CO_3^{--} with Na^+ as Na_2CO_3
8. Combine remaining Na^+ and Cl^- as NaCl
9. Disregard potasium unless specifically analyzed for solubilities of these salts will usually never been a problem.

1. Various information for hypothetical combination

- Calcium chloride, magnesium chloride and sodium chloride occur in all natural formation brines.
- Never add SO_4 as $CaSO_4$ to synthesize brine containing Na_2CO_3 used to satisfy carbonate requirements

Results:

$$Na_2CO_3 + CaSO_4.2H_2O \rightarrow CaCO_3 \downarrow + Na_2SO_4 + H_2O$$

ppt.

- Most common precipitations: $CaSO_4$, $MgCO_3$, $CaCO_3$ and $BaSO_4$
- mg/L = (ppm) x (specific gravity)

2. Hypothetical combinations for building synthetic brine

For reconstruction the synthetic formation brine compositions from water analysis data, the following factors in Table 1 can be used:

3. Example of building synthetic formation brine

Given Water Analysis Data of formation water are as follows: (Table 2).

Table 1
Composition factors for building synthetic brine

Composition	Cation factor	Anion factor
NaCl	Na x 2.5421	Cl x 1.6485
$CaCl_2$	Ca x 2.7619	Cl x 1.5653
$MgCl_2.6H_2O$	Mg x 8.3625	Cl x2.8673
$BaCl_2.2H_2O$	Ba x 1.7786	Cl x 3.4451
KCl	K x 1.9067	Cl x 2.1029
Na_2SO_4	Na x 3.0892	SO_4 x 1.4786
$CaSO_4$	Ca x 3.3967	SO_4 x 1.4172
$CaSO_4.2H_2O$	Ca x 4.2957	SO_4 x 1.7923
$MgSO_4.7H_2O$	Mg x 10.1382	SO_4 x 2.5658
$NaHCO_3$	Na x 3.6541	HCO_3 x 1.377
Na_2CO_3	Na x 2.3051	CO_3 x 1.7662
$Na_2B_4O_7$	Na x 4.3762	B x 4.6531
Na_2SO_3	Na x 2.7412	SO_3 x 1.5742
$MgSO_4$	Mg x 4.9512	SO_4 x 1.2530
NH_4Cl	NH_4 x 2.9654	Cl x 1.5088
NaJ	Na x 6.5200	J x 1.1811
NaOH	Na x 1.7398	OH x 2.3518
$FeCl_3.6H_2O$	Fe x 4.8400	Cl x 2.5414
$FeSO_4$	Fe x 2.7200	SO_4 x 1.5813
$BaCl_2$	Ba x 1.5163	Cl x 2.9369
$FeCl_3$	Fe x 2.9045	Cl x 1.5251

Table 2
Formation water analysis data

Component	Anion (mg/L)	Component (mg/L)	Cation (mg/L)
(1) Potasium (K^+)	0.0	(6) Chloride (Cl^-)	12789.0
(2) Natrium (Na^+)	9279.8	(7) Sulfat ($SO_4^=$)	214.0
(3) Calsium (Ca^{++})	200.5	(8) Bicarbonat (HCO_3^-)	3336.4
(4) Magnesium (Mg^{++})	109.4	(9) Carbonat ($CO_3^=$)	76.4
(5) Fero (Fe^{++})	0.0	(10) Hydrokside (OH^-)	0.0
Temperature (° F) = 68		Total solids = 25987.5	
Spec.gravity (gram/cc) = 1.0223		pH = 8.3	

Reconstruction of formation brine based on water analysis data are as follows:

* $CaCl_2$ required = (3) x 2.7619 mg/L = (11)
= 200.5 x 2.7619 mg/L = 553.76 mg/L

* Cl^- used = (11) x 0.6589 mg/L =(12)
= 553.76 x 0.6589 mg/L = 364.87 mg/L

* $MgCl_2.6\,H_2O$ required = (4) x 8.6589 mg/L = (13)
= 109.4 x 8.3608 mg/L = 914.67 mg/L

* Cl^- used = (13) x 0.3489 mg/L = (14)
= 914.67 x 0.3489 mg/L = 319.13 mg/L

* $NaHCO_3$ required =(8) x 1.3768 mg/L = (15)
= 3336.4 x 1.3768 mg/L = 4593.6 mg/L

* Na^+ used = (15) x 0.2737 mg/L = (16)
= 4593.6 x 0.2737 mg/L = 1257.3 mg/L

* $Na_2\,SO_4.10\,H_2O$ required = (7) x 3.3600 mg/L =(17)
= 214 x 3.3600 mg/L = 719.04 mg/L

* Na^+ used = (17) x 0.1428 mg/L = (18)
= 719.04 x 0.1428 mg/L = 102.67 mg/L

* $Na_2CO_3.10\,H_2O$ required =(9) x 4.9310 mg/L =(19)
= 76.4 x 4.9310 mg/L = 376.73 mg/L

* Na^+ used = (19) x 0.1600 mg/L = (20)
= 376.73 x 0.1608 mg/L = 60.578 mg/L

Total Na+ used = (16) + 18) + 20) = (21)
= 1257.3 + 102.67 + 60.578 mg/L
= 1420.548 mg/L

* Na^+ remnant = (2) - (21)
= 9278.8 - (21) 1420.548
= 7849.452 mg/L

* NaCl required = (22) x 2.5421 mg/L = (23)
= 7849.452 x 2.5421 mg/L
= 19954.09 mg/L

* Cl^- used = (23) x 0.6066 mg/L = (24)
= 19954.09 x 0.6066 mg/L
= 12104.15 mg/L

Cl^-remnant = (6) - (12) + (14) + (24) = (25)
= 12789 - (364.87 + 319.13 + 12104.15) mg/L
= 12789 - 12788.15 mg/L = 0.85 mg/L.

In this calculation the lowest Cl^- remnant is the most accuracy water analysis data.

Based on above data calculated, the synthetic formation brine can be reconstructed as follow :

- **$CaCl_2$ = (11) = 563.76 mg/L**
- **$MgCl_2$. 6H2O = (13) = 914.67 mg/L**
- **$NaHCO_3$ = (15) = 4593.6 mg/L**
- **Na_2SO_4. $10H_2O$ = (17) = 719.04 mg/L**
- **Na_2CO_3. $10H_2O$ = (19) = 378.73 mg/L**
- **NaCl = (23) = 19954.09 mg/L.**

4. Scale calculations

Langelier, Larson & Buswall and Skilman, Mc Donald and Stiff presented a general concept on the use of formation water compositions data for monitoring the occurence of scale in the near wellbore or for quantitative analysis of scale components.

a. Langelier saturation index (SI)

Saturation Index value can be calculated by equation :

SI = pH - pHs
$pHs = K + pC^{++} + pAlk$

where:

pH = true water pH
pHs = pH at saturated condition
K = empirical constant, which is defined from plot of Ionic strength (μ) vs T
pCa^{++} = - log moles Ca^{++} per liter
$pAlk$ = - log equivalent total Alkalinity per liter.

For interpretation data calculated following catagories are given:

- If SI value > 0, → shows scalling tendency
- If SI value < 0, → water has corrosion characteristics.

b. Larson & Buswall saturation index (I)

Saturation index value is defined by equation:

$$I = pH + log\ Ca^{++} + log\ Alk - K - 9.3 - \frac{2.5\mu}{1+10.8\mu}$$

It is noticed that for Larson & Buswall equation in ionic strength calculation, the ppm Alk should be converted to Ca^{++} ppm. Conversion factor of equivalent total Alkalinity to ppm Ca^{++} equals 1.22

Rough interpretation of the data calculated using this equation are as follows:

- If $I > 0 \rightarrow$ Saturated water
- If $I < 0 \rightarrow$ Corrosion water

Empirical constant (K) for both equation is defined from plot Ionic strength (μ) versus Temperature. The ionic strength is calculated using equation:

$$\mu = \frac{1}{2}\,(C_1.Z_1^2 + C_2Z_2^2 + \ldots\ldots\ldots Cn.Zn^2)$$

where :

C = *ion concentration in moles/1000 gram*

Z = *valency number.*

5. Case study of scale calculation

Using previous data as shown in Table 2, the occurence of scalling tendency are calculated using both equation as follows: (Table 3).

a. Application of Langelier equation

$$\mu = \frac{1}{2}(C_1,Z_1^2 + C_2Z_2^2 \ldots\ldots\ldots\ldots Cn.Zn^2)$$

$$= \frac{1}{2}\ ((0.3946)(1)^2 + (0.0049)(2)^2 +$$

$$(0.0044)(2)^2 + (0.3524)(1)^2 +$$
$$(0.0022)(2)^2 + (0.0535)(1)^2 +$$
$$(0.0012)(2)^2 = 0.4257$$

For $\mu = 0.4257$ using plot of μ vs K at 68° F :

K is equal 3.28 (from Figure 3 and Figure 4)

$pCa^{++} = -\log 0.0049 = 1/0.0049 = \log 204 = 2.310$

$pAlk = \log 0.0535 = \log 1/0.0535 = \log 18.6916$
$= 1.272$

$SI = 8.3 - (3.20 + 2.310 + 1.272) = + 1.518$

$SI > 0$ *indicate Scalling Tendency of* $CaCO_3$

Table 3
Formation water analysis data

Component	0(mg/L)	(ppm)	(mole/L)
Potasium (K^+)	0.0	0.0	0.0
Natrium (Na^+)	9279.8	9076.6	0.3946
Calsium (Ca^{++})	200.5	196.1	0.0049
Magnesium (Mg^{++})	109.4	107.0	0.0044
Fero (Fe^{++})	0.0	0.0	0.0
Chloride (Cl^-)	12789.0	12510.0	0.3524
Sulfate ($SO_4^=$)	214.0	209.3	0.0022
Bicarbonate (HCO_3^-)	3336.4	3263.6	0.0535
Carbonate ($CO_3^=$)	76.4	74.7	0.0012
Hydroxide (OH^-)	0.0	0.0	0.0
Temperature (° F) = 68 Total solids = 25987.5			
Spec.Gravity (gram/cc) = 1.0223 pH = 8.3			

b. Application of Skillman, Mc Donald and Stiff

Calcium Sulfate solubility can be defined using equation:

$$S = 1000\sqrt{(X^2 - K) - X}$$

where:

X = (moles/L Ca^{++}) - (moles/L SO_4)
= 0.0049 - 0.0022 = + 0.0027

μ = calculated previously equals 0.4257

K is defined from plot various μ vs temperature (from Figure 5) equals 9.7×10^{-4}

$S = 1000\sqrt{(+0.0027)^2 + 9.7 \times 10^{-4})} - 0.0027$
= - 1.723 meq/L

Ca = 196.1/20 = 9.805 meq/L

SO_4 = 209.3/48 = 4.463 meq/L

$S <$ meq/L $Ca^{++} <$ meq/L SO_4 = ---> Corrosion water.

III. FIELD WORK

Several factors that define actual, in-system conditions can be determined only by work on-location. They include: plugging solids actually present, dissolved gases (hydrogen sulfide, carbon dioxide and oxygen), oil content, iron content and bacterial activity.

Several methods concerning the above factors determinations are as follows :

A. *Plugging Solids*

Special procedures based on membrane (millipore) filter apparatus are used to make quantitative determination of plugging solids actually present. A small side stream of water is flowed through the apparatus until sufficient sample has accumulated. The filter used is 70 mm diameter, 0.8 micron pore opening.

B. *Oxygen Content*

The magna Oxymeter (a procedure originated by Shell Development Corporation) is used to measure dissolved oxygen content of water. This method is sufficiently accurate and sensitive for all usual purpose. This meter is not normally used if hydrogen sulfide is present.

C. *Hydrogen Sulfide (H_2S)*

The procedure involves chemically "fixing" hydrogen sulfide as the sample is taken. Hydrogen sulfide is later liberated in the laboratory by another reaction and the determination is completed.

D. *Carbon Dioxide (CO_2)*

The present of this gas is determined as free CO_2 by a rapid chemical test at the sampling point. The sample is titrated with sodium hydroxide or sodium carbonate in the present of phenolphthalin indicator.

E. *Oil Content*

The water sample is extracted with trichlorethane as the sample is taken. Photometric procedures then are used to measure the amount of oil in the solvent. A small one ounce sample of lease crude is required so a calibration standard can be run.

F. *Iron Content*

Hydrochloric acid is added to samples taken for iron content determinations. Acid dissolved any iron that is precipitated and ensures that none was dissolved precipitates. The amount of iron in the precipitated state under system conditions is determined when the millipore filter residue is analyzed. Iron dissolved under system conditions is the difference between the acidified sample content and the iron on the millipore. Knowledge of iron behavior is neccessary both for corrosion and plugging studies.

G. *Sulfate Reducing Bacteria*

A special procedure that measures activity of these bacteria has been developed. This requires field inoculation of laboratory prepared samples. The term "activity" is the result of the number present (the "count"), types present and the environmental effects provided by the water. A "count" simply is an enumeration under arbitrary conditions. "Activity" can be interpreted in practical terms much more readily than a "count".

H. *Additional Water Samples*

Another important purpose of field work is to collect the other samples needed for laboratory analysis. Special procedures are followed to enhace accuracy of the data.

IV. INTERPRETATION DATA

The interpretation of field and laboratory data is made to define problems in the water system that will result in poor injectivity and resultant lost of recoverable oil. Information methods will include:

- Analysis of System in Operation
- Water Plant Design Studies.

A. *Analysis of System in Operation includes:*

- The Material Balance Principle
- Critical Content of Plugging Materials.

1. The material balance principle

The principle is the technical basis for definition of water system performance. As noted under field work, samples are taken and analyzed at each point in the system where a change in water character could occur.

This point includes:

- Each water at its source
- Before and after filters
- After point of chemical injection
- At one or more injection wells.

Plugging solids analyses and complete water analyses from each test point are studied to determine system behavior. Suppose, for example, that precipitated iron is found to be increasing as water flows through the system. There are several possible explanations : Iron that originally was dissolved could be precipitated because of oxidation, mixing of incompatible waters, bacterial activity or reaction with hydrogen sulfide.

On the other hand, the iron may originate from corrosion and not be a native constituent of the water. If corrosion is occurring, part of the iron may enter a precipitated form and part may stay in solution. It is not uncommon to have both corrosion and natively present iron in the same water.

Having quantitative data on both dissolved and precipitated iron at each test point, material balance analysis will explain what is happening. In this manner, the behavior of all constituents of the plugging solids is determined.

Other common example of plugging materials include precipitated carbonates, sulfates, siliceous materials and hydrocabon or nonhydrocarbon organics.

2. Critical content of plugging materials

The first step of intepretation, as described above, is to construct a quantitative description of actual system conditions and behavior. The next step is to determine if these conditions are satisfactory. No water is entirely free of plugging materials, but many reservoirs have an appreciable tolerance for them. The most economical operation results when water quality is maintained at the level that is just good enough.

There is a critical content of plugging materials for each reservoir. As long as solids are kept below the critical, no plugging will occur, regardless of how much water is injected. If the solids exceed the critical content, plugging will occur in proportion to the amount of solids present.

B. *Water Plan Design Studies*

Design studies use much the same technical procedures as studies of plants that are in operation. The principle difference is that fewer test points are required, but more work of an interpretative nature is involved. The water to be used must be accessible for test.

Not frequently, a tentative or final plant design will be adopted before the water source is developed. In this case, water quality studies have a greatest value in conjunction with plant start-up. Design assumptions can be verified or modified, and all desirable changes can be made promptly.

V. CONCLUSIONS

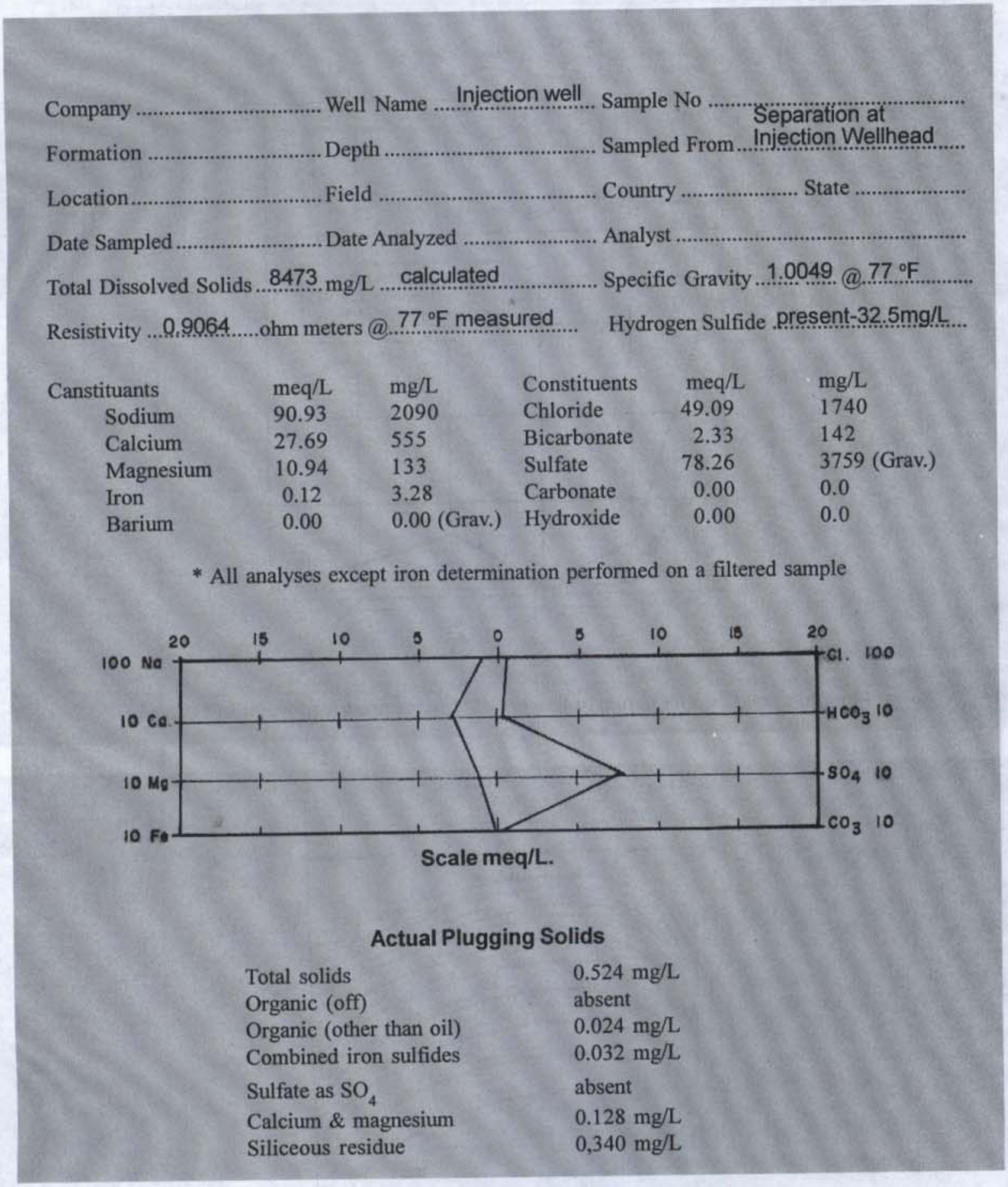
1. If it is concluded that water system conditions are less than satisfactory, the causes of the problem will have been defined in the study process.
2. The study process creates a direct basis for choice of remedy.
3. The solutions to water quality problems include many kinds of chemical treatments and mechanical measures.

REFERENCES

1. **E.T. Chanlet,** 1973, *Environmental Protection*, McGraw Hill, Series in Water Resources and Environmental Engineering, New York.
2. **J.R.Holum,** 1977, "Topic and Term in Environmental Problems", *Willey Interscience Publication*, New York.
3. **ACS (American Chemical Society)**, 1978, "Cleaning Our Environment" 2nd Ed, *American Chemical Society Publication*, Washington DC.
4. **Gark S.K.**, 1979, *Sewage and Waste Disposal Engineering*, Vol-II, Delhi, Khana Publisher.
5. **Badaruddin Machmud,** 1992, "Pengendalian Pencemaran Air", *Makalah* pada Konperensi Nasional PII dari Puslitbang Departemen Pekerjaan Umum, Surabaya.
6. **Lund Hebert F.**, 1971, *Industrial Pollution Control Handbook*, Mc Graw Hill Book, Company.
7. **Emdi,** 1990, *Kependudukan dan Lingkungan Hidup Suatu Tinjauan,* Kantor Menteri Negara Kependudukan dan Lingkungan, Jakarta.
8. **N.N.**,1972, "Core Laboratories", *Special Core Analysis Section,* April.

Appendixes

1. Water analysis data.
2. Plugging solids under actual in-line conditions for produced water injection.
3. Value of "K" at various ionicstrength for calcium carbonate.
4. Conversion of Mg/l calcium and alkalinity into pCa and pAlk.
5. Ionic strength calculation curves.



Company .... Well Name Injection well Sample No ....

Formation .... Depth .... Sampled From Separation at Injection Wellhead

Location .... Field .... Country .... State ....

Date Sampled .... Date Analyzed .... Analyst ....

Total Dissolved Solids 8473 mg/L calculated .... Specific Gravity 1.0049 @ 77 °F

Resistivity 0.9064 ohm meters @ 77 °F measured Hydrogen Sulfide present-32.5mg/L

Canstituants	meq/L	mg/L	Constituents	meq/L	mg/L
Sodium	90.93	2090	Chloride	49.09	1740
Calcium	27.69	555	Bicarbonate	2.33	142
Magnesium	10.94	133	Sulfate	78.26	3759 (Grav.)
Iron	0.12	3.28	Carbonate	0.00	0.0
Barium	0.00	0.00 (Grav.)	Hydroxide	0.00	0.0

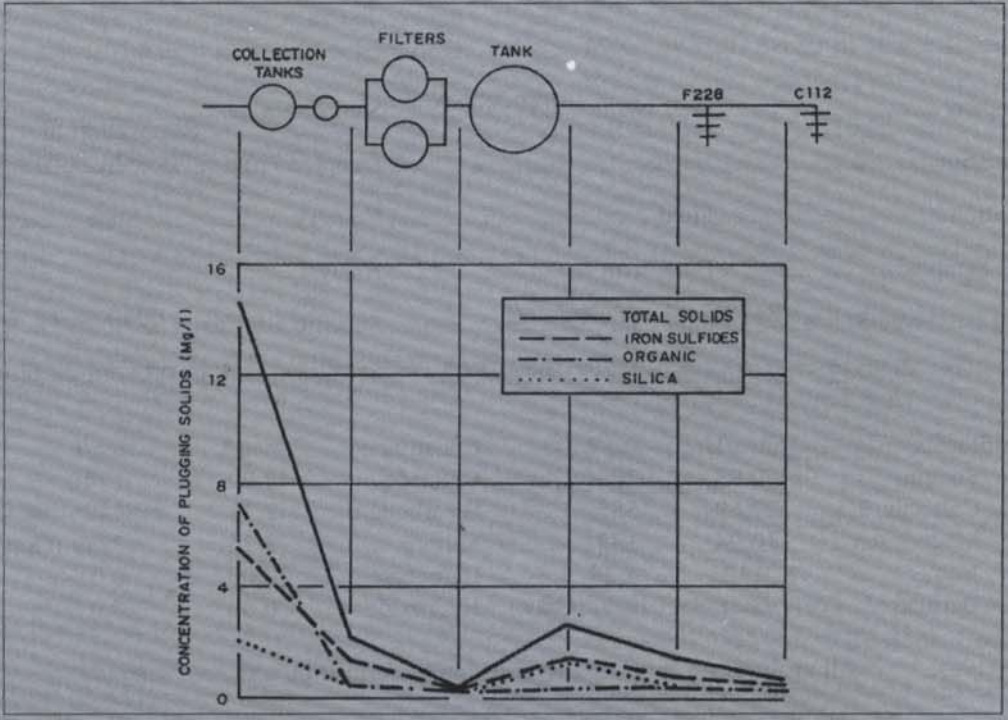
* All analyses except iron determination performed on a filtered sample

Scale meq/L.

Actual Plugging Solids

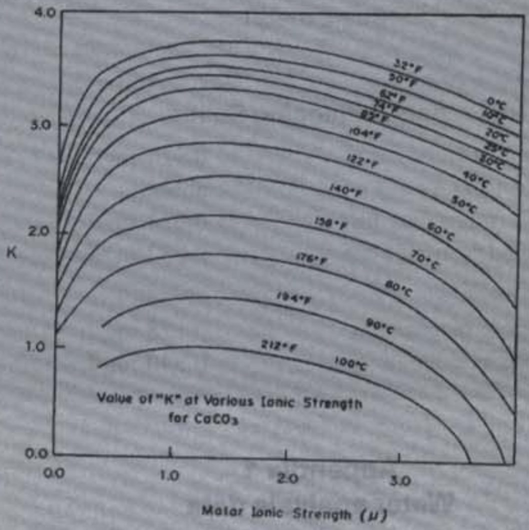
Total solids	0.524 mg/L
Organic (off)	absent
Organic (other than oil)	0.024 mg/L
Combined iron sulfides	0.032 mg/L
Sulfate as SO_4	absent
Calcium & magnesium	0.128 mg/L
Siliceous residue	0,340 mg/L

Appendix 1
Water analysis data



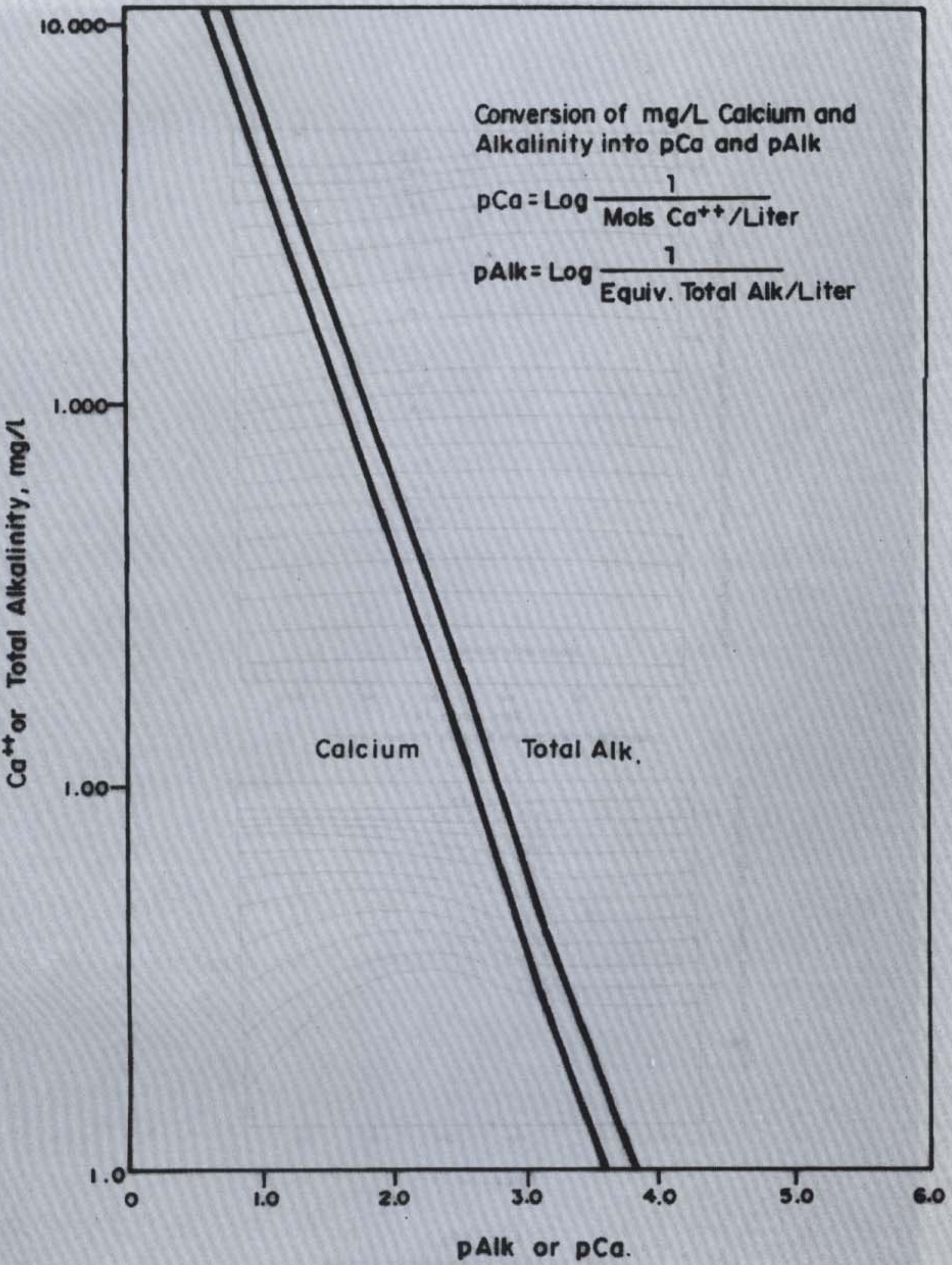
Appendix 2

Plugging solids under actual in-line conditions for produced water injection

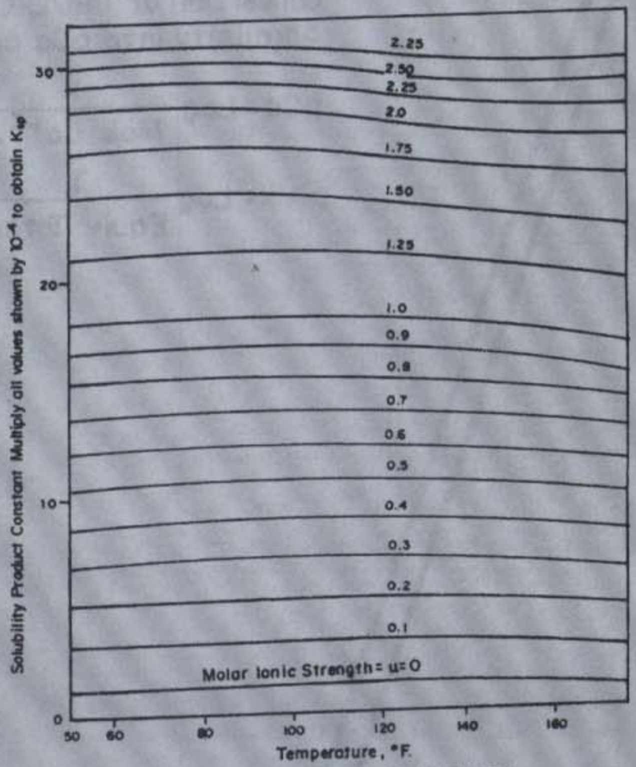


Appendix 3

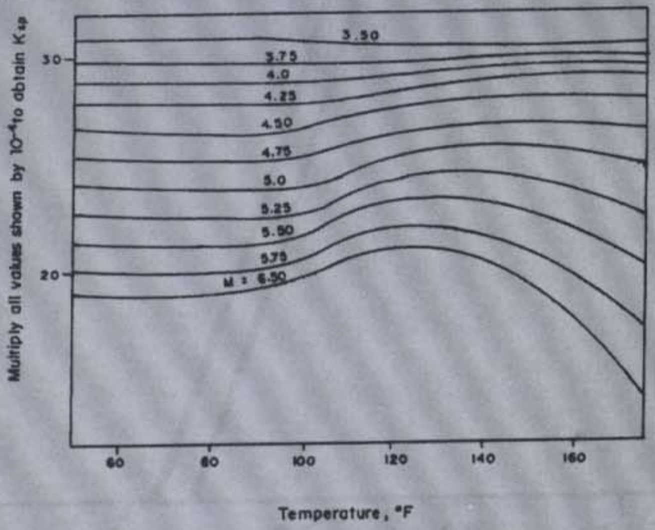
Vallue of "K" at various ionic strength for calciumcarbonate


Conversion of mg/L Calcium and Alkalinity into pCa and pAlk
pCa = Log 1 / Mols Ca++/Liter
pAlk = Log 1 / Equiv. Total Alk/Liter
Calcium
Total Alk.
10.000
1.000
1.00
1.0
0
1.0
2.0
3.0
4.0
5.0
6.0
Ca++ or Total Alkalinity, mg/l
pAlk or pCa.

Appendix - 4



Calcium Sulfate (Gypsum) Solubility Product Instants



Appendix 5
Ionic strength calculation curves