

CO₂ FORMATION DAMAGE STUDY

First Annual Report

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Las Cruces, New Mexico



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First Annual Report

John T. Patton, *Project Manager*
Department of Chemical Engineering
New Mexico State University
Las Cruces, New Mexico 88003

Contributors:

Patrick Phelan
Stan Holbrook

Royal Watts, *Technical Project Officer*
Morgantown Energy Technology Center
P.O. Box 880
Morgantown, West Virginia 26505

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OVERVIEW

Objective: Learn how to avoid or minimize formation damage due to CO₂ injection processes. The study is to determine the types of chemical and physical changes that can occur in carbonate or other reservoirs because of injected carbon dioxide (CO₂) and/or its chemical additives and the effects on oil recovery due to those changes.

Summary: During 1980 significant progress was made in determining possible mechanisms of damage and in describing them using theoretical considerations. Preliminary experimental results have permitted a well defined experimental plan to be developed. Most of the apparatus has been designed and assembly of some systems has been completed.

A literature search made at the inception of the project found no documented reports of CO₂ damage to oil reservoirs. The search was then expanded to include studies relating to our proposed damage mechanisms. Over 100 references were collected. They are presented with abstracts, author index, and subject category in Appendix A.

1. INTRODUCTION

1.1 General

For more than 30 years oil recovery experts have known that carbon dioxide possesses a unique ability to displace crude oil from reservoir rock. Although many gases have been tested for their crude-displacing efficacy, only carbon dioxide has the ability to reduce residual oil saturations to near zero and also produce significant quantities of tertiary oil in reservoirs that have been previously water flooded to the economic limit. Early studies provided the fundamental understanding required to explain the high efficiency of carbon dioxide, but as long as the price of crude remained depressed, most, if not all, field applications of CO₂ appeared to be unprofitable.

Oil displacement by gas can occur under both miscible and immiscible phase conditions. CO₂ is unique in that it can effectively displace oil in both modes with the determining factor being largely the depth of the reservoir which controls the pressure at which the flood is conducted. All factors being equal, it is more desirable to conduct the flood under miscible conditions than immiscible conditions if possible.

1.2 Concern About Possible Reservoir Damage

Miscible conditions imply high concentrations of CO₂ at the oil-CO₂ interface. Some workers reported [4,5] that traces of black solids were formed when mixtures of CO₂ and oil exceeded 70 mole percent CO₂ in laboratory experiments. These observations, and the common observation that addition of a light hydrocarbon to crude oil causes asphaltene to precipitate, gave rise to suspicions that reservoir damage might occur during CO₂ floods.

Less-tangible evidence has been provided by some of the pilot tests of CO₂-enhanced oil recovery which have been conducted. Injectivity problems were encountered in some cases, and damage to the reservoir was suspected, but other explanations could usually be advanced, so that no conclusions were possible.

1.3 History of Project

With increased interest in CO₂-enhanced recovery and the suspicions about possible damage, the Department of Energy (DOE) contracted with the Chemical Engineering Department at New Mexico State University to study the problem.

The project was initiated September 28, 1979 and is to be completed September 28, 1981. The total cost is estimated to be \$450,000, of which DOE will contribute \$305,492, with the New Mexico Department of Energy and Minerals and New Mexico State University contributing the balance. During the first year the following five tasks were accomplished:

- a) a group of expert consultants from the oil industry, was established,
- b) plausible mechanisms of CO₂ damage were identified,
- c) the literature was searched for reports of such damage,
- d) an experimental program was developed to test plausible mechanisms, and
- e) necessary equipment and supplies were assembled.

2. POSTULATED DAMAGE MECHANISMS

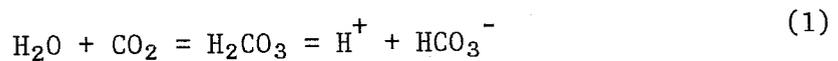
2.1 Introduction

When technical experts from the oil industry met at New Mexico State University in 1979, they agreed that the most likely kind of damage which CO₂ flooding might cause would be plugging of the reservoir rock. Several plausible mechanisms were hypothesized. Of those, two were chosen for study, because they could be investigated by laboratory experiments, and the experiments could be completed within the life of the project. The two were:

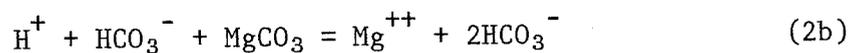
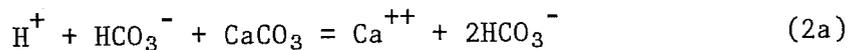
- a. Pluggage due to carbonate deposition.
- b. Deposition of solids from the crude oil.

2.2 Pluggage by Carbonates

Carbonic acid (H₂CO₃) would be expected to form whenever CO₂ encounters water in the reservoir. The CO₂ would dissolve in the water and form carbonic acid according to the well-known reaction depicted by Equation 1.



The carbonic acid could dissolve calcium carbonate or magnesium carbonate as shown by Equations 2a and 2b.



As CO₂ is injected under high pressure, the equilibrium of Equation 1 would be forced to the right, and the acid concentration [H⁺] would increase. As the concentration of carbonic acid increased, Equilibria 2a and 2b would similarly be forced to the right and the calcium or magnesium carbonate would dissolve. Reservoir damage might occur as the calcium carbonate, which dissolved in the high-pressure

region of the reservoir migrated to remote, low-pressure regions of the reservoir and precipitated. This reprecipitation would occur as carbon dioxide bubbled out of solution near the producing well, causing Equilibrium 1 to shift to the left which, in turn, would cause Equilibria 2a and 2b to shift to the left. That is, calcium bicarbonate and magnesium bicarbonate would decompose into CO_2 , water, and calcium carbonate and magnesium carbonate, both solids.

As the calcium carbonate or magnesium carbonate precipitated, it could form tiny particles in the bulk liquid, or it might form as a scale on the walls of the pores in the reservoir rock. The effect on permeability cannot be predicted from theoretical considerations, although one would expect that permeability would decrease. If, however, the scale deposited preferentially in pores of large diameter or in the large-diameter sections of non-uniform pores, the reduction in permeability would be minimal. These possibilities would have to be determined experimentally.

2.3 Pluggage by Asphaltene Deposition

Trace amounts of black solids have been observed during phase-equilibrium studies involving CO_2 and oil [4,5]. These black solids or semisolids seem to be different from the black solids which precipitate when low-molecular-weight hydrocarbons such as pentane or hexane are poured into crude oils [6].

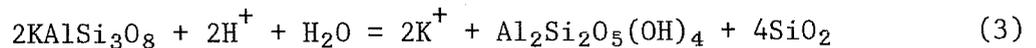
During a CO_2 flood, these black solids might form in at least three different ways. The first way might be analogous to a "salting out" effect. That is, the high concentration of carbon dioxide might change the polarity or solubility characteristics of the crude oil enough that high-molecular-weight components of

the crude would precipitate. The second way would involve removal of solubilizing hydrocarbons (those in the range C₆ to C₃₀) from the crude as CO₂ swept the reservoir. Thus, the relatively insoluble components (i.e., those having high molecular weights) would be left behind. The third way could occur at the producing well where, as the mixture of carbon dioxide and oil flashed, the components having very high molecular weight that had been carried to the producing well would be left behind as an asphaltic residue. The transport process may be considered analogous to liquid chromatography. The deposition process would be analogous to vacuum distillation of a mixture to dryness.

2.4 Other Damage Mechanisms

Review of the literature suggested other mechanisms which, however, are beyond the scope of the present project.

Decomposition of sandstone--Carbonates and feldspars in sandstones might be attacked by carbonic acid. If very tiny grains of insoluble minerals were released as cementing material dissolved, the grains might be swept along and lodge in the pores. Alternately, the feldspars might be converted to clays in accord with Equation 3, and the clays would swell as they absorbed water



thereby plugging the pores in the rock.

Deposition of calcium or barium sulfate--This mechanism does not involve CO₂ directly. Rather, it would arise from the difference in pressure between injection well and producing well. The solubility of these minerals can be increased just by increasing the pressure on the water which is in contact with them. This is

because the molar volumes of CaSO_4 and BaSO_4 in solution are less than their respective molar volumes in the crystalline state. When pressure is applied to the water and the crystals, some of the solid dissolves in an attempt to relieve the stress in accord with the famous Principle of LeChatelier. Thus, the compounds would dissolve in water near the injection well, then the solution would move out into the reservoir where, as the pressure decreased the crystals of CaSO_4 and BaSO_4 would form again. As with calcium carbonate, the precipitated solid might plug pores in the reservoir rock. Note that according to this mechanism, CO_2 does not participate directly; the effect of its acidity in this case is probably negligible, because pH has little effect on the solubility of calcium and barium sulphate.

Formation of emulsions or immobile phases--The phase equilibria involving just CO_2 and crude oil are being investigated by numerous workers [1-5], but little is known about ternary mixtures which include water. It seems possible that under certain conditions, immobile phases or emulsions might form as the CO_2 front swept through a reservoir, because at the interface, CO_2 , oil and water would be present simultaneously.

3. EXPERIMENTAL

This section describes our experimental plans and some preliminary experiments which were performed in the course of developing the experimental plans.

3.1 Pluggage Due to Carbonates

Laboratory studies will be of two types:

- (1) Batch experiments using mixed Ca^{++} and CO_3^{--} solutions in contact with CaCO_3 solids.
- (2) Continuous flow of a supersaturated solution of Ca^{++} and CO_3^{--} through a column packed with CaCO_3 solids.

3.1.1 Batch Experiments

Apparatus--A 400-ml beaker, containing marble chips (200-300 μm average diameter) and 100 ml of 3% (wt.) NaCl solution will be employed (See Figure 1). An electrically-driven agitator will be used to keep the marble chips suspended.

Procedure--From buret A, aqueous CaCl_2 solution (0.04 M, in 3% NaCl) will be introduced into the beaker at 5 ml/min while Na_2CO_3 solution (0.04 M, in 3% NaCl) will be introduced at the same rate from buret B.

After 50 ml of each solution has been added, the marble chips will be separated from the solution and rinsed with cold, distilled water to remove any particles of CaCO_3 precipitate which may loosely adhere. The rinsings will be combined with the solution, then the mixture will be acidified with hydrochloric acid and diluted to 2,000 ml. Total Ca^{++} will be measured using a specific-ion electrode (Orion) calibrated to compensate for the presence of Na^+ .

Anticipated results--From a mass-balance on Ca^{++} , the fraction of CaCO_3 which precipitates as a scale on the marble surfaces

can be calculated. By repeating this experiment with various masses of marble chips (10 g, 25 g, 50 g, and 100 g), we can determine whether CaCO_3 has an increasing tendency to precipitate on surfaces rather than form particles of precipitate in the bulk liquid. In the limit, when the ratio of surface area to liquid volume tends to infinity (as it would in a carbonate reservoir), any tendency to form a scale on surfaces would become the dominant mechanism.

An alternative result would be that when Ca^{++} and $\text{CO}_3^{=}$ solutions are mixed, a supersaturated solution is formed (after some initial deposition of CaCO_3 precipitate, perhaps). This possibility can be detected by monitoring the Ca^{++} concentration in the beaker during the experiment using a specific-ion electrode. If the solution is found to be supersaturated, its time of contact with the chips will be extended until an appreciable amount of the Ca^{++} has precipitated.

3.1.2 Continuous Flow Experiments

Apparatus--A glass column (40 mm i.d.) packed with sieved marble chips will be employed (See Figure 2). Aqueous solutions of CaCl_2 (0.01 M) and Na_2CO_3 (0.01 M) in 3% NaCl will be metered at constant rates using adjustable speed diaphragm pumps A and B. (For very low flow rates, the solutions may be introduced dropwise, but continuously, through the top). A manometer will be employed to measure the pressure drop across the column. The effluent will be collected for later analysis.

Procedure--The Ca^{++} and $\text{CO}_3^{=}$ solutions will be introduced at equal rates (1 to 20 ml/min). The total flow will be confirmed

by measuring the effluent flow rate. Periodically, the effluent will be sampled, acidified with HCl, and analyzed for total calcium using a specific-ion electrode calibrated to compensate for the presence of Na^+ .

The pressure drop will be recorded periodically until it has increased appreciably, then the experiment will be stopped.

The contents of the column will then be emptied into a large beaker and the chips separated from the solution. The chips will be rinsed with distilled water to remove any loosely-held particles of CaCO_3 precipitate they may have retained. The rinsings will be combined with the solution that was held in the column, and the mixture acidified (HCl) and diluted to known volume. The total Ca^{++} will be determined using a calcium specific-ion electrode.

Anticipated results--By analyzing the combined rinsings, we can calculate how much of the solid CaCO_3 which formed inside the column was present as particles in the voids among the marble chips. The total mass of CaCO_3 collected within the column (as particles and as scale on the chips) will be calculated from a mass balance on Ca^{++} . The difference will reveal how much of the CaCO_3 precipitated as scale. This can be compared with the mass of particles to determine the tendency toward scale formation vs. the tendency toward particle formation.

The concentration of CaCO_3 solution entering the column can be calculated from the concentrations of Ca^{++} and CO_3^{--} feed

solutions. By comparing the inlet concentrations with the effluent concentrations, we can calculate the rate at which CaCO_3 precipitate is accumulating within the column. This rate can be correlated with the change in pressure drop across the column and, hence, with the change in permeability.

If the marble chips are sufficiently large so the channels within the packed bed are sufficiently large, the particles of CaCO_3 precipitate which form in the liquid phase may pass out the bottom of the column. Thus, the only CaCO_3 precipitate which will accumulate within the column will be scale on the marble chips.

The residence times of the solutions in the column can be calculated from the feed rate and the void fraction. The nominal surface area of chips having a given diameter can be calculated approximately from their density and the mass of chips used. Thus, the product (surface area) x (residence time) can be calculated approximately for each experiment. The fraction of CaCO_3 precipitate which forms as scale can be correlated against this product, perhaps, and a trend discerned. Extrapolation to large values of the product, as expected for flow through a carbonate reservoir, may yield a limiting value.

Additional experiments--The above experiments will be repeated using a series of solution feed rates so as to vary residence time. A second series of experiments will employ marble chips of varying sizes, though for any particular experiment, the chips will be of uniform size.

The void fraction will be determined by filling the column with brine, then displacing it with carbon tetrachloride that has

been colored with iodine so the water- CCl_4 interface may be easily observed.

The mixing pattern within the column will be investigated by coloring one of the solutions with KMnO_4 and observing how quickly the color becomes dispersed as it passes along the column.

For those runs in which the CaCO_3 accumulation is expected to be great, the marble chips will be contained within a plastic sleeve lining the glass column. Thus, if the precipitate cements the chips together, they can still be easily removed. In this case, the mass of aggregate will be cut into thin sections using a diamond saw and the sections examined under a microscope to see how the cementation occurred. This may tell us whether the CaCO_3 scale forms uniformly over the surface or preferentially in places where flow is especially slow or especially fast.

The rate of precipitation may depend strongly upon the nature of the rock surfaces as well as upon the surface area. This possibility will be investigated by repeating some of the experiments using columns packed with chips of limestone or dolomite, or beads of glass or Teflon, instead of marble.

3.1.3 Preliminary Experiments

Batch experiments--Precipitation is apparently not instantaneous, nor is the rate independent of the surface area. When we mixed solutions of CaCl_2 and Na_2CO_3 in the presence of limestone chips, not only did the calcium ion concentration decrease with time after the solutions were mixed (indicated by specific-ion electrode response monitored over a 15-min period) but the small particles of CaCO_3 which were formed initially, gradually disappeared as the larger particles grew. The latter observation was apparent when mixtures, prepared

under identical conditions, were allowed to react, with continual stirring, for different lengths of time (15 min and 60 min, respectively). When the mixtures were filtered through papers of identical porosity, more solid CaCO_3 was seen in the filtrate from the first mixture than from the second. The filtrate from the first was noticeably turbid while that from the second was clear.

When the experiment was repeated using marble chips of smaller diameter (but same total mass) so that a greater surface area was available, the concentration of Ca^{++} ion in solution decreased more rapidly and less Ca^{++} was found in the filtrate.

Flow experiments--When Ca^{++} and $\text{CO}_3^{=}$ solutions (each 0.01 M; equivalent to 500 ppm CaCO_3 when combined) were passed through 20-mm (i.d.) columns filled with marble chips (50-90 mesh), the effluent concentration varied with the column length as shown in Figure 3. This graph suggests that supersaturation in CaCO_3 solutions decreases very slowly once the concentration is below 250 ppm. The experiments were not run for long enough periods to cause significant amounts of CaCO_3 to precipitate, so nothing can be said about the fraction of CaCO_3 that formed as scale.

3.1.4 Limitations of the Experimental Design

With four possible exceptions, the experiments described above adequately duplicate the reservoir environment in which formation damage by CO_2 is likely to occur.

Pressure gradient--The pressure gradient across a reservoir may be difficult to duplicate with a packed column. In a reservoir, the gradient would probably be in the range 0.5-2 psi/ft. By contrast, the pressure drop across the unconsolidated pack is expected to vary between 0.01 and 0.1 psi/ft.

Precipitation kinetics--The rate of formation of CaCO_3 particles or scale may be so slow that the solutions or mixtures will be supersaturated and pass through the packed columns without causing pluggage. It is possible, then, that the experimental design might understate the significance of this mechanism. Kinetics will be investigated and to the extent that time units of hours and days are significant, the kinetics will be noted and quantified.

Pore geometry--The pore-size distribution and pore geometry in the packed column may not adequately match the pore size and geometry of the reservoir. If at all feasible, an attempt will be made to use authentic cores once the experimental techniques have been perfected.

Degree of supersaturation--In view of the high surface area and long residence time expected in a reservoir, supersaturation of the calcium carbonate solution would probably be very small. In most of our experiments, supersaturation will probably be significant. Thus, the rate of precipitation and the character of the precipitate may be affected. We will try to determine the importance of this factor by repeating some experiments using inlet Ca^{++} concentrations which are relatively close to equilibrium solubility, and running the experiments for long periods.

3.2 Deposition of Insoluble Materials from Crude

Laboratory studies will be of two types:

- (1) Precipitation of solids by dissolving CO_2 in crude under high pressure.
- (2) Extraction of solublizing components from crude by contacting the crude repeatedly with supercritical CO_2 , leaving solids or semisolids behind.

3.2.1 Precipitation of Solids

In these experiments we would try to make solids precipitate from crude, in much the same way that asphaltenes are usually produced when pentane is poured into crude oil. It is likely that the solids produced by adding CO₂ to crude would depend on the concentration of CO₂ in the CO₂-crude mixture.

Apparatus--A high-pressure, Jergurson sight-glass with steel, housing having a capacity of 800 ml, will be connected to reservoirs of crude oil and CO₂ as shown in Figure 4. The sight-glass will serve as a contacting vessel (Vessel 1). A pressure gage (PI-2) will be used to determine the pressure after CO₂ has been introduced into the oil. Beneath the contacting vessel will be a high-pressure filter (Millipore). The filter (F-1) can be isolated from the system by means of valves V1 and V2, if necessary. A variety of filter elements will be available; their pore diameters will be 0.5 μm, 1.2 μm, 5 μm and 8 μm. A sight-glass (SG) in the line between the vessel and the filter will permit visual observation of the mixture which enters the filter. All lines will be ¼-inch stainless steel tubing.

Vessel 2, downstream of the filter, will be pressurized with CO₂ and will help control the differential pressure across the filter element at 1-10 psi. The entire assembly will be kept in a thermally controlled environment at 25± 1°C (77± 1.8°F).

Procedure--The system will first be purged with CO₂ to remove air and moisture. A 200-ml sample of crude oil, previously filtered through a 2-μm filter, will be transferred into Vessel 1. Next, CO₂ will be transferred into the vessel, and the vessel will be pressurized with CO₂ to 2000 psia.

The contents of Vessel 1 will be equilibrated by shaking it at 25°C (77°F). The contents will be inspected visually to see if any solids have formed. If no precipitate is seen, more CO₂ will be added, and the vessel will be shaken again.

When precipitate is noted, the contents of Vessel 1 will be filtered. The pressure drop across the filter will be controlled by keeping the CO₂ in Vessel 2 at a pressure that is only slightly lower than that in Vessel 1.

If the pressure drop across filter F-1 becomes too high, indicating that plugging has occurred, the flow will be interrupted and the 0.5 μm filter element replaced with a more porous filter element. If the new element also becomes plugged, it too, will be replaced until the 8 μm filter element has been tested for evidence of plugging.

Similar experiments will be performed using CO₂ and oil in different ratios. Later another set of analogous experiments will be performed at a higher temperature, about 52°C (125°F).

Control experiments--The operability of the apparatus will be verified before experiments using CO₂ are begun. A crude, known to contain asphaltenes, will be introduced into the vessel and an excess of pentane will be added. The mixture containing freshly-precipitated asphaltenes will be passed through filter F-1 under the same conditions of temperature and pressure to be used during the CO₂-crude experiments later. The pressure drop across the filter will be measured with a transducer and kept at about 1 psi.

In a second experiment, crude will be contacted with nitrogen instead of CO₂ and filtered under the conditions to be used later.

Anticipated results--The experiment using pentane-generated asphaltenes will demonstrate that particulates in the size-range of interest can be captured by the filter.

By contrast, during the control experiment using nitrogen, nothing should collect on the filter. If anything is collected, that will indicate that the oil is still contaminated with foreign matter, despite the preliminary filtration. (An alternate, though less-likely cause could be that the presence of high-pressure nitrogen is itself sufficient to form insoluble solids).

The pressure drop across the filter will vary with time if any solid or semisolid is being collected on the filter. The amount of precipitate which forms may vary with the ratio of CO₂ to crude.

If plugging is indeed observed, then that mixture of CO₂ and crude will be passed through a thin section of reservoir rock (sliced from a core) to confirm that reservoir damage would occur.

3.2.2 Extraction with Multiple Contacting

It may be that the high-molecular-weight components in oil become insoluble once the lower-molecular-weight components (solvent) have been removed. Accordingly, multiple contacting of crude with CO₂ may be required to produce solids.

Apparatus--A high-pressure, Jergurson sight-glass with steel, housing, having a capacity of 800 ml, will be connected to reservoirs of crude oil and CO₂ as shown in Figure 5. The primary difference between the apparatus shown in Figure 5 and that depicted in Figure 4 is the provision to sample the CO₂ phase and analyze it by gas chromatography.

Procedure--The prefiltered and preweighed crude will be transferred into the high-pressure sight-glass (Vessel 1 in Figure 5). Carbon dioxide will be added until CO₂ in the mixture exceeds 70 mole percent, then the mixture will be equilibrated at 25°C (77°F). After equilibration, a sample will be withdrawn from the upper (CO₂-rich) phase and analyzed by gas chromatography. Precipitates can be seen by looking through the sight-glass. If no precipitate is observed, we shall bleed off some of the CO₂ then refill the sight glass with CO₂ as before. After equilibration, the CO₂-rich phase will again be sampled and the liquid phase observed for any evidence of precipitation.

The procedure will be repeated at least ten times or until a precipitate has been observed. In either case, the mixture will be filtered, and any material which is collected will be saved for later analysis.

To determine the effect of temperature, the experiment will be repeated using the same crude oil but at 52°C (125°F).

For those crudes which form a precipitate on contact with CO₂, we would repeat the experiments using a thin section of core in place of the filter to confirm that plugging occurs.

Anticipated results--We expect that asphaltic precipitates will form only after the solubilizing (lower-molecular-weight) species have been removed. Extracting the "solvent" is a more severe treatment than just dissolving CO₂ in the crude. But by performing this alternate experiment, perhaps we can determine whether precipitates will ever form within a reservoir during a CO₂ flood.

Gas chromatography of the CO₂-rich phase will reveal which components are being extracted from the oil, and their relative amounts.

3.2.3 Preliminary Experiments

Control experiment--Asphaltenes which were produced by adding pentane to crude oil were successfully filtered from the mixture at atmospheric pressure. The solids tended to stick to the walls of the vessel and tubing, but were dislodged by shaking and swirling the mixture. A noticeable amount of finely-divided, black particulates was collected on the 5- μ m absolute filter element, but the filter element did not become clogged as the 200 ml of mixture passed through.

Pressure drop across the element was not measured; the high-pressure mixture was carefully bled through the filter by regulating the flow using valve V-2 just below the filter; hence most of the pressure drop probably occurred across the valve.

CO₂-crude mixture--When 100 ml of Maljamar crude that had been previously filtered through a 2- μ m filter to remove sediments was treated with CO₂ at 25°C in the 800-ml Vessel 1 (Figure 5), four results were noted:

- (1) No particles were observed in the crude until the pressure exceeded 1400 psi.
- (2) The particles tended to adhere to the walls of the vessel and tubing, but were dislodged by shaking and swirling the mixture before filtering.
- (3) As the contents were filtered by bleeding the mixture to atmospheric pressure, the flow rate gradually decreased until, after half the crude had been filtered, flow stopped. Pluggage of the 5- μ m filter element was complete and no flow

occurred, even though the pressure drop across the filter was nearly 2000 psi.

- (4) When the pressure in Vessel 1 was reduced to atmospheric and the filter element was inspected, no particulates or solids were evident! The filter element was merely stained black.

Although several explanations may be proposed, these results suggest that CO₂ causes precipitation of gummy materials, which, if they migrate with the CO₂ front, can cause pluggage.

3.2.4 Limitations of the Experimental Design

With four possible exceptions, the experiments described above adequately duplicate the reservoir environment in which formation damage by CO₂ is likely to occur.

Pressure-gradient--The pressure gradient across a reservoir may be difficult to duplicate with filter membranes. In a reservoir, the gradient would probably be in the range 0.5-2 psi/ft. By contrast, the pressure drop across the filter element, whose thickness is only 0.001 inch, is expected to be nearly 12,000 psi/ft.

Precipitates--Solids which precipitate from crude may be quite gummy and not suited to the simulated filtration techniques.

Precipitation kinetics--The rate of formation of semisolids or solids from crude may be so slow that the solutions or mixtures will be supersaturated and pass through the filters without causing pluggage. It is possible, then, that the experimental design might understate the significance of this mechanism. Kinetics will be investigated and to the extent that time units of hours and days are significant, the kinetics will be noted and quantified.

Pore Geometry--The pore-size distribution and pore geometry in the filter elements may not adequately match the pore size and geometry of the reservoir. If at all feasible, an attempt will be made to demonstrate that the damage mechanisms, identified using filters, will also occur in reservoirs by repeating the experiments with actual cores taken from oil reservoirs or outcrops having similar characteristics. In these experiments, time cannot be scaled accurately, so an attempt will be made to modify the experimental design to properly scale the kinetics anticipated under reservoir conditions.

3.3 Applicability of Expected Results

It is expected that both the deposition of carbonate and the formation of waxes or asphaltene-like materials will be demonstrated as potentially damaging to oil-bearing formations. The results of this study can be applied to actual field applications by proper cognizance of the factors responsible for the formation damage and their susceptibility to corrective action.

Asphaltenes--For example, precipitation of asphaltenes, near the injection well, could be avoided by displacing residual oil away from the well using a light, aromatic solvent followed by complete displacement with a micellar fluid. Such a displacement should leave the pores totally filled with an aqueous medium that would cause no damage.

Asphaltene damage to the producing wellbore can be lessened, if not eliminated, by recycling an aromatic solvent down the annulus concurrently with production. By periodically giving the producing well a squeeze treatment with an aromatic solvent containing properly

selected surfactant additives, it should be possible to repair any damage that has been generated around the producing wellbore.

Carbonates--The deposition of calcium carbonate in the vicinity of the injection well can best be avoided by a mild acidizing prior to initiating CO₂ injection. Once the high pressure drop has moved away from the area around the wellbore, there should be little or no tendency for damage to the formation due to the injection of high pressure CO₂.

Carbonate deposition is thought to present more of a problem in the producing well and here the solution is not readily obvious. If pressure drop is shown to be the major parameter governing damage at the production well, then hydraulic fracturing could be the remedy. Other remedies may become apparent as data are obtained. For example, acidizing of the wellbore, followed by reverse-wetting surfactants which render the mineral surfaces incapable of nucleating calcium carbonate precipitation, is a possibility. Another remedy might be some sort of inhibitor squeeze treatment which would establish the required level of sequestering agent in the reservoir around the wellbore and thereby delay or eliminate calcium ion precipitation.

4. LITERATURE SEARCH

4.1 Results

Six computer-accessible data bases were searched for references related to the title subject. No documented cases of CO₂ damage during field tests were found. Some laboratory studies were found which pertained to plausible mechanisms of damage, but which did not describe CO₂ damage explicitly.

Of the articles collected, those relating to the dissolution of carbonate and sulfate rocks and to the reprecipitation of carbonate and sulfate compounds were the most plentiful. For example, reports of scale formation in oil field water-handling equipment are numerous, and countless studies concerning this problem have been made. Only two articles mentioning asphaltene deposition in CO₂-crude mixtures were found [4,5].

Abstracts of the articles are presented in serial order in Appendix A with full citation information. An alphabetical author index is also presented in Appendix A, as is a listing of the references by subject.

4.2 Data Bases Searched

The electronic data search system called ORBIT, provided by System Development Corporation, was employed. The six data bases which were searched are described in Appendix B.

Manual searches were performed using the following indices, 1970-1979, inclusive:

Engineering Index

Comprehensive Index of American Association of Petroleum Geologists

International Petroleum Abstracts

and J. Petroleum Technology annual indices.

4.3 Search Technique

The computerized data bases were searched by submitting lists of keywords to the computer which compared them with the words in the title, abstract and keyword list for each reference. The keyword lists are presented in Appendix C. Citations that were found in this manner were examined in detail. Those which appeared relevant to formation damage were retrieved manually from the literature and read in their entirety.

4.4 Unpublished Accounts of Reservoir Damage

Representative of five oil companies which have CO₂-flood projects were contacted. Their production departments will not attribute any operating problems (such as unexpected pressure changes) to CO₂ damage. For most problems, several alternate explanations are generally more plausible.

5. CONTACTS WITH PETROLEUM INDUSTRY

At the inception of the project (late 1979) a consulting group made up of experts from industry was established and invited to New Mexico State University to discuss their experiences and suggest possible mechanisms of CO₂ damage. It was concluded that plugging of the reservoir rock was the most likely type of damage, and it might occur in either of three ways. The first would involve dissolution of calcium carbonate rock in carbonic acid, followed by reprecipitation of calcium carbonate in the vicinity of the producing well. The second would involve deposition of asphaltenes as the carbon dioxide dissolved in the oil. The third would arise from the formation of an immobile phase(s) at the CO₂-oil interface where CO₂, oil and water are simultaneously present under high pressure.

It was agreed to limit investigations to the first two mechanisms listed above. Studies relating to the third are already in progress elsewhere [1-5]. The scope of the project was also limited to theoretical and experimental investigations; no field trials are envisioned. Furthermore, tests will employ actual crude oils, not synthetic mixtures. If any cases of CO₂ damage are demonstrated, remedies will be sought and tested.

Informal contacts with oil industry personnel continued throughout the year. Our personnel consulted with several industry representatives during the Joint SPE/DOE Symposium on Enhanced Oil Recovery, held in Tulsa, April 20-21, 1980. During the same period our personnel visited the production laboratories of Amoco (Tulsa) and Shell (Houston) to discuss our experimental design and designs for apparatus.

The advisory committee has grown since 1979. The present members are:

Mr. Stan Walker - Chevron	Mr. Chapman Chronquist - G.U.R.C.
Dr. Gary Charlson - Atlantic Richfield	Dr. K. S. Lee - Shell
Dr. Loyd Jones - Amoco	Dr. Lowell Smith - Amoco
Dr. Franklyn Orr - Petroleum Recovery Research Center, New Mexico Institute of Technology, Socorro	

Amoco has been one of the most vigorous supporters of our research and, recently, has volunteered to provide an additional member of our advisory committee for the CO₂ Formation Damage project. Dr. Lowell Smith, who heads their overall CO₂ field program, has agreed to advise us in non-proprietary areas of his expertise.

All the members of this committee have been generous with their advice, and equally so with their time and money, by serving without any reimbursement. In addition, advisory companies have volunteered both information and material which greatly benefitted the project. Dr. Loyd Jones, for example, has supplied unpublished data relative to the effect of pressure on the solubility of certain salts which might damage formations. Shell has donated dolomite cores for use in quantifying the plugging effect of carbonates and asphaltenes. Amoco Production has donated several high-pressure transfer cylinders which were badly needed for the execution of the experimental program.

6. ACKNOWLEDGEMENTS

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The authors gratefully acknowledge the cooperation and assistance of the Bartlesville Energy Research Center, and Mr. Ken Spence in particular, for securing a sample of crude oil from the Bartlett Field.

Thanks too, to Dr. Franklin Orr of the Petroleum Recovery Research Center, New Mexico Institute of Mining and Technology, New Mexico for numerous ideas and much useful advice regarding experimental techniques.

7. REFERENCES

1. Orr, F. M., Yu, A. D. and Lien, C. L., "Phase Behavior of CO₂ and Crude Oil in Low Temperature Reservoirs," SPE 8813, presented at First Joint SPE/DOE Symposium on Enhanced Oil Recovery, Tulsa, April 1980.
2. Hutchinson, C. A., Jr. and Braun, P. H., "Phase Relations of Miscible Displacement in Oil Recovery," AIChE J 7 (March 1961) 64-72.
3. Huang, E. T. S. and Tracht, J. H., "The Displacement of Residual Oil by Carbon Dioxide," SPE 4735, presented at the SPE 3rd Symposium on Improved Oil Recovery, Tulsa, April 1974.
4. Shelton, J. L. and Yarborough, L., "Multiple Phase Behavior in Porous Media During CO₂ or Rich-Gas Flooding," J. Pet. Tech. 19 (September 1977) 1171-1178.
5. Simmon, R., Rosman, A. and Zana, E., "Phase Behavior Properties of CO₂ Reservoir Oil Systems," Soc. Pet. Eng. J. 18 (February 1978) 20-26.
6. Orr, F. M., Petroleum Recovery Research Center, Socorro, N.M., private communication, December 1979.

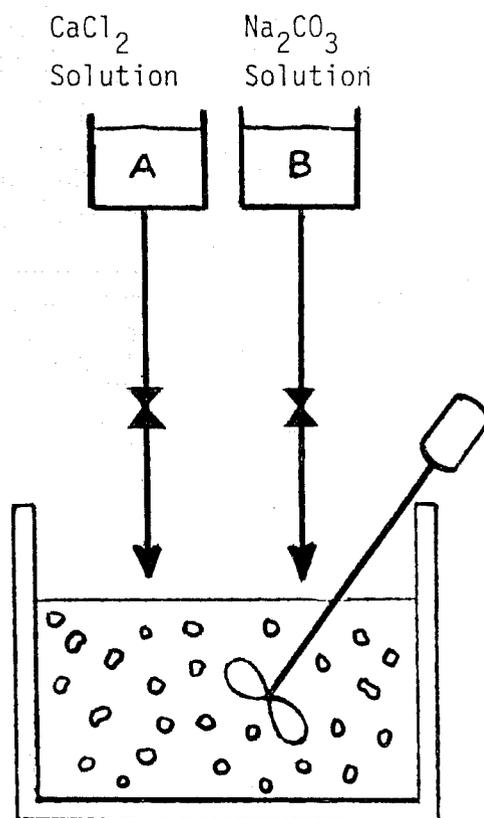


FIGURE 1 APPARATUS FOR BATCH EXPERIMENTS

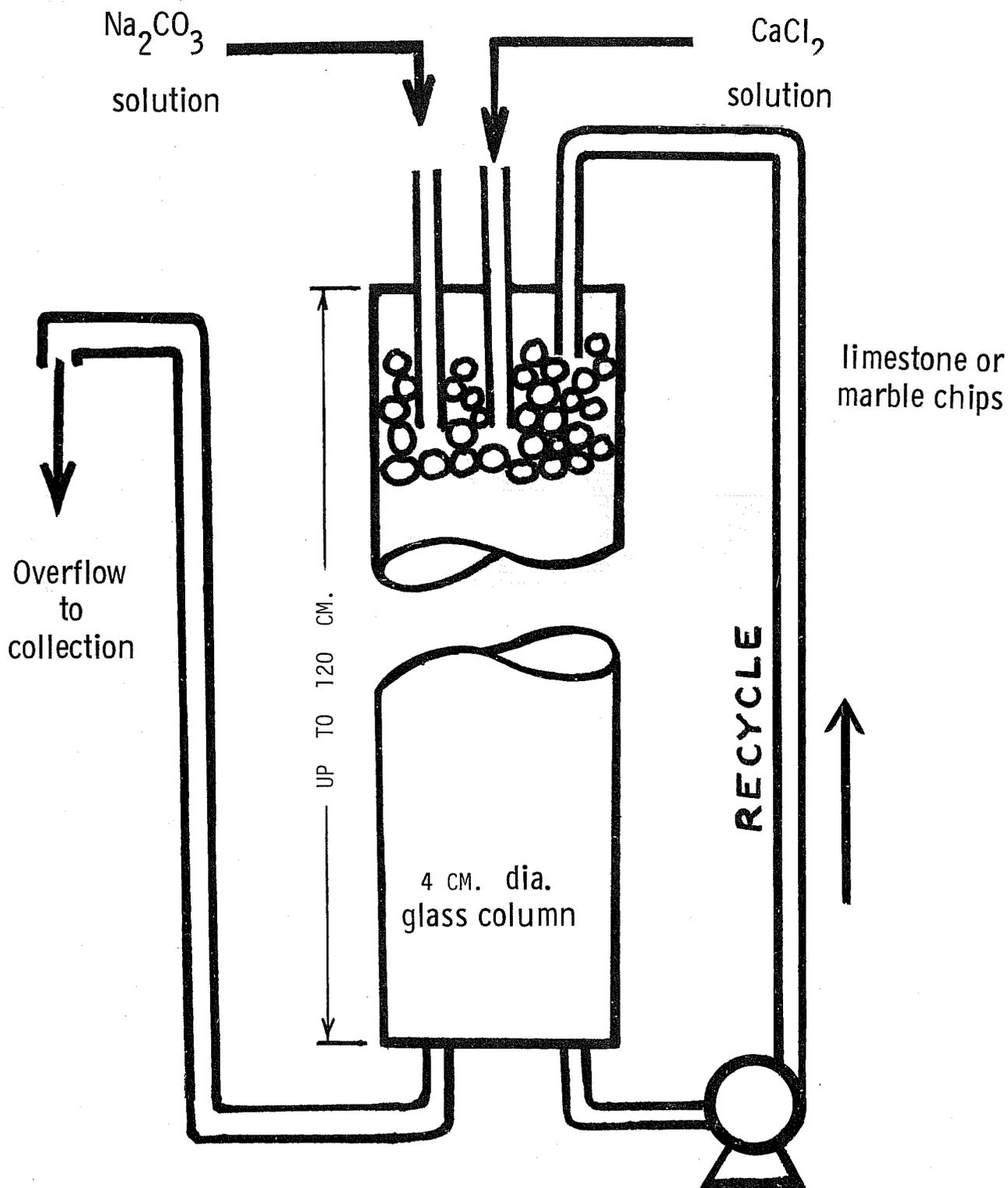
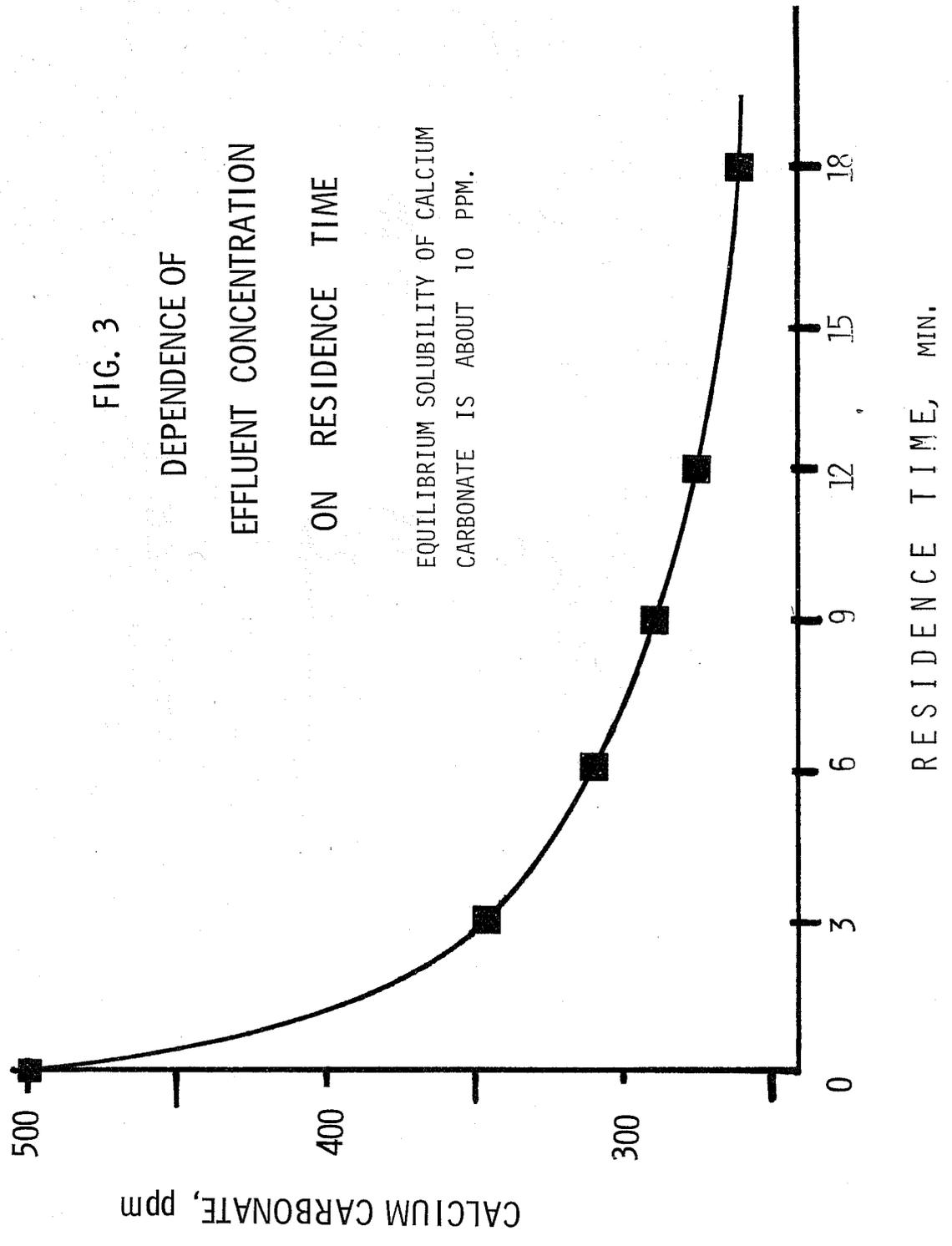


FIG. 2 APPARATUS FOR CONTINUOUS FLOW EXPERIMENTS

FIG. 3
DEPENDENCE OF
EFFLUENT CONCENTRATION
ON RESIDENCE TIME

EQUILIBRIUM SOLUBILITY OF CALCIUM
CARBONATE IS ABOUT 10 PPM.



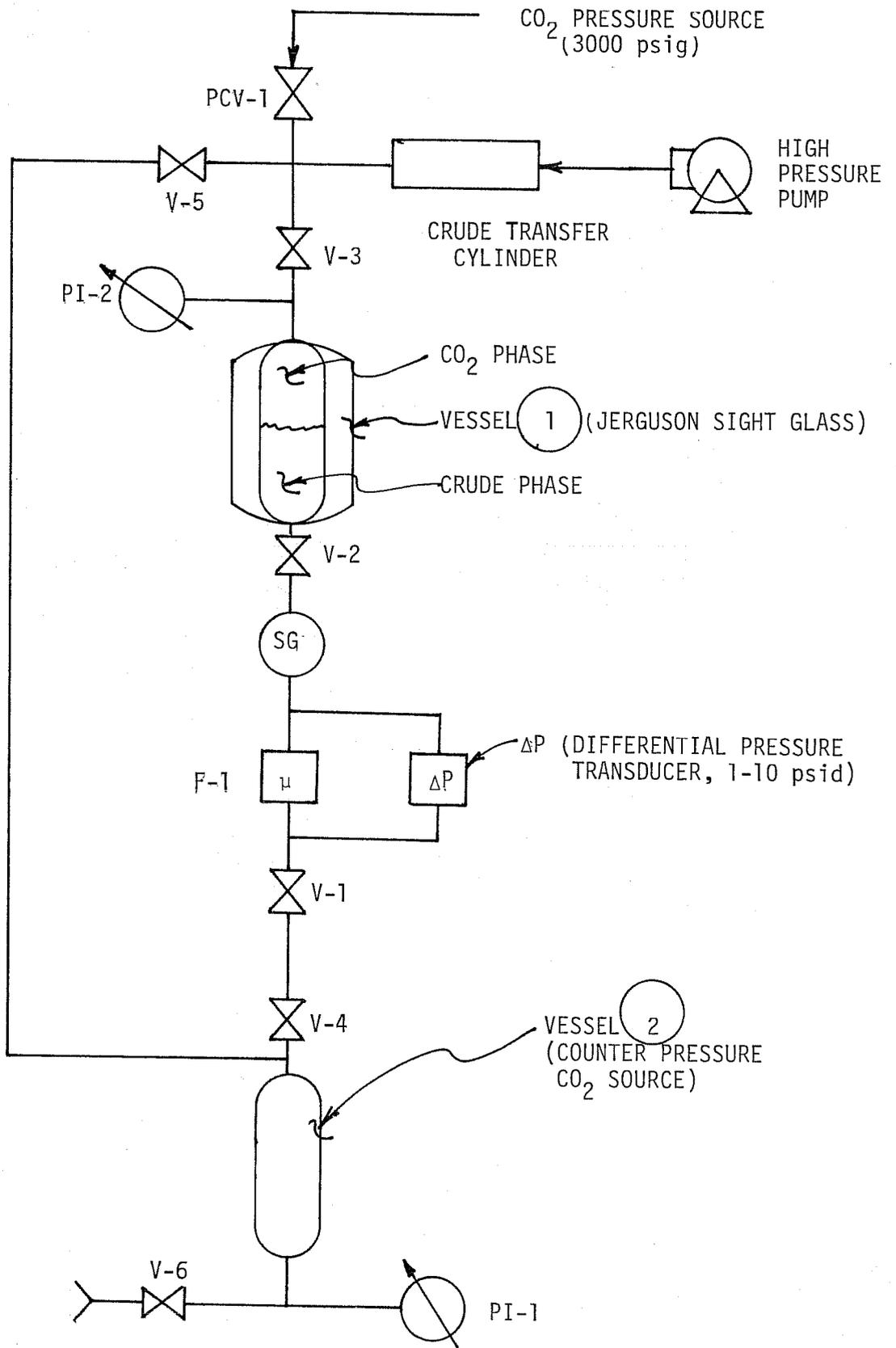


FIGURE - 4
APPARATUS FOR BATCH EXPERIMENTS

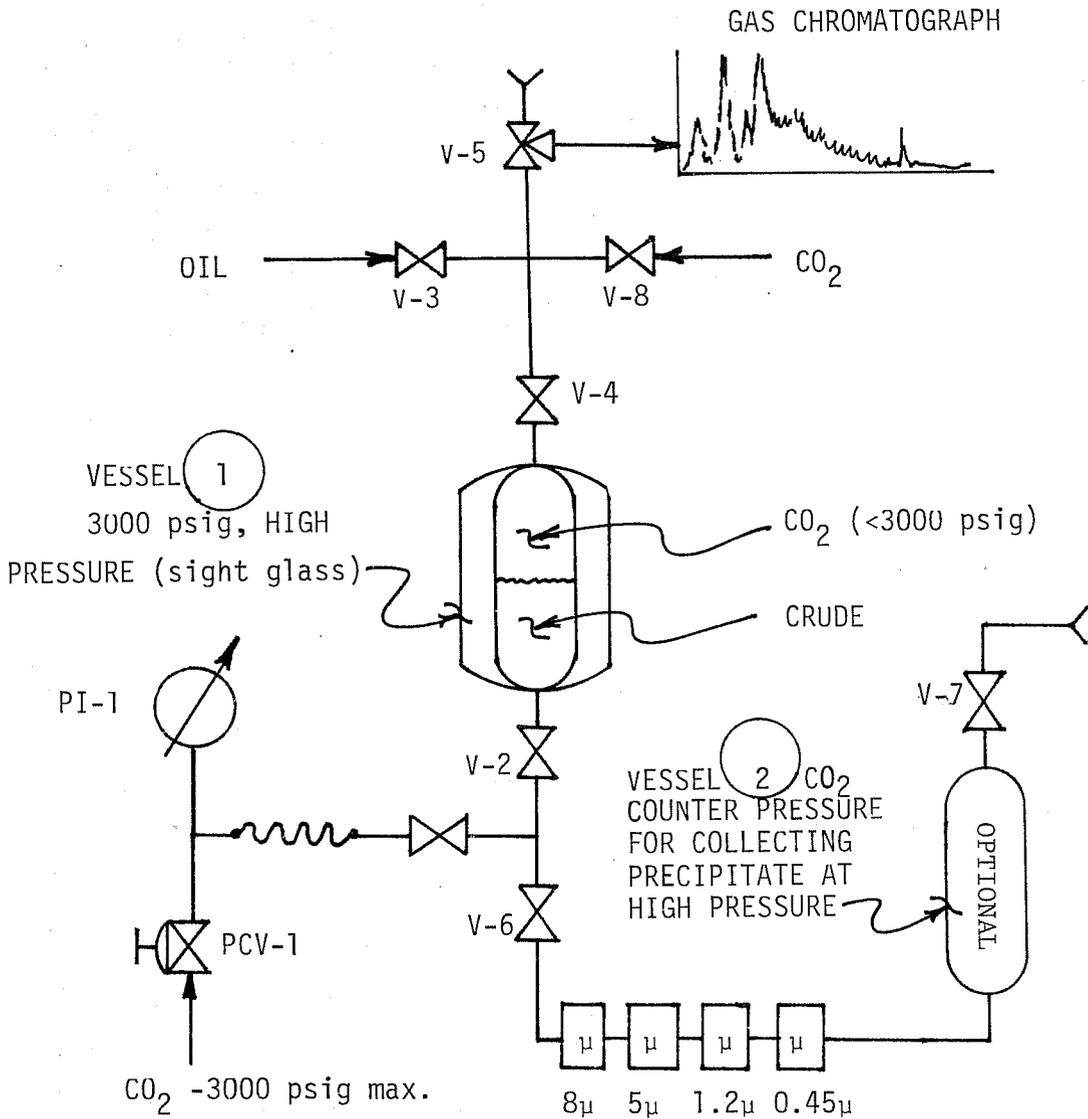


FIGURE - 5
EXTRACTION WITH MULTIPLE
CONTACTING

APPENDIX A. COMPILATION OF LITERATURE

CO₂ Formation Damage Study

References are listed, with abstracts, in serial order, on the following pages. An alphabetical index by author is also provided.

Classification by Subject

The following table lists the references by major subject area. The numbers listed there are serial numbers. The subject areas are:

- I. Field Trials
- II. Laboratory Studies, including articles which present experimental results by other workers
- III. Theoretical Studies
- IV. CO₂ - Crude Equilibria and Displacements by CO₂
- V. Carbonate Solubility or Precipitation
- VI. Sulfate Solubility or Precipitation
- VII. Scale Inhibitors
- VIII. Feldspar Decomposition, Clays, Sandstone Decomposition, Related Geochemical Topics

Table A-1

References by Subject

I.	Field Trials	7,8,13,17,24,26,32,36,54,56-59,63-65,68,74,75,88,92,97,98
II.	Lab Studies	8,9,11,12,14-16,18,19,21-24,27-29,31,32,34-37,39-44, 47-53,55-57,59,63,67,69,70,72,77-85,87,89,91-96,99, 101-105,107-111
III.	Theoretical	10,11,18,20,23,25,27,33,38,44-47,62,73,76,81,86,91,104,112
IV.	CO ₂ -Crude Equilibria	16-18,20,21,32,33,70,80,91-96,98,102
V.	Carbonate Solubility	11-14,19,34,36,37,40,45,47,51,54,56,59,64,73-76,78,79 84-86,88,99,111,112
VI.	Sulfate Solubility	8-11,15,22-24,35-38,40-46,48-50,52,53,56,59,62,64,75, 77,82,83,86,87,89,101
VII.	Scale Inhibitors	13,24,35,37,40,52,54,55,56,57,58,59,63,64,65,66,68, 69,72,75
VIII.	Feldspar Decomposition, Geochemistry Topics	25-29,31,39,67,81,97,100,103-110

REFERENCES BY AUTHOR

13. Beasley, A. E. and I. McKinney, 'Prevention of Calcium Carbonate Scale Deposition in Mill Water Systems,' Society of Mining Engineers, March 1973, pp. 32-37.
67. Bernard, G. G., 'Effect of Clays, Limestone, and Gypsum on Soluble Oil Flooding,' Journal of Petroleum Technology, Feb. 1975, pp. 179-180.
34. Bernard, G. G., 'Effect of Calcium Carbonate Supersaturation of Flood Water on Rock Permeability,' Producers Monthly, July 1957, pp. 32-36.
36. Bernard, G. G., 'A Survey on the Use of Incompatible Flood Waters,' Producers Monthly, February 1957, pp. 34-37.
25. Berner, R. A., 'Rate Control of Mineral Dissolution Under Earth Surface Conditions,' American Journal of Science, Vol. 278, No. 9 (1978), pp. 1235-1252.
26. Berner, R. A. and G. R. Holdren, Jr., 'Mechanism of Feldspar Weathering-II. Observations of Feldspar from Soils,' Geochim. Cosmochim. Acta, Vol. 43, No. 8 (1979), pp. 1173-1186.
54. Bezemer, C. and K. A. Bauer, 'Prevention of Carbonate Scale Deposition: A Well-Packing Technique with Controlled Solubility Phosphates,' Journal of Petroleum Technology, April 1969, pp. 505-514.
50. Blount, C. W. and F. W. Dickson, 'Gypsum-Anhydrite Equilibria in Systems $\text{CaSO}_4\text{-H}_2\text{O}$ and $\text{CaCO}_3\text{-NaCl-H}_2\text{O}$,' American Mineralogist, Vol. 58, 1973, pp. 323-331.
89. Bock, E., 'On the Solubility of Anhydrous Calcium Sulphate and of Gypsum in Concentrated Solutions of Sodium Chloride at 25°C, 30°C, 40°C, and 50°C,' Can. J. Chem., Vol. 39 (1961), pp. 1746-1751.
55. Bsharah, L., 'Test Unit Evaluates Scale Inhibitors,' Oil and Gas Journal, April 7, 1969, pp. 166-170.
35. Burcik, E. J., 'The Inhibition of Gypsum Precipitation by Sodium Phosphates,' Producers Monthly, Nov. 1954, pp. 42-44.
110. Busenburg, E., 'The Products of the Interaction of Feldspars with Aqueous Solutions at 25°C,' Geochim. Cosmochim. Acta, Vol. 42 (1978), pp. 1679-1686.
31. Busenberg, E. and C. V. Clemency, 'The Dissolution Kinetics of Feldspars at 25 Degrees C and at 1 Atm CO_2 Partial Pressure,' Geochim. Cosmochim. Acta, Vol. 40, No. 1 (1976), pp. 41-49.
68. Canapary, R. C., 'How to Control Refinery Fouling,' Oil and Gas Journal, Oct. 9, 1961, pp. 114-118.

106. Chafetz, H. S., 'Surface Diagenesis of Limestone,' J. of Sed. Pet., Vol. 42 (1972), pp. 325-329.
71. Chorley, R. J., 'The Role of Water in Rock Disintegration,' in: Introduction to Fluvial Processes, Methuen, London (1969), pp. 53-74.
61. Correns, C. W., 'Experiments on the Decomposition of Silicates and Discussion of Chemical Weathering,' Tenth Annual Conference on Clays and Clay Minerals, pp. 443-459.
75. Cowan, J. C. and D. J. Weintritt, 'Water-Formed Scale Deposits,' Gulf Pub. Co., Houston (1976), pp. 343-376.
37. Crawford, P. B., 'Sequestration and Chelation,' Producers Monthly, July 1957, p. 17.
9. Davis, J. W. and A. G. Collins, 'Solubility of Barium and Strontium Sulfates in Strong Electrolyte Solutions,' Environmental Science and Technology, Vol. 5, No. 10 (Oct. 1971), pp. 1039-1043.
60. DeBiesse, Y., G. de Lomballerie and F. Leandri, 'Etude Experimentale du Drainage d'une Huile Legere par Gaz Carbonique ou Eau Carbonatee,' Revue de L'Institut Francais du Petrole, Vol. 23, No. 4 (April 1968), pp. 486-507.
87. Dickson, F. W., C. W. Blount and G. Tunell, 'Use of Hydrothermal Solution Equipment to Determine the Solubility of Anhydrite in Water from 100°C to 275°C and from 1 Bar to 1000 Bars Pressure,' Am. J. of Science, Vol. 261 (1963), pp. 61-78.
7. Dixon, B. P. and L. E. Newton, Jr., 'Reinjection of Large Volumes of Produced Water in Secondary Operations,' Journal of Petroleum Technology, July 1965, pp. 781-788.
42. Doremus, R. H., 'Crystallization of Slightly Soluble Salts From Solution,' Journal of Physical Chemistry, Vol. 74, No. 7 (April 2, 1970), pp. 1405-1408.
44. Doremus, R. H., 'Precipitation Kinetics of Ionic Salts From Solution,' Journal of Physical Chemistry, Vol. 62 (1958), pp. 1068-1075.
65. Earlougher, R. C. and W. W. Love, 'Sequestering Agents for Prevention of Scale Deposition in Oil Wells,' Journal of Petroleum Technology, April 1957, pp. 17-20.
76. Edmond, J. M. and J. M. T. M. Gieskes, 'On the Calculation of the Degree of Saturation of Sea Water with Respect To Calcium Carbonate Under In Situ Conditions,' Geochim. Cosmochim. Acta, Vol. 34 (1970), pp. 1261-1291.
78. Ellis, A. J., 'The Solubility of Calcite in Carbon Dioxide Solutions,' Amer. J. Sci., Vol. 257 (May 1959), pp. 354-365.

3. Ellis, A. J. and I. M. McFadden, 'Partial Molal Volumes of Ions in Hydrothermal Solutions,' Geochim. Cosmochim. Acta, Vol. 36 (1972), pp. 413-426.
14. Englander, H. E., 'Conductometric Measurement of Carbonate Scale Inhibitors Effectiveness,' Journal of Petroleum Technology, July 1975, pp. 827-834.
64. Featherston, A. B., R. G. Mihram, and A. B. Waters, 'Minimization of Scale Deposits in Oil Wells by Placement of Phosphates in Producing Zones,' Journal of Petroleum Technology, March 1959, pp. 29-32.
69. Frazier, A. W., J. G. Huddle, and W. R. Power, 'New, Fast Approach To Reduced Preheat-Exchanger Fouling,' Oil and Gas Journal, May 3, 1956, pp. 117-122.
53. Fulford, R. S., 'Effects of Brine Concentration and Pressure Drop on Gypsum Scaling in Oil Wells,' Journal of Petroleum Technology, Vol. 20, June 1968, pp. 559-564.
15. Gainey, R. J., C. A. Thorp and E. A. Cadwallader, 'Calcium Sulfate Seeding Prevents Calcium Sulfate Scale,' Ind. and Eng. Chem., Vol. 55, No. 3 (March, 1963).
18. Gardner, J. W., F. M. Orr, and P. D. Patel, 'The Effect of Phase Behavior on CO₂ Flood Displacement Efficiency,' SPE 8367, presented at SPE 54th Annual Fall Meeting; Las Vegas, Nev. (Sept. 23-26, 1979).
86. Garrels, R. M. and M. E. Thompson, 'A Chemical Model for Sea Water at 25°C and One Atmosphere Total Pressure,' Amer. J. Science, Vol. 260 (1962), pp. 57-66.
85. Garrels, R. M., M. E. Thompson and R. Siever, 'Control of Carbonate Solubility by Carbonate Complexes,' Amer. J. Science, Vol. 259 (1961), pp. 24-25.
22. Glater, J., L. Ssutv and J. W. McCutchan, 'Laboratory Method For Predicting Calcium Sulfate Scaling Thresholds,' Env. Sci. and Tech., Vol. 1, No. 1 (Jan. 1967), pp. 41-45.
32. Government, Department of Energy (Formerly Energy Research and Development Administration), 'Enhanced Oil and Gas Recovery and Improved Drilling Methods,' DOE Quarterly Publications (1975, 1976, 1977, 1978, 1979).
41. Gunn, D. J. and M. S. Murthy, 'Kinetics and Mechanisms of Precipitations,' Chemical Engineering Society, Vol. 27 (1972), pp. 1293-1313.
51. Hawley, J. and Z. M. Pytkowicz, 'Solubility of Calcium Carbonate in Seawater at High Pressures,' Geochim. Cosmochim. Acta, Vol. 33 (1969), pp. 1557-1561.
33. Herbeck, E. F., R. C. Heinty and J. R. Hastings, 'Fundamentals of Tertiary Oil Recovery, Part 5 - Carbon Dioxide Miscible Process,' Petroleum Engineering, May 1976, pp. 114-120.

28. Holdren, G. R., Jr., and R. A. Berner, 'Mechanism of Feldspar Weathering-I, Experimental Studies,' Geochim. Cosmochim. Acta, Vol. 43, No. 8 (1979), pp. 1161-1172.
80. Holm, L. W., 'Oil Recovery Process,' U. S. Patent 3,065,790, Official Gazette, Vol. 784, No. 4 (Nov. 27, 1962), p. 1240.
98. Holm, L. W., 'Carbon Dioxide Solvent Flooding for Increased Oil Recovery,' Petroleum Transactions, Vol. 216 (1959), pp. 225-231.
16. Huang, E. T. S. and J. H. Tracht 'The Displacement of Residual Oil by Carbon Dioxide,' SPE 4735, presented at the SPE 3rd Symposium on Improved Oil Recovery; Tulsa, Okla. (April 1974).
29. Huang, W. H., 'Experimental Studies of Kinetics and Mechanisms of Simulated Organo-Chemical Weathering of Silicate Minerals,' Ph.D. Dissertation, Univ. of Missouri, Columbia, Missouri (1970).
105. Huang, W. H. and W. C. Kiang, 'Laboratory Dissolution of Plagioclase Feldspars in Water and Organic Acids at Room Temperature,' American Mineralogist, Vol. 57 (1972), pp. 1849-1859.
20. Hutchinson C. A., Jr., and P. H. Braun, 'Phase Relations of Miscible Displacement in Oil Recovery', A.I.Ch.E. Journal, March 1961, pp. 66-72.
45. Kaschier, D., 'Nucleation at Time-Dependent Supersaturation,' Surface Science, Vol. 22 (1970), pp. 319-324.
40. Kleber, J. P., 'The Use of Calgon in Primary Production and Water Flooding,' Producers Monthly, January 1951, pp. 18-24.
5. Kolthoff, I. M. and V. A. Stenger, 'Error in Quantitative Neutralizations,' in: Volumetric Analysis, Vol. 1, 2nd ed., Interscience, New York (1954).
6. Kolthoff, I. M. and V. A. Stenger, 'Neutralization and Ionic Combination Reactions,' in: Volumetric Analysis, Vol. 1, 2nd ed., Interscience, New York (1954).
4. Kolthoff, I. M. and H. A. Laitinen, 'Acids and Bases; the pH of Aqueous Solutions,' in: pH and Electrotitration, 2nd ed., John Wiley, New York (1947).
27. Kramer, K. F., 'Oxygen Compound Acidity and Oxygen Polarization as a Control in Silicate Weathering,' Ph.D. Dissertation, Florida State University, Gainesville, Florida (1968).
39. Krynine, P. D., 'Mineralogy Of Water Flooding,' Producers Monthly, December 1938, pp. 10-13.
81. Lagache, M., 'New Data on the Kinetics of the Dissolution of Alkali Feldspars at 200 Degrees C in CO₂ Charged Water,' Geochim. Cosmochim. Acta, Vol. 40, No. 2 (1976), pp. 157-161.

56. Lasater, R. M., T. R. Gardner, and T. M. Glasscock, 'Scale Deposits Are Controlled,' Oil and Gas Journal, Jan. 15, 1968, pp. 83-93.
100. Legand, H. E. and V. T. Stringfield, 'Differential Erosion of Carbonate-Rock Terranes,' Southwest Geology, Vol. 13, No. 1 (1971), pp. 1-17.
19. Lowe, L. C., M. C. McPhillips and A. C. Riddiford, 'On the Wetting of Carbonate Surfaces by Oil and Water,' Journal of Canadian Petroleum Technology, April-June 1973, pp. 33-40.
49. Madgin, W. M. and D. A. Swales, 'Solubilities in the System CaSO_4 - $\text{NaCl-H}_2\text{O}$ at 25° and 35°,' J. Appl. Chem., Nov. 1956, pp. 482-487.
77. Marshall, W. L., R. Slusher and E. V. Jones, 'Solubility and Thermodynamic Relationships for CaSO_4 in $\text{NaCl-H}_2\text{O}$ Solutions from 40° to 200°C., 0 to 4 Molal NaCl ,' J. of Chem. and Eng. Data, Vol. 9 (1964) pp. 187-191.
48. Metler, A. V. and A. G. Ostroff, 'The Proximate Calculation of the Solubility of Gypsum in Natural Brines from 28° to 70°C.,' Environ. Science and Tech., Vol. 1 (1967), pp. 815-819.
57. Miles, L., 'New Well Treatment Inhibits Scale,' Oil and Gas Journal, June 8, 1970, pp. 96-99.
12. Miller, J. P., 'A Portion of the System Calcium Carbonate-Carbon Dioxide-Water, with Geological Implications,' American Journal of Science, Vol. 250, March 1952, pp. 161-203.
88. Nakayama, F. S., 'Calcium Activity, Complex and Ion-Pair in Saturated CaCO_3 Solutions,' Soil Science, Vol. 106 (1968), pp. 429-434.
111. Nancollas, G. H. and K. Sawada, 'The Formation of Scales of Calcium Carbonate Polymorphs. The influence of Magnesium Ion and Inhibitors,' SPE 9992, SPE Fifth International Symposium on Oilfield and Geothermal Chemistry, Stanford, California, pp. 167-177.
2. Nancollas, G. H. and M. M. Reddy, 'The Kinetics of Crystallization of Scale-Forming Minerals,' Society of Petroleum Engineers Journal, April 1974, pp. 117-126.
52. Nancollas, G. H., A. E. Eralp and J. S. Gill, 'Calcium Sulfate Scale Formation: A Kinetic Approach,' Society of Petroleum Engineers Journal, April 1978, pp. 133-138.
82. Nancollas, G. H., and S. T. Liu, 'Crystal Growth and Dissolution of Barium Sulfate,' Soc. of Pet. Eng. of AIME, 1975, pp. 69-79.
99. Nathan, C., 'Vaterite in Lake Water,' Nature Physical Science, Vol. 231, No. 24 (June 14, 1971), p. 158.
102. Nathan, C., 'Solubility Studies on High Molecular Weight Paraffin Hydrocarbons Obtained from Petroleum Rod Waxes,' Petroleum Transactions, AIME, Vol. 204 (1955), pp. 151-155.

103. Nixon, R. A., 'Differences in Incongruent Weathering of Plagioclase and Microcline-Cation Leaching Versus Precipitates,' Geology, Vol. 7 (1979), pp. 221-224.
107. Nooner, D. W., J. Oro, J. M. Gilbert, L. V. Ray and J. E. Mann, 'Ubiquity of Hydrocarbons in Nature: Aliphatic Hydrocarbons in Weathered Limestone,' Geochim. Cosmochim. Acta, Vol. 36 (1972), pp. 953-959.
91. Orr, F. M., Jr., A. D. Yu, and C. L. Lien, 'Phase Behavior of CO₂ and Crude Oil in Low Temperature Reservoirs,' First Joint SPE/DOE Symposium on Enhanced Oil Recovery, Tulsa, Oklahoma, April 20-23, 1980, pp. 17-32.
72. Ostroff, A. G. and A. V. Metler, 'Apparatus for Testing Scale and Corrosion Inhibitors,' Producers Monthly, May 1965, pp. 8-12.
73. Ostroff, A. G., 'Compatibility of Waters for Secondary Recovery,' Producers Monthly, March 1963, pp. 2-9.
1. Owen, B. B. and S. R. Brinkley, 'Calculations of the Effect of Pressure Upon Ionic Equilibria in Pure Water and in Salt Solutions,' Chemistry Reviews, Vol. 29 (1941), pp. 461-471.
108. Perkins, A. T., 'Decomposition of Silicate Minerals by Acid Extractions Chemical Composition and Exchange Capacity,' Transactions Kansas Academy of Sci., Vol. 67, (1964), pp. 486-495.
17. Perry, G. E., A. J. Guillory, J. D. Baron and M. B. Moranville, 'Weeks Island 'S' Sand Reservoir B Gravity Stable Miscible CO₂ Displacement, Iberia Parish, Louisiana,' Fourth Annual DOE Symposium on Enhanced Oil and Gas Recovery, Tulsa, Oklahoma, Aug. 29-31, 1978.
21. Peterson, A. V., 'Optimal Recovery Experiments with Nitrogen and Carbon Dioxide,' Pet. Eng. Int., Nov. 1978, pp. 40-50.
109. Petrovic, R., R. A. Berner and M. B. Goldhaber, 'Rate Control in Dissolution of Alkali Feldspars - I. Study of Residual Feldspar Grains by X-ray Photoelectron Spectroscopy,' Geochim. Cosmochim. Acta, Vol. 40 (1976), pp. 537-548.
93. Pilat, S. and M. Godlewicz, 'Method of Treating Mineral Oils,' U. S. Patent No. 2,315,131 (Jan. 30, 1934).
94. Pilat, S. and M. Godlewicz, 'Method of Separating High Molecular Mixtures,' U. S. Patent No. 2,188,013 (April 27, 1936).
30. Pytkowicz, R. M., 'Rates of Inorganic Calcium Carbonate Nucleation,' Geological Notes, 1964, pp. 196-199.
59. Ralston, P. H., 'Scale Control with Aminomethylene phosphonates,' Journal of Petroleum Technology, August 1969, pp. 1029-1036.

97. Reed, M. G., 'Formation Permeability Damage by Mica Alteration and Carbonate Dissolution,' Journal of Petroleum Technology, Vol. 29 (September 1977), pp. 1056-1060.
104. Rodgers, G. P. and H. D. Holland, 'Weathering Products Within Microcracks in Feldspars,' Geology, Vol. 7 (1979), pp. 278-280.
70. Shelton J. L. and F. N. Schneider, 'The Effects of Water Injection on Miscible Flooding Methods Using Hydrocarbons and Carbon Dioxide,' Society of Petroleum Engineers Journal, June 1975, pp. 217-226.
96. Shelton, J. L. and L. Yarbrough, 'Multiple Phase Behavior in Porous Media During CO₂ or Rich-Gas Flooding,' Journal of Petroleum Technology, September 1977, pp. 1171-1178.
95. Simon, R., A. Rosman, and E. Zana, 'Phase-Behavior Properties of CO₂-Reservoir Oil Systems,' Society of Petroleum Engineers Journal, February 1978, pp. 20-26.
74. Slaton, L., R. Laster, and J. Knox, 'Scale Deposition and Removal,' Producers Monthly, September 1965, pp. 8-10.
63. Sloat, B. 'Controlled Solubility Phosphates--A Versatile Solution to Oilfield Scale Problems,' Journal of Petroleum Technology, November 1960, pp. 30-36.
24. Smith, C. F., T. J. Nolan and P. L. Czenshaw, 'Removal and Inhibition of Calcium Sulfate Scale in Waterflood Projects,' J. Petroleum Technology, Nov. 1968, pp. 1249-1256
58. Spriggs, D. M. and G. W. Hover, 'Field Performance of a Liquid Scale Inhibitor Squeeze Program,' Journal of Petroleum Technology, July 1972, pp. 812-816.
92. Stalkup, F. I., 'Carbon Dioxide Miscible Flooding: Past, Present, and Outlook for the Future,' Fifth Symposium on Improved Methods for Oil Recovery, Soc. Pet. Engrs. of AIME; Tulsa, Oklahoma (April 16-19, 1978), pp. 39-50.
47. Stiff, H. A. and L. E. Davis, 'A Method for Predicting the Tendency of Oil Field Waters to Deposit Calcium Carbonate,' Pet. Trans., Vol. 195 (1952), pp. 213-216.
46. Stiff, H. A. and L. E. Davis, 'A Method for Predicting the Tendency of Oil Field Waters to Deposit Calcium Sulfate,' Pet. Trans., Vol. 195 (1952), pp. 25-28
79. Stumper, R., 'Physicochemical Investigations of the Precipitation of Calcium Carbonate from Water,' Angew. Chem., Vol. 48, No. 7 (1935), pp. 117-124.

101. Tate, J. F., R. L. Venable and C. C. Nathan, 'The Solubility of Gypsum in Oil Field Brines,' ACS National Meeting (1964).
43. Templeton, C. C., 'Solubility of Barium Sulfate in Sodium Chloride Solutions from 25 to 95 Degrees Centigrade,' Journal of Chemical and Engineering Data, Vol. 5, No. 4 (Oct. 1960), pp. 514-516.
23. Templeton, C. C. and J. C. Rodgers, 'Prediction of Anhydrite Precipitation in Field Water-Heating Systems,' J. Pet. Tech., April 1968, pp. 423-432.
83. Uchameyshvili, N. Y., S. D. Malinin and N. I. Khitarov, 'Solubility of Barite in Concentrated Chloride Solutions of Some Metals at Elevated Temperatures in Relation to Problems of the Genesis of Barite Deposits,' Geokhimiya, Vol. 3 (1966), pp. 951-961.
10. Vetter, O. J., 'How Barium Sulfate is Formed: An Interpretation,' Journal of Petroleum Technology, December 1975, pp. 1515-1524.
66. Vetter, O. J., 'The Chemical Squeeze Process--Some New Information On Some Old Misconceptions,' Journal of Petroleum Technology, March 1973, pp. 339-352.
62. Vetter, O. J. and R. C. Phillips, 'Prediction of Deposition of Calcium Sulfate Scale Under Downhole Conditions,' Soc. of Pet. Eng., SPE 2620, 44th Annual Fall Meeting, Denver, Colo. (Sept. 28 - Oct. 1, 1969).
112. Vetter, O. J. and V. Kandarpa, 'Prediction of CaCO₃ Scale Under Downhole Conditions,' SPE 8991, SPE Fifth International Symposium on Oilfield and Geothermal Chemistry, Stanford, California, pp. 155-165.
11. Walton, A. G., 'The Nucleation of Sparingly Soluble Salts from Solution,' Analytica Chemica Acta, Vol. 29 (1963), pp. 434-441.
8. Weintritt, D. J. and J. C. Cowan, 'Unique Characteristics of Barium Sulfate Scale Deposition,' Journal of Petroleum Technology, October 1967, pp. 1381-1394.
84. Weyl, P. K., 'The Solution Kinetics of Calcite,' J. of Geology, Vol. 66 (1958), pp. 163-175.
38. Yuster, S. T., 'The Gypsum Problem in Water Flooding,' Producers Monthly, April 1939, pp. 27-35.

SERIAL LISTING OF ABSTRACTS

1. Owen, B. B., and Brinkley, S. R.: "Calculations of the Effect of Pressure Upon Ionic Equilibria in Pure Water and in Salt Solutions", Chem. Reviews Vol. 29 (1941) pp. 461-471.

Abstract

Tables of standard partial molal and ionic volumes, and their pressure coefficients, are given for aqueous solutions at 25° C. These are used to estimate the effect of pressure upon the ionization constants of water and weak acids, and the solubility constants of several minerals.

2. Nancollas, G. H. and Reddy, M. M.: "The Kinetics of Crystallization of Scale Forming Minerals", Soc. of Pet. Eng. J. (April, 1974) pp. 117-126.

Abstract

This article examines the kinetics of the crystallization of sparingly soluble minerals such as calcium carbonate, calcium sulfate, and barium sulfate, which frequently cause scaling problems in oil fields. For all three electrolytes, the crystal growth is surface controlled and follows a second-order rate law with an activation energy for the growth process of 10 to 20 kcal/mol. The growth of calcium sulfate seeded crystal above 100°C. demonstrates the importance of characterizing polymorphic transformation processes. Phosphonate scale inhibitors show differing modes of inhibition in systems precipitating CaCO_3 and CaSO_4 .

3. Ellis, A. J. and McFadden, I. M.: "Partial Molal Volumes of Ions in Hydrothermal Solutions", Geochimica et Cosmochimica Acta, vol. 36 (1972) pp. 413-426.

Abstract

Partial molal volume data are reported for NaHCO_3 and NaHS up to 200°C ., derived from solution density measurements. A summary is given of molal volumes of ions of principal interest in natural hydrothermal equilibria. Examples are given of the use of these data to calculate the effect of pressure on equilibria involving ions (H_2S and H_2CO_3 ionization; CaCO_3 , CaSO_4 solubility). In the latter case the agreement between the calculated and experimental solubility is very good to at least 250°C and 1000 bars.

4. Kolthoff, I. M., and Laitinen, H. A.: "Acids and Bases; The pH of Aqueous Solutions", pH and Electrotitration, 2nd ed. (1947) pub. John Wiley, pp. 8-11.

Abstract

A method for calculating the hydrogen ion concentration of a dibasic acid is shown on pages 8 to 11 of this book. This method can also be used with bases. A table of ionization constants and pK values is presented for some acids and bases at room temperature.

5. Kolthoff, I. M., and Stenger, V. A.: "Error in Quantitative Neutralizations", Volumetric Analysis, Vol. 1, 2nd ed. (1954) Interscience, N.Y., pp. 151-152.

Abstract

A method for calculating the error encountered when titrating a dibasic acid is presented on pages 151 to 152 of this book.

6. Kolthoff, I. M., and Stenger, V. A., "Neutralization and Ionic Combination Reactions" Volumetric Analysis, 2nd ed. (1954) pub. Interscience, N.Y., pp. 26-29.

Abstract

A method for calculating the hydrogen ion concentration (pH) of a solution containing two weak acids is presented on pages 26 to 29 of this book. Two sets of sample calculations are included.

7. Dixon, B. P., and Newton, L. E., Jr.: "Reinjection of Large Volumes of Produced Water in Secondary Operations", Journal of Pet. Tech. (July, 1965) pp. 781-788.

Abstract

A study was made of the operating performance histories and pressure-maintenance logs of four waterflood projects in the Permian Basin area, where large volumes of produced water have been reinjected into the producing formations. The projects reviewed include a wide range of characteristics: (1) open and closed water systems, (2) volumes of injected water from 2,200 to 12,500 B/D, (3) sand and limestone formations, (4) depths of 1,300 to 6,750 ft. (5) average permeabilities from 17 to 275 md, (6) bare and protected facilities, and (7) 10- to 50-year project life.

Each project exhibited performance data which indicated that reinjection of large volumes of produced water provides a good source of injection fluid, results in practical and prudent salt water disposal and, in many cases, results in conservation of fresh water for future domestic needs.

8. Weintritt, D. J., and Cowan, J. C.: "Unique Characteristics of Barium Sulfate Scale Deposition", Jour. of Pet. Tech., (October, 1967) pp. 1381-1394.

Abstract

Methods of studying oilfield mineral scale deposition in the laboratory do not work for barium sulfate because only small nonadhering crystals are formed. On the other hand, barium sulfate scale found in down-hole or surface equipment is strongly adhering and may contain very large crystals. Results suggest that most of the difference derives from the extremely low solubility of barium sulfate. Firm adherence of scale and the consistent development of oriented crystals 100 microns and larger suggest a relationship between scale adherence and crystal growth.

Data from this study indicate some reasons for barium sulfate's occurring as a deposit in oilfield waters. The unique characteristics as well as the associative properties of barium sulfate scale as related to calcium carbonate and calcium sulfate are shown.

9. Davis, J. W., and Collins, A. G.: "Solubility of Barium and Strontium Sulfates in Strong Electrolyte Solutions", Environ. Science and Tech., Vol. 5, No. 10, (Oct., 1971) pp. 1039-1043.

Abstract

Knowledge of the solubilities of $BaSO_4$ and $SrSO_4$ in solutions containing $NaCl$, $CaCl_2$, $MgCl_2$, and $NaHCO_3$ is needed to solve geologic and petroleum production problems. Samples of the sulfates were tagged with ^{35}S and prepared by precipitation. The solubility was measured in various concentrations of the major solutes by use of a liquid scintillation technique to detect the SO_2 in solution. The observed solubilities plotted against ionic strength of the solution are similar for strong electrolytes. They reach a maximum at concentration levels beginning at ionic strength of near 1. The sulfate solubility in synthetic brines (principally $NaCl$) confirms the ionic strength-sulfate solubility relationships.

10. Vetter, O. J. G.: "How Barium Sulfate is Formed: An Interpretation", Jour. of Pet. Tech., (Dec., 1975) pp. 1515-1524.

Abstract

Basic thermodynamic relations are used to predict the locations and rates of $BaSO_4$ scale formation under field conditions. When kinetics are considered, the prediction method is much improved. However, the inclusion of hydrodynamic factors in the predictive model makes it possible to explain the full range of $BaSO_4$ scale formation in the oil field.

11. Walton, A. G.: "The Nucleation of Sparingly Soluble Salts from Solution", Anal. Chim. Acta, Vol. 29, (1963) pp. 434-441.

Abstract

An examination of some of the latest ideas in the nucleation of salts from solution shows that many of the older precipitation data may be interpreted in a similar manner. Former difficulties which resulted from the interplay of heterogeneous and homogeneous nucleation processes have been resolved and the implications in the optimization of grain size in precipitates examined. Some of the possible future developments relating the interfacial tension to the environment of the nucleus are outlined and calculated values for some of the required parameters obtained both from previously published and unpublished data are presented.

12. Miller, J. P.: "A Portion of the System Calcium Carbonate - Carbon Dioxide - Water, With Geological Implications", Am. Jour. of Sci., Vol. 250 (March, 1952) pp. 161-203.

Abstract

The solubility of CaCO_3 in water depends on the presence of CO_2 , the concentration of which is a function of temperature and pressure of CO_2 in equilibrium with the water. As CO_2 -pressure increases at constant temperature the solubility of CaCO_3 increases, and at constant CO_2 pressure the solubility of CaCO_3 increases with decreasing temperature.

In the investigation conducted in this article, 259 determinations of solubility were made at temperatures ranging from 0° to 105°C and at CO_2 - pressures ranging from 1 to 100 bars. Three types of CaCO_3 - optical grade calcite, solenhofen limestone, and Venus mercenaria shells - were used for the experiments. Solvents were distilled water, 0.5 M NaCl solution, and standard sea water.

13. Beasley, A. E. and McKinney, I.: "Prevention of Calcium Carbonate Scale Deposition in Mill Water Systems", Society of Mining Engineers (March, 1973) pp. 32-37.

Abstract

This article examines various aspects of the scale deposition problem in mill water systems. Topics discussed include 1) the causes of scale deposition and 2) the methods used to combat the scale problem.

14. Englander, H. E.: "Conductometric Measurement of Carbonate Scale Inhibitors Effectiveness", Journ. of Pet. Tech. (July, 1975) pp. 827-834.

Abstract

This paper discusses the use of electrolytic conductometry for determining quantitatively an oil field brine's capacity to precipitate calcium carbonate under given conditions, and for determining the optimum dosage of scale inhibitor for specific brines.

Electrolytic conductometry involves the measurement of a solution's conductance. A change in a sample's dissolved calcium carbonate concentration causes a small, reproducible change in the solution's conductance. The amount of calcium carbonate precipitated can be determined from the change in conductance using a precalibrated graph. Correlations between laboratory tests and field data have shown that electrolytic conductometry is a useful tool for predicting scaling quantitatively.

15. Gainey, R. J., Thorp, C. A. and Cadwallader, E. A.: "Calcium Sulfate Seeding Prevents Calcium Sulfate Scale", Ind. and Eng. Chem., Vol. 55, No. 3 (March, 1963) pp. 39-43.

Abstract

Laboratory and pilot plant tests were conducted to determine the feasibility of preventing calcium sulfate scale formation in an evaporator by maintaining a sludge of calcium sulfate particles in the evaporator. This technique is based on the theory that the precipitating calcium sulfate will have a natural affinity to collect on the surface of the calcium sulfate particles introduced into the evaporator rather than on the evaporator surface. The results of these laboratory and pilot plant tests show that this technique effectively eliminates calcium sulfate scale formation in an evaporator.

16. Huang, E. T. S. and Tracht, J. H., "The Displacement of Residual Oil by Carbon Dioxide", SPE 4735, presented at the SPE 3rd Symposium on Improved Oil Recovery; Tulsa, Okla. (April, 1974).

Abstract

Displacement of a 36° API West Texas oil from watered-out cores with carbon dioxide was investigated at reservoir conditions of 90°F and 1250 psig. Phase behavior of the CO₂-West Texas oil system was also investigated. The objectives of the study were (1) to determine the oil recovery efficiency, and (2) to improve understanding of the oil recovery mechanisms, especially in relation to the phase behavior.

The phase behavior studies indicate that CO₂ efficiently swells the oil and forms two equilibrium liquid phases with the oil. Significant amounts of light and intermediate hydrocarbons are shown to be extracted into the CO₂-rich liquid phase from the oil phase. The CO₂ displacement studies conducted on watered-out cores indicate that a continuous CO₂ drive can achieve a maximum recovery of 69 percent of residual oil from a 6-ft Berea core and 65 percent from a 20 ft. sand-packed core. The minimum CO₂ slug size required in a water-propelled CO₂ drive for maximum recovery is 0.42 pore volume for the Berea core and 0.27 pore volume for the sand-packed core. In both cases, the required slug sizes are slightly greater than residual oil saturations.

An analysis of the results of the phase behavior and displacement studies indicates that CO₂ swelling and CO₂ extraction of oil are the dominant mechanisms responsible for recovering residual oil.

17. Perry, G. E., Guillory, A. J., Baron, J. D. and Moranville, M. B.: "Weeks Island 'S' Sand Reservoir B Gravity Stable Miscible CO₂ Displacement, Iberia Parish, Louisiana", presented at the 4th² Annual DOE Symposium on Enhanced Oil and Gas Recovery; Tulsa, Okla., (Aug. 29-31, 1978).

Abstract

Shell Oil Company in conjunction with the Department of Energy is conducting a gravity-stable field test of the miscible CO₂ process. The test is being conducted in a 12,800-foot deep Gulf Coast reservoir. The future producing well was drilled in December of 1977. The residual hydrocarbon saturation has been investigated using logging devices and cores.

Shell has investigated the miscibility and phase behavior of the CO₂ and reservoir crude. Injection facilities have been constructed and CO₂ injection has been targeted for the Second Quarter of 1978.

18. Gardner, J. W., Orr, F. M. and Patel, P. D.: "The Effect of Phase Behavior on CO₂ Flood Displacement Efficiency", SPE 8367, presented at SPE 54th Annual Fall Meeting; Las Vegas, Nev. (Sept. 23-26, 1979).

Abstract

The relationship between phase behavior and displacement efficiency regarding the displacement of Wason crude oil by CO₂ is examined at two different pressures - the lower one at which three co-existing hydrocarbon phases are encountered. At both pressures experimental phase behavior data, consisting primarily of phase volume fractions observed in both single contact and multiple-contact experiments, are presented. Pseudo-ternary representations of the phase behavior are incorporated into a simple, one dimensional, finite difference simulator to relate the phase behavior to displacement efficiency. At the appropriate dispersion level, displacement efficiencies computed with the model are consistent with high oil recovery efficiencies obtained experimentally in slim-tube displacements, and indicate the displacement efficiency of the process should be high in certain consolidated media as well.

19. Lowe, L. C., Phillips, M. C., and Riddiford, A. C.: "On the Wetting of Carbonate Surfaces By Oil and Water", Journal of Canadian Pet. Tech. (April, 1973) pp. 33-40.

Abstract

The relaxation of initially advancing and receding contact angles has been studied for two basic systems, water/saturated air/marble, and aqueous solution/oil/marble, and static advancing contact angles have been studied in the water/air/marble system. All experiments were conducted at room temperature, but other experimental conditions have been varied so as to permit comparison between these laboratory results and certain aspects of the recovery of oil from limestone fields. A preliminary study also has been made to elucidate which components of crude oil affect the wettability of calcium carbonate, and assess the stability of the adsorbed layers to solvent attack and to oxidation.

20. Hutchinson, C. A., Jr., and Braun, P. H. "Phase Relations of Miscible Displacement in Oil Recovery", A.I.Ch.E. Journal (March, 1961) pp. 66-72.

Abstract

Miscible displacement as an oil recovery process has received wide interest in the literature recently. Essentially, three basic processes have been proposed for attaining miscible displacement in our oil reservoirs: high-pressure gas, enriched gas, and miscible-slug processes.

The present paper relates and compares the phase relations and mass transfer mechanisms of these various basic, miscible-displacement processes. It also discusses the effects of the various operating variables, such as pressure, temperature, injected gas composition, etc., on the applicability of the process and considers the pertinent conditions that restrict the application of each process. It is to be recognized that at times a miscible displacement may be attempted but not attained, or unforeseen conditions may destroy miscibility once it has been attained. The authors discuss the results of such conditions. The mechanisms of the miscible displacement processes are explained in a conceptual analysis based on the triangular phase diagram. Although the multicomponent reservoir fluid system cannot be represented rigorously from a thermodynamics standpoint by these diagrams, they are useful for conceptual analysis. Their limitations are presented by the authors along with data supporting the concepts developed.

24. Smith, C. F., Nolan, T. J., and Czenshaw, P. L.: "Removal and Inhibition of Calcium Sulfate Scale in Waterflood Projects", J. Pet. Tech. (Nov., 1968) pp. 1249-1256.

Abstract

The problem of preventing calcium sulfate scale deposition has become increasingly important in the last few years due to the increasing use of waterflood as a means of secondary recovery. Many methods have been proposed for removing or preventing scale deposition. A few chemicals and treatment methods have been effective, but there are many ineffective scale-removal agents and inhibitors still on the market today. This paper describes the results of a laboratory testing program that evaluated 98 potential-scale inhibitors and 20 scale-removal agents. The paper also describes a field-testing program in which various removal methods and inhibitor placement techniques were evaluated in 19 wells, and it compares field and laboratory results.

25. Berner, R. A.: "Rate Control of Mineral Dissolution Under Earth Surface Conditions", Am. Journ. of Sci., Vol. 278, No. 9 (1978) pp. 1235-1252.

Abstract

Dissolution of minerals by water is an important Earth surface geochemical process. Actual dissolution rates generally cannot be accurately predicted from laboratory experiments, because experiments ordinarily fail to reproduce the composition and structure of natural mineral surfaces, especially with regard to adsorbed, trace-inhibitor species, and poorly-understood biological factors are usually ignored. Laboratory experiments can be helpful, however, in distinguishing rate-limiting mechanisms, or in other words, whether dissolution is primarily controlled by surface reactions or by transport of ions away from the surface.

Although much work has been done in predicting, from thermodynamic calculations, whether or not dissolution can occur, little attempt has been made to describe how dissolution occurs under natural conditions. The purpose of this paper is to point out some of the factors that control the rate of dissolution and to yield a better understanding of the applicability of chemical kinetics to the solution of geochemical problems.

26. Berner, R. A. and Holdren, G. R. Jr. "Mechanism of Feldspar Weathering-II. Observations of Feldspars from Soils", Geochim. Cosmochim. Acta, Vol. 43, No. 8 (1979), pp. 1173-1186

Abstract

Examination of the surface morphology (via scanning electron microscopy) and surface composition (via X-ray photoelectron spectroscopy) of sodic plagioclase and potash feldspar grains taken from four different soils, provides little or no evidence for the existence of a tightly-adhering, protective, surface layer of altered composition on the feldspar surface. Grains, from which all adhering clay has been removed by ultrasonic cleaning, exhibit the same chemical composition in the outermost few tens of angstroms as the underlying feldspar. Aluminum-rich 'clay' coatings which continue to adhere to the grains after ultrasonic treatment are patchy, highly hydrous, and unlikely to act as major diffusion-limiting, and thus protective, barriers. Attack by dissolution of the feldspar surface is non-uniform and follows a definite etching sequence characterized by the development and growth of distinctive etch-pits. This dissolution sequence can be reproduced by treating fresh feldspars in the laboratory with strong HF-H₂SO₄ solutions and, thus, the sequence is unaffected by the composition of the attacking solution. All of our results suggest that the dissolution of feldspar during weathering is controlled by selective chemical reaction at the feldspar-solution interface and not by uniform diffusion through a protective surface layer.

27. Kramer, K. F.: "Oxygen Compound Acidity and Oxygen Polarization as a Control in Silicate Weathering", Ph.D. Dissertation, Florida State University, Gainesville, Florida (1968).

Abstract

This work discusses the solution chemistry involved in silicate alteration. It employs an acid-base model based on anion polarization. The model was developed for oxygen compounds.

28. Holdren, G. R. Jr., and Berner, R. A.: "Mechanism of Feldspar Weathering-- I. Experimental Studies," Geochim. Cosmochim. Acta, Vol. 43, No. 8 (1979) pp. 1161-1172

Abstract

It has been widely accepted that a chemically altered, protective surface layer regulates the dissolution, and hence the weathering, of plagioclase feldspars under Earth's surface conditions. In this study, we examine this hypothesis in detail with the aid of scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS). Using these techniques, we have been unable to find any direct evidence suggesting the presence of a chemically-altered coating on feldspar surfaces which have been weathered in the lab. Instead, our results suggest that the mechanism controlling feldspar weathering is a surface-controlled reaction.

Based on SEM observations and measurements of rate of release of silica, we postulate that the process of feldspar dissolution proceeds in two stages in the lab. Initially, one observes the dissolution of ultrafine (1 μm diameter) particles which are produced during grinding of the sample, and which adhere tenaciously to the surfaces of larger grains. This is the stage which results in the non-linear rates of dissolution which are commonly observed in the lab (parabolic kinetics). Secondly, the dissolution occurs at sites of excess surface energy such as at dislocations or similar crystal defects. This process yields linear rates of dissolution, and it dominates the weathering of feldspars in the field.

29. Huang, W. H.: "Experimental Studies of Kinetics and Mechanisms of Simulated Organo-Chemical Weathering of Silicate Minerals", Ph.D. Dissertation, Univ. of Missouri; Columbia, Missouri (1970).

Abstract

Freshly fractured olivine, augite, muscovite, labradorite, and microcline in particle sizes $297 \mu - 149 \mu$ in diameter, after washing, were shaken at room temperature in deionized water, CO_2 charged water, 0.01 M acetic acid and 0.01 M aspartic acid (weakly complexing organic acids), 0.01 M salicylic acid and 0.01 M tartaric acid (strongly complexing organic acids), in closed systems. Samples of solute were drawn at 0.36, 1.2, 5.1 and 21.2 days and analyzed for Si, Al, Fe, Mg, Ca, Na, K, pH and conductivity.

30. Pytkowicz, R.M., "Rates of Inorganic Calcium Carbonate Nucleation", Geological Notes, 1964, pp. 196-199.

Abstract

The induction period for the inorganic precipitation of calcium carbonate was examined over a wide range of supersaturations. Results suggest that inorganic precipitation in average sea water would require about 10^5 years. If most of the bicarbonate were converted to carbonate, precipitation could occur in 50 hours. The power dependence of the rate of nucleation on the carbonate concentration is second order in the absence of magnesium and sixth order in its presence; this indicates that magnesium inhibits the precipitation of calcium carbonate.

31. Busenberg, E. and Clemency, C. V.: "The Dissolution Kinetics of Feldspars at 25°C. and 1 atm. CO₂ Partial Pressure", Geochim. Cosmochim. Acta., Vol. 40², No. 1 (1976) pp. 41-49.

Abstract

The dissolution kinetics of 5% by weight suspensions of two potassium feldspars and six plagioclases were studied for 400-1200 hr at 1 atm P_{CO₂}. The less than 37 μm particles had surface areas ranging from 0.83 to 1.84 m²/g. At frequent intervals, the pH of the stirred suspensions were measured in the reaction cell as the solutions were sampled. The filtered aqueous samples were acidified and then were analyzed for Si, Al, K, Na, Ca, Mg, and Fe.

The following sequence of events was recognized in the artificial weathering of all the feldspars: (1) an initial ion-exchange stage lasting approximately 1 min during which the surface cations were replaced by hydrogen ions from the bulk solution, (2) an up-to-4-day, non-parabolic stage characterized by the very rapid release of cations and silicic acid into the bulk solution, (3) a diffusion-controlled parabolic stage lasting approximately 19 days, and (4) a steady-state stage characterized by the very slow release of cations and silicic acid. All the rate constants for all the feldspars were evaluated at the pH of about 5. The calculated parabolic rate constants range from 3.4×10^{-14} to 9.3×10^{-13} mole/cm²/sec^{1/2}; the linear rate constants range from 3.2×10^{-17} to 2.5×10^{-15} mole/cm²/sec, and the apparent diffusion coefficients range from 1×10^{-22} to 5×10^{-21} cm²/sec.

32. Department of Energy (Formerly Energy Research and Development Administration): "Enhanced Oil and Gas Recovery and Improved Drilling Methods", D.O.E. quarterly publications (1975, 1976, 1977, 1978, 1979).

Abstract

These reports, which are issued quarterly by the U.S. Department of Energy, contain useful information on the objectives, background, and technical progress of DOE sponsored field projects and supporting research. A number of topics are covered, including chemical flooding, carbon dioxide injection, thermal/heavy oil projects, Western Gas studies, Eastern Gas studies, improved drilling methods, residual oil studies, environmental studies, and petroleum technology.

The CO₂ field projects include Granny's Creek Field, West Va., Griffithsville Field, West Va., Rock Creek Field, West Va., and Weeks Island Reservoir, La. Supporting research is being performed on corrosion problems, oil recovery, and displacement of residual oil.

33. Herbeck, E. F., Heintz, R. C. and Hastings, J. R.: "Fundamentals of Tertiary Oil Recovery, Part 5 - Carbon Dioxide Miscible Process", Pet. Eng. (May, 1976) pp. 114-120.

Abstract

Miscibility in a CO₂ flood process is achieved only after several contacts between the injected CO₂ and the reservoir fluid. The minimum miscibility pressure in the case of CO₂ is less than 1,500 psi for many reservoirs. CO₂ can also extract heavier components of hydrocarbons in the range of C6 to C30 and achieve miscibility even with crude oils that have little intermediate (C2 to C6) components. This makes the process more versatile. It is particularly suited for reservoirs containing crude oils with 25 API and above. A practical upper limit of operating pressure in a CO₂ injection process is 6000 psi; the lower limit is 1500 psi. The density of CO₂ is close to that of crude oil and approaches that of water under some reservoir conditions. As a result, effects of gravity override are minimized in this process. The process also gives better sweep efficiency than hydrocarbon-miscible processes because CO₂ viscosity is two to four times higher than that of hydrocarbon solvents, over usual ranges of pressure. However, alternate CO₂ and water injection is often necessary to achieve a reasonable miscibility ratio. CO₂ with water forms carbonic acid, which is highly corrosive. Special metal alloys and coatings may be required for facilities. Dual-injection systems for water and CO₂ are usually used. Availability and cost of CO₂ are important economic factors that should be considered in this process.

34. Bernard, G. C.: "Effect of Calcium Carbonate Supersaturation of Flood Water on Rock Permeability", Producers Monthly (July, 1957) pp. 32-36.

Abstract

A laboratory investigation was carried out to determine the maximum amount of CaCO_3 supersaturation that can be carried in a flood-water without plugging injection wells. It appears that up to 60 ppm of CaCO_3 supersaturation can be tolerated in a floodwater entering the reservoir in the temperature range of 80 to 130°F. Thus, it is likely that the closed system will be satisfactory for many floodwaters that were formerly thought to require calcium carbonate stabilization. Since the closed system is considerably more economical to build and to maintain than the open system, application of this information may result in reduced floodwater treating costs.

35. Burick, E. J.: "The Inhibition of Gypsum Precipitation by Sodium Polyphosphates", Prods. Monthly (Nov., 1954) pp. 42-44.

Abstract

Experiments were conducted to determine the effectiveness of several dehydrated sodium polyphosphates in inhibiting gypsum precipitation in an aqueous solution. Results show that the sodium polyphosphates are effective as inhibitors in concentrations far below the concentration actually needed to form complexes with all of the calcium ions. The polyphosphates apparently work by adsorbing on the surface of the gypsum crystals to prevent further growth, rather than by tying up all of the calcium ions.

The experiments were conducted with inhibitor concentrations of 50, 25, and 12.5 ppm and time periods of 1 hr., 10 hr., and 11.5 days. Several of the polyphosphates inhibited precipitate formation past the 10 hr. period, but all the solutions had precipitated after 11.5 days.

36. Bernard, G. S.: "A Survey on the Use of Incompatible Flood Waters", Producers Monthly (Feb., 1957) pp. 34-37.

Abstract

Experimental data indicate that incompatible waters do not react in, nor decrease the permeability of, a reservoir. Apparently, during the displacement process the main body of injection water does not mix with the main body of interstitial water.

A questionnaire was prepared requesting information concerning field experience with injection waters that were incompatible with interstitial waters, during water flooding of oil reservoirs. This was sent to fifty persons who had had considerable experience with all phases of water flooding. In the questionnaires that were returned, five water floods were reported in which incompatible waters had been used without any injurious effects. Thus far, no case has been reported in which the use of incompatible waters had a deleterious effect.

It is concluded that there is little danger of plugging a reservoir rock by injecting into it a water which is incompatible with the reservoir interstitial water.

37. Crawford, P. B.: "Sequestration and Chelation", Producers Monthly (July, 1957) p. 17.

Abstract

This article briefly discusses how the polyphosphates prevent calcium and barium ions from precipitating in flood waters. Equilibrium data for several of the reactions involving the polyphosphates and calcium ions are presented and explained. Diagrams showing the structures of several of the polyphosphates are shown.

38. Yuster, S. T.: "The Gypsum Problem in Water Flooding", The Producers Monthly (April, 1939) pp. 27-35.

Abstract

The factors involved in the precipitation of calcium sulfate (gypsum) from aqueous solutions are examined to determine which factors are responsible for calcium sulfate scaling in water flood projects. The three factors discussed are temperature change, evaporation of solvent, and chemical precipitation.

Calculations are presented to show the relative contributions of each of these factors to the total scaling problem. Results show that temperature change and evaporation of solvent are of minor importance. Chemical precipitation due to the mixing of incompatible waters is probably the major contributor to calcium sulfate scaling in water flood projects.

39. Krynine, P. D.: "Mineralogy of Water Flooding", The Producers Monthly (Dec., 1938) pp. 10-13.

Abstract

In order to predict the behavior of a reservoir during a water flood, it is important to know not only the porosity and permeability of the reservoir, but to understand the structural factors within the reservoir which determine these values. The structural factors involved fall into the three general categories of the structure and texture of the sand; the physical properties of the surface of the walls of the voids, which include wettability and adsorption; and the chemical properties of the reservoir, which includes the solubilities of the various constituents found in the reservoir. Methods for determining and evaluating these structural factors are presented in this article.

40. Kleber, J. P.: "The Use of Calgon in Primary Production and Water Flooding", Producers Monthly (January, 1951) pp. 18-24.

Abstract

Calgon is a molecularly dehydrated phosphate which has proved to be effective in overcoming many scaling and corrosion problems encountered in the petroleum industry. The most important of these problems may be listed as follows:

1. The deposition of relatively insoluble salts such as calcium carbonate, barium sulfate, and strontium sulfate resulting from the mixing of various waters and brines.
2. The deposition of calcium carbonate scale resulting from the loss of carbon dioxide due to pressure reduction or temperature changes.
3. The deposition of calcium carbonate scale resulting from the addition of alkali in treating the brine or fresh water prior to injection.
4. The deposition of soluble iron or manganese resulting from the exposure of the water to the air or to oxidizing, disinfecting agents such as chlorine.
5. The deposition of iron oxide and the decreased life of lines and equipment due to the corrosive action of oxygen or carbon dioxide.

41. Gunn, D. J. and Murthy, M. S.: "Kinetics and Mechanisms of Precipitations", Chem. Eng. Sci., Vol. 27 (1972) pp. 1293-1313.

Abstract

The kinetics of crystal growth of a number of sparingly-soluble salts have been studied. The crystallization of barium sulphate was studied in detail; the concentration of the crystallizing solution and the surface area of the precipitate were measured as the crystallization proceeded, and the particle size distribution was measured at the termination of the growth period.

The induction period was measured for three, sparingly-soluble salts at a number of different concentrations. The rate of growth of barium sulphate was found to show a third-order dependence on concentration when the crystals were small. For larger crystals at low supersaturations the dependence was found to be first order.

The measurements of concentration, surface area and particle size distribution were used to calculate the rates of primary and secondary nucleation of barium sulphate. Other evidence concerning secondary nucleation is presented and found to be consistent with the kinetic measurements.

The development of crystal shape is related to diffusion in the solution and the surface reaction. It is shown that the induction period may be simply related to the rate of growth of small crystals.

42. Doremus, R. H.: "Crystallization of Slightly Soluble Salts from Solution", Journ. of Phys. Chem., Vol. 74, No. 7 (April 2, 1970) pp. 1405-1408.

Abstract

The rate of crystallization of barium sulfate from aqueous solution was studied simultaneously using two methods, electrical conductivity of the solution and light scattering from the particles. From these measurements the particle size was estimated and the interface growth coefficient was calculated. The results indicated that the particles coagulated in the later stages of precipitation. Results of several authors on crystallization of salts from solution are compared. The order of the crystallization process depends upon the stoichiometry of the salt and its supersaturation. The effect of supersaturation may result from different growth processes on different crystal faces. The interface growth coefficients for different salts, orders of crystallization, and supersaturation are compared. These coefficients are usually not a function of order or supersaturation, but do depend upon the type of salt crystallizing.

43. Templeton, C. C.: "Solubility of Barium Sulfate in Sodium Chloride Solutions from 25° to 95°C." Journ. of Chem. and Eng. Data, Vol. 5, No. 4 (Oct., 1960) pp. 514-516.

Abstract

The deposition of barium sulfate as scale from highly concentrated brines produced from oil wells is a fairly common occurrence. As part of a study of this scale-formation problem, the concentration solubility product of barium sulfate in the $\text{BaSO}_4 - \text{NaCl} - \text{H}_2\text{O}$ system has been determined at several temperatures between 25°C and 95°C for sodium chloride molalities between about 0.1 and 5.0.

44. Doremus, R. H.: "Precipitation Kinetics of Ionic Salts from Solution", Journ. of Phys. Chem., Vol. 62 (1958) pp. 1068-1075.

Abstract

Mechanisms for ionic crystal growth from solution are discussed and compared to experimental measurements of salt precipitation rates. In the systems considered the crystal growth rate is shown to be controlled by an interface process, rather than by bulk diffusion of solute. An adsorbed surface-layer on the growing salt particles is proposed as the first stage in crystal growth from solution, and this proposal is shown to be consistent with the experimental results. It is concluded that in the systems considered, nucleation occurs rapidly and the number of salt particles is constant during the measured growth period, and that factors as well as solute supersaturation influence the nucleation process.

45. Kaschier, D.: "Nucleation at Time-Dependent Supersaturation", Surface Science, Vol. 22 (1977) pp. 319-324.

Abstract

Homogeneous nucleation taking place at time-dependent supersaturation is considered. Expressions are derived for the nucleation rate and for the total number of nuclei formed in the system. After simple modification these expressions may also be used in the case of heterogeneous nucleation. Finally, a linear supersaturation change during the process is considered as an example.

46. Stiff, H. A. and Davis, L. E.: "A Method For Predicting the Tendency of Oil Field Waters to Deposit Calcium Sulfate", Pet. Trans., Vol. 195 (1952) pp. 25-28.

Abstract

A graphic method was developed which can be used to predict the tendency of oil field waters to precipitate calcium sulfate under a variety of conditions. Application of this method is made to the prediction of sulfate scale formation in heater treaters, boilers, oil wells, cooling systems and water injection wells.

47. Stiff, H. A. and Davis, L. E.: "A Method for Predicting the Tendency of Oil Field Waters to Deposit Calcium Carbonate", Pet. Trans. Vol. 195 (1952) pp. 213-216.

Abstract

The authors previously presented a method for predicting the tendency of oil field waters to deposit calcium sulfate. The present paper gives a similar method for calcium carbonate.

Methods for predicting calcium carbonate scaling tendencies in fresh waters have been available for some time, but these could not be used for brines. By experimentally deriving the value of the K term in the Langelier equation, a method has been developed which applies to waters of high salt content. A statistical study is included which shows that the experimentally derived values of K are in good agreement with actual conditions. Several applications of the final equation to production practice are given.

48. Metler, A. V., and Ostroff, A. G.: "The Proximate Calculation of the Solubility of Gypsum in Natural Brines from 28° to 70° C.", Environ. Science and Tech. (1967) Vol. 1, pp. 815-819.

Abstract

Formulas are derived for calculation of the solubility of calcium sulfate in various concentrations of sodium, magnesium, calcium, chloride, and sulfate ions in solution at 28°, 38°, 50°, and 70° C. Corrections are included to account for the effect of a wide concentration range of excess common ion (Ca^{++} or SO_4^{--}). Results are compared with a large number of solubility determinations in solutions of widely varying salt content. Examples demonstrating the use of these formulas are given.

49. Madgin, W. M. and Swales, D. A.: "Solubilities in the System $\text{CaSO}_4 - \text{NaCl} - \text{H}_2\text{O}$ at 25° and 35°", J. Appl. Chem. (Nov., 1956) pp. 482-487.

Abstract

Solubilities of both gypsum and anhydrite in solution with sodium chloride, varying in concentration up to saturation, have been determined at 25° and for gypsum only at 35°. Sodium chloride lowers the temperature (42°) at which both forms of calcium sulphate have the same solubility and the salt concentration to cause this at 25° has been determined. The influence of small amounts of sodium sulphate, in addition to sodium chloride, has also been investigated.

It has been found that calcium sulphate, never present as much as 1% by weight, has very little, if any, influence on the solubility of sodium chloride.

50. Blount, C. W., and Dickson, F. W.,: "Gypsum-Anhydrite Equilibria in Systems $\text{CaSO}_4\text{-H}_2\text{O}$ and $\text{CaCO}_3\text{[sic]-NaCl-H}_2\text{O}$ ", Am. Mineralogist, Vol. 58 (1973) pp. 323-331.

Abstract

The equilibria of gypsum and anhydrite with solution and vapor were studied by the use of solubilities, which were in part gained from downward extrapolation of solubilities measured at high temperatures to avoid kinetic difficulties encountered below 70°C. The 4-phase invariant equilibrium of gypsum, anhydrite, simple H_2O solution, and vapor is set at $56^\circ\text{C} \pm 3^\circ\text{C}$ and 124 ± 9 torr. The pressure change required to increase the univariant equilibrium temperature of gypsum, anhydrite and H_2O solution 1°C is about 78 bars, which agrees well with values calculated from thermochemistry. The 3-phase univariant equilibrium of gypsum, anhydrite, and vapor ranges from 124 torr at 56°C to 13.6 torr at 20°C . The effect of NaCl concentration on the 4-phase univariant equilibrium of gypsum, anhydrite, $\text{NaCl-H}_2\text{O}$ solution, and vapor, is to lower the equilibrium temperature from that of the invariant point, 56°C for zero NaCl concentration, to: 48°C , 2 molal NaCl; 36°C , 4 molal NaCl; and 20°C , molal NaCl. The uncertainty in the temperatures in NaCl solutions is $\pm 4^\circ\text{C}$.

51. Hawley, J. and Pytkowicz, Z. M.: "Solubility of Calcium Carbonate in Seawater at High Pressures", Geochim. Cosmochim. Acta, Vol. 33 (1969) pp. 1557-1561.

Abstract

The solubility product of calcium carbonate in seawater at high pressure was determined at 2°C . Results were used to study the degree of calcium carbonate saturation in the Pacific Ocean, and to determine the change in molal volume upon solution of calcium carbonate.

52. Nancollas, G. H., Erlap, A. E., and Gill, J. S.: "Calcium Sulfate Scale Formation: A Kinetic Approach", Soc. of Pet. Eng. Jour. (April, 1978) pp. 133-138.

Abstract

The growth and phase transformation of calcium sulfate dihydrate and hemihydrate crystals were studied at temperatures from 70° to 130°C. At 70°C the second-order rate constant for dihydrate crystal growth did not change by more than 20 percent over a pH range of 3.2 to 9.2. It was also independent of ionic strength up to 2.0 M. Growth in stable supersaturated calcium sulfate solution was completely inhibited by $7. \times 10^{-7}$ M phytic acid for about 24 hours at 70°C. The seeded crystallization of calcium sulfate hemihydrate at temperatures from 90 to 140°C and the phase changes from alpha to beta hemihydrate were investigated by X-ray diffraction, specific surface area analysis, and scanning electron microscopy. Organic phosphonates were found to be effective inhibitors of crystal growth of all the phases at high temperatures.

53. Fulford, R. S.,: "Effects of Brine Concentration and Pressure Drop on Gypsum Scaling in Oil Wells", J. of Pet. Tech., Vol. 20 (June, 1968) pp. 559-564.

Abstract

This article studies the effects of brine concentration and pressure drop on gypsum scaling in oil wells. The study reveals that the amounts of scale formed at a given pressure drop and temperature depend on the amount of sodium chloride and other salts dissolved in the brine. The quantity of gypsum deposited increases with salt concentration to a maximum, then decreases until, with strong brines, no scale is formed.

54. Bezemer, C. and Bauer, K. A.,: "Prevention of Carbonate Scale Deposition: A Well-Packing Technique With Controlled Solubility Phosphates", J. of Pet. Tech. (April, 1969) pp. 505-514.

Abstract

This article looks at the prevention of carbonate scale deposition using polyphosphate well packs. Equations and graphs are presented for selecting the kind and amount of polyphosphate to be used for scale prevention. Results of field tests conducted on wells in the south Sumatran fields (Indonesia) are presented. Results show that the method has been successful in preventing scale in these wells.

55. Bsharah, L.,: "Test Unit Evaluates Scale Inhibitors", The Oil and Gas Journ. (April 7, 1969) pp. 166-170.

Abstract

This article presents a method for testing the effectiveness of scale inhibitors. A diagram of the testing apparatus is shown and procedures for its use are presented. Results of tests conducted to evaluate the effectiveness of numerous scale inhibitors are shown.

56. Lasater, R. M., Gardner, T. R., and Glasscock, F.M., : "Scale Deposits are Controlled", The Oil and Gas Journ. (Jan. 15, 1968) pp. 88-93.

Abstract

The usual techniques for applying scale inhibitors to wells usually uses the scale inhibitor in its solid form. There are instances however, where the scale inhibitor could be more effectively applied as a liquid.

This article looks at the effectiveness of liquid scale inhibitors in preventing scale deposits in wells. Results of laboratory tests using several liquid scale-inhibitors with CaSO_4 and CaCO_3 are shown. The results of field tests conducted on several producing wells are reported.

57. Miles, L.: "New Well Treatment Inhibits Scale", The Oil and Gas Journ. (June 8, 1970) pp. 96-99.

Abstract

Scale formation in producing and injection wells is a problem frequently encountered in the petroleum industry. This article discusses the effectiveness of one scale inhibitor, ArcoHib S-232, at combatting this problem. Results of laboratory and field tests are presented.

58. Spriggs, D. M. and Hover, G. W.: "Field Performance of a Liquid Scale Inhibitor Squeeze Program", J. of Pet. Tech. (July, 1972) pp. 812-816.

Abstract

This article presents the field test results of a liquid scale-inhibitor squeeze program. The results were collected from 100 liquid squeezes performed in 60 wells. The production performance of these wells indicates that the inhibitor squeeze program has been effective in preventing scale buildup.

59. Ralston, P.H.: "Scale Control with Aminomethylenephosphonates", J. of Pet. Tech. (Aug., 1969) pp. 1029-1036.

Abstract

This article discusses the use of aminomethylenephosphonates (AMP) in controlling scale in producing wells. Topics include information on the properties of AMP, the mode of action of AMP as a scale inhibitor, and laboratory and field test results.

Laboratory results show the effectiveness of AMP in controlling water-formed deposits. Calcium sulfate, barium sulfate, and calcium carbonate can be controlled with 0.2 to 20 mg/l of AMP based products.

Field results confirm that AMP-type compositions (1) inhibit scale from produced, injection, and heater-treater waters, (2) possess desirable solution stability for surface and down-hole applications and (3) improve profitability in oil recovery by reducing maintenance and workover costs.

60. DeBiesse, Y., de Lamballerie, G. and Leandri, F.: "Étude Expérimentale du Drainage d'une Huile Légère par Gaz Carbonique ou Eau Carbonatée," Revue de L'Institut Français du Pétrole, Vol. 23, No. 4 (April 1968), pp. 486-507.

Abstract

Draining a petroleum-bearing layer either by means of carbon dioxide followed by carbonate-containing water or by carbonate-containing water alone is a variant of the waterflooding process which, in the case of heavy and viscous oils, is known to bring about spectacular improvements in recovery.

Experiments of the same process applied to particularly light and fluid oil such as that from the Fz. 4 reservoir in the Zarzaitine field were made in the laboratory by Entreprise de Recherches et d'Activités Pétrolières.

They showed that the expected increase in recovery - which is quite appreciable in the case of CO₂ drainage - was only moderate when drainage was brought about by carbon-dioxide-containing water. This is because carbon dioxide does very little to decrease the viscosity and volume expansion of the oil even though both of these factors are usually considered to be preponderant in an interpretation of the process. On the other hand, the noteworthy decrease in the interfacial tension between oil and water containing dissolved CO₂ may play an important role, especially if drainage is done in an unconsolidated medium.

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61. Correns, C.W.: 'Experiments on the Decomposition of Silicates and Discussion of Chemical Weathering' Tenth Annual Conference on Clays and Clay Minerals, pp. 443-459.

Abstract

Experimental investigations of chemical weathering in which powders of potassium feldspar, albite, leucite, muscovite, tremolite, olivine, and volcanic glass are treated with pure water and with dilute solutions of sulfuric, carbonic, and hydrochloric acid have been performed in an apparatus in which the mineral powder is exposed to a circulating water flow. The experiments have been continued recently by treating kaolinite and montmorillonite. The course of decomposition of these minerals depends on water flow rate, grain size, temperature, and pH of the solutions. These experiments in open systems are compared with investigations reported in the literature and with the conditions of natural weathering.

62. Vetter, O. J. and Phillips, R. C.: "Prediction of Deposition of Calcium Sulfate Scale Under Downhole Conditions", Soc. of Pet. Eng., SPE 2620, 44th Annual Fall Meeting, Denver, Colo. (Sept. 28 - Oct. 1, 1969).

Abstract

This paper describes the use of fundamental thermodynamic relations to determine where and how much CaSO_4 scale is deposited under bottomhole conditions. The simplifications used in the calculations are explained and a method for proving the validity of published solubility data is submitted. Experimental solubility data, published by different authors, are used for the presented calculations. Some fundamental relationships concerning the behavior of CaSO_4 under downhole conditions are given. These relationships have proved to be valuable in fighting scale.

63. Sloat, B., "Controlled Solubility Phosphates - A Versatile Solution to Oilfield Scale Problems", Journal of Pet. Tech., (November, 1960) pp. 30-36.

Abstract

Water flooding has focused attention on the problem of scale in producing wells. Four reasons why scale forms are discussed. A new theory which will help explain the severe scale build-up that occurs in any producing wells at the time of water breakthrough is presented.

A recently-developed family of scale preventives, the controlled-solubility phosphates, is described chemically and physically. Factors which influence the performance of these unique phosphates in oilfield brines are evaluated in terms of laboratory test data. Case histories of producing wells treated with controlled-solubility phosphates are summarized. The importance of bottom-hole temperature, the role of produced-fluid mineral characteristics and the value of knowing down-hole flow conditions are pointed out. Economic considerations well known to engineers and production men are used to compare the cost of conventional treatment and the cost of the new controlled-solubility phosphate scale-prevention approach.

64. Featherston, A. B., Mihram, R. G., Waters, A. B.: "Minimization of Scale Deposits in Oil Wells by Placement of Phosphates in Producing Zones", J. of Pet. Tech., (March, 1959) pp. 29-32.

Abstract

Deposition of compounds such as calcium carbonate, calcium sulfate and barium sulfate in formation flow channels, on tubing, casing and producing equipment has continuously plagued the oil industry. Although polyphosphates have a long history in scale inhibition, only relatively recently have the extremely-slow-solubility, di-metallic polyphosphates been injected into producing zones in conjunction with fracturing.

As a result of such treatments, scale deposition in the formation in addition to the wellbore and producing equipment has been checked in some cases for over a year. Characteristics to be considered when selecting a phosphate for this type treatment have been outlined with the effect each has on scale prevention and on length of time they will be effective.

65. Earllougher, R. C. and Love, W. W.: "Sequestering Agents for Prevention of Scale Deposition in Oil Wells", J. of Pet. Tech., (April, 1957) pp. 17-20.

Abstract

This article discusses the field performance of phosphate sequestering agents in the prevention of scale deposition in oil wells. Soluble phosphates are mixed with the sand injected into the producing formation during fracturing treatments. More than 30 wells have been treated by this special fracturing method, and production data indicate that the problem of formation plugging by mineral deposition is being effectively overcome.

66. Vetter, O. J.: "The Chemical Squeeze Process - Some New Information on Some Old Misconceptions", J. of Pet. Tech. (March, 1973) pp. 339-552.

Abstract

This article discusses new information learned about the chemical squeeze process. Among the things learned through a series of tests was that adsorption isotherms, contrary to common theory, are not very important to the process, and some factors that have been largely ignored (flow velocity, for example) are very important.

67. Bernard, G. C.: "Effects of Clays, Limestone, and Gypsum on Soluble Oil Flooding", J. of Pet. Tech. (Feb., 1975) pp. 179-180.

Abstract

This study is concerned with the effect of rock minerals (clays, limestone, and gypsum) on soluble-oil flooding. Flooding experiments were conducted in sandpacks containing from 0 to 2 percent of either gypsum, montmorillonite clay, or calcium carbonate. The oil recovery efficiency is calculated at various bed compositions and the results compared graphically.

68. Canapary, R. C.: "How to Control Refinery Fouling", The Oil and Gas Journ. (Oct. 9, 1961) pp. 114-118.

Abstract

This article discusses the techniques used to control fouling of refinery equipment. Topics presented include a review of the causes of fouling and a discussion of the chemicals that can be used and the operational changes that can be made to help solve the problem.

69. Frazier, A. W., Huddle, J. G. and Power, W. R.: "New, Fast Approach To Reduced Preheat-Exchanger Fouling", The Oil and Gas Journ. (May 3, 1965) pp. 117-122.

Abstract

This paper presents a laboratory test procedure for determining the fouling tendency of refinery process streams. The information obtained from the laboratory test can be used to predict where fouling problems will occur in plant equipment and to predict the effectiveness of anti-fouling chemicals. Results of the laboratory test compare favorably with plant operating data.

70. Shelton, J. L. and Schneider, F. N.: "The Effects of Water Injection on Miscible Flooding Methods Using Hydrocarbons and Carbon Dioxide", Am. Inst. of Min., Met., and Pet. Eng., (June, 1975) pp. 217-226.

Abstract

The effects of mobile water saturations on oil recovery and solvent requirements were studied in miscible displacement tests on sandstone cores. It was found that (1) oil, if trapped by mobile water, cannot be easily contacted by solvent, and the amount of oil is directly related to measureable relative-permeability characteristics; (2) miscible displacement performances for secondary and tertiary conditions are equivalent; (3) long-core tests describe the movement of fluid banks that would occur in field floods; and (4) flooding response for solvent developed from multiple contact of crude oil with carbon dioxide or rich gas in long cores is the same as that for liquid solvents with first-contact miscibility.

71. Chorley, R.J., 'The Role of Water in Rock Disintegration', in: Introduction to Fluvial Processes, Methuen, London (1969), pp. 53-74.

Abstract

The properties of water which promote the decomposition of rocks and minerals are discussed. The weathering of igneous minerals is described; included are orthoclase, plagioclase, muscovite mica, quartz, ferromagnesium minerals, biotite and hornblende.

72. Ostroff, A. G. and Metler, A. V.: "Apparatus for Testing Scale and Corrosion Inhibitors", Producers Monthly (May, 1965) pp. 8-12.

Abstract

An apparatus is described for the simultaneous testing of scale and corrosion inhibitors. The apparatus assembly provides for evaluation of inhibitory efficiency under flowing conditions over a range comparable to actual oil field conditions of temperature, pressure, pH, flow rate, and composition of corrodant. Any type of steel or other alloy can be tested. Results of tests with several specific chemicals and with several proprietary materials are presented.

73. Ostroff, A. G.: "Compatibility of Waters for Secondary Recovery", The Producers Monthly (March, 1963) pp. 2-9.

Abstract

The water used for water floods in oil recovery projects may come from many different sources. It is important that mixed waters be chemically compatible or else problems will be encountered with deposits precipitated from incompatible waters. This article contains information on the calcium carbonate and iron scale problems. Procedures for testing for incompatibility are reviewed and methods for predicting incompatibility are discussed.

74. Slaton, L., Lasater, R. and Knox, J.: "Scale Deposition and Removal"
Producers Monthly, (Sept., 1965) pp. 8-10

Abstract

Scale deposition in injection wells and producing wells occurs primarily as a result of: pressure drop, temperature changes, incompatible waters, microbial reactions, improper well treatments. Scale removal requires consideration of type of scale, connate waters, and previous treatment.

Several examples of scale problems encountered in industry and their solutions are discussed.

75. Cowan, J. C. and Weintritt, D. J.: "Water-Formed Scale Deposits",
Gulf Pub. Co., Houston, TX. (1976) pp. 343-376.

Abstract

The scale problem in the petrochemical industry is discussed on pages 343-376 of this book. Topics include a discussion of the various types of scale encountered in the petrochemical industry and the use of scale inhibitors to combat the problem.

76. Edmond, J. M. and Gieskes, J. M. T. M.: "On the Calculation of the Degree of Saturation of Sea Water with Respect To Calcium Carbonate Under In Situ Conditions", Geochim. Cosmochim. Acta, Vol. 34 (1970) pp. 1261-1291.

Abstract

A discussion is presented of the computation of the in situ degree of saturation of sea water with respect to calcite or aragonite, Ω , using apparent thermodynamic constants. It is found that when the various reported values of the constants are recomputed so as to be strictly comparable, the resulting concordance is generally good. A systematic error in Ω of not more than 10 percent is estimated to result from the uncertainties in the constants. This is equivalent to an error of 1 per cent in the measured values of A_t or ΣCO_2 , where A_t is the alkalinity by titration and ΣCO_2 is the total carbon dioxide concentration. A profile of A_t and ΣCO_2 from the Brazil Basin in the equatorial South Atlantic is used as an example of the computation procedure.

77. Marshall, W. L., Slusher, R., and Jones, E. V.: "Solubility and Thermodynamic Relationships for CaSO_4 in $\text{NaCl-H}_2\text{O}$ Solutions from 40° to 200° C., 0 to 4 Molal NaCl ", J. of Chem. and Eng. Data Vol. 9 (1964) pp. 187-191.

Abstract

The solubility of metastable $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ has been determined at 40° and 60°C ., of metastable $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ at 125°C ., and CaSO_4 (anhydrite) at 125° , 150° , 175° , and 200°C in $\text{NaCl-H}_2\text{O}$ solutions varying from 0 to 4 molal NaCl . These data, combined with additional literature values, agreed with Debye-Huckel theory at all temperatures and over the range of concentration (except at the highest concentrations at temperatures below 100°C .) when a function of the ionic strength, I , is $I^{\frac{1}{2}}/(1 + AI^{\frac{1}{2}})$, where $A = 1.5$, was used. This agreement lends confidence to the application of Debye-Huckel theory to this system at varying temperatures using a constant value for A . The solubility product, K° , for the reaction,

$$\text{CaSO}_4(\text{solid}) = \text{Ca}^{+2} + \text{SO}_4^{-2},$$

decreased from 63.0×10^{-6} at 25°C . to 0.114×10^{-6} at 200°C ., giving values of ΔF° varying from $+5.75$ to $+15.0$ kcal./mole, respectively. Values of ΔH° and ΔS° changed from -1.9 to -18 kcal./mole and from -26 to -70 cal. mole $^{-1}$ deg. $^{-1}$, respectively, over the same range of temperature. For $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ at 60°C ., $K^\circ = 35.7 \times 10^{-6}$ was obtained and for $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ at 125°C ., $K^\circ = 9.49 \times 10^{-6}$.

78. Ellis, A. J.: "The Solubility of Calcite in Carbon Dioxide Solutions", Amer. J. Sci., Vol. 257 (May, 1959) pp. 354-365.

Abstract

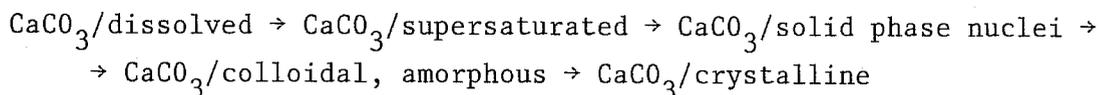
The solubility of calcite in water is reported for temperatures between 100 and 300°, at partial pressures of carbon dioxide ranging from 1-40 atmospheres. Values for the solubility product and the free energy of solution of calcite are derived.

From a study of the kinetics of solution of a single calcite crystal at these temperatures the Arrhenius energy of activation was found to be very low. The rate-determining step is suggested to be a diffusion or desorption process.

79. Stumper, R.: "Physicochemical Investigations of the Precipitation of Calcium Carbonate From Water", Angew. Chem., Vol. 48, No. 7 (1935) pp. 117-124.

Abstract

In order for CaCO_3 to precipitate the following conditions must be met. 1) The free CO_2 content must fall below the equilibrium value for "pertinent carbonic acid" or the partial pressure of CO_2 in the gas phase must fall below the CO_2 partial pressure corresponding to this value. 2) The ion product, $[\text{Ca}^{++}][\text{CO}_3^{--}]$ must exceed the solubility product. 3) The supersaturation of the solution in CaCO_3 must be eliminated. The chief factors regulating the precipitation of CaCO_3 from pure $\text{Ca}(\text{HCO}_3)_2$ solutions are, in general, the partial pressure of CO_2 and the rate of formation of the solid phase:



The precipitation of CaCO_3 from supersaturated solutions begins only after an induction period has passed. Between this period (I) and the initial concentration (C) there is a simple relationship:

$$C \cdot I^{\frac{1}{2}} = \text{const.}$$

The induction period is very sensitive to the presence of foreign substances.

80. Holm, L. W.: "Oil Recovery Process", U. S. Patent 3,065,790 (Nov. 27, 1962).

Abstract

This patent describes a process for producing a petroleum oil from an oil-bearing, limestone rock reservoir, by injecting carbon dioxide into the well. The process involves injecting 500 to 3500 s.c.f. of carbon dioxide per barrel of oil in place, to provide an elevated pressure of not less than 700 p.s.i. in the reservoir. An aqueous drive fluid is then injected into the reservoir until breakthrough of the fluid occurs at the producing well. Oil can then be produced from the reservoir until the pressure is depleted.

81. Lagache, M.: "New Data on the Kinetics of the Dissolution of Alkali Feldspars at 200°C. in CO₂ Charged Water", Geochim. Cosmochim. Acta., Vol. 40, No. 2 (1976), pp. 157-161.

Abstract

The kinetics of the dissolution of several feldspars were studied experimentally at 200°C as a function of the surface area and time. The molalities of Na⁺ and K⁺ have been plotted against the product of the surface area and time. For two feldspars (albite and adularia) the rates of dissolution of Na⁺ and K⁺ are smooth, continuous functions of surface area-time, which implies that they are controlled by the composition of the fluid.

The comparison between the dissolution of pure sodium or potassium feldspars and that of an intermediate feldspar (sanidine) shows that the intermediate feldspar dissolves as if it were composed of sodium and potassium feldspar grains in the proportions corresponding to its composition.

A mechanism proposed by others to describe the method of dissolution is reviewed. This mechanism proposes that the dissolution could be described by a process of diffusional mass transfer through a surface layer of reaction products.

The present experiments do not agree with such an interpretation of the mechanism of dissolution.

82. Nancollas, G. H., and Liu, S. T.: "Crystal Growth and Dissolution of Barium Sulfate", Soc. of Pet. Eng. of AIME (1975), pp. 69-79.

Abstract

The kinetics of crystallization and dissolution of barium sulfate seed crystals have been investigated conductimetrically. Growth is characterized by an initial surge, due to secondary nucleation, followed by a rate which is proportional to the square of the supersaturation. Studies have been made using seed material of differing morphology and in all cases the crystallization is surface controlled. A surface reaction also appears to be rate determining for the corresponding dissolution process, but the overall rate constant is considerably greater than that for growth. Crystallization and dissolution have been studied in the presence of potential phosphonate and polyphosphate scaling inhibitors and, in some cases, both processes are markedly inhibited. The incorporation of the anti-scalant into the developing crystals may pose problems in their down-hole application.

83. Uchameyshvili, N. Y., Malinin, S. D., and Khitarov, N. I.:
"Solubility of Barite in Concentrated Chloride Solutions of Some
Metals at Elevated Temperatures in Relation to Problems of the
Genesis of Barite Deposits", Geokhimiya, Vol.3 (1966) pp. 951-961.

Abstract

The solubility of barite in chloride solutions depends both on the concentration and on the type of chloride. For pure water and 0.25 N solutions of KCl and NaCl, the solubility of barite passes a maximum in the temperature interval 100-300° C. However, in solutions of CaCl₂, MgCl₂ and 2 N NaCl, barite solubility increases continuously with temperature, and in a 1 N NaCl solution the solubility curve has an inflection. The authors propose that the dissolution of barite in CaCl₂, MgCl₂ (>1N) may be accompanied by the formation of new phases (CaSO₄, MgSO₄, and Na₂SO₄); only CaSO₄ was observed directly. On the basis of experimental solubility data and data from fluid inclusion study, it is suggested that anhydrite paragenetically preceded barite, in a barite deposit in the Caucasus.

84. Weyl, P. K.: "The Solution Kinetics of Calcite", J. of Geology, Vol. 66, (1958), pp. 163-175.

Abstract

The solution alteration of a limestone depends on the rate at which water entering the rock becomes saturated. This rate is governed by the rate of transport of solute away from the solid-liquid interface, where the solution is always saturated. For laminar flow in a straight circular capillary of radius a , the solution will be 90 per cent saturated after penetrating a distance $0.572\gamma a^2/D$, where γ is the average flow velocity of the fluid and D is the diffusion constant of the solute in the solution. Under normal conditions below the water table, γ and a are sufficiently small that the water in a limestone is always saturated with respect to calcium carbonate. Solution alteration can therefore take place only where the water first enters the rock or where the solubility changes.

85. Garrels, R. M., Thompson, M. E., and Siever, R.: "Control of Carbonate Solubility by Carbonate Complexes", Am. J. of Science, Vol. 259, (1961), pp. 24-25.

Abstract

Activity coefficients of HCO_3^- and CO_3^{--} were determined in aqueous solutions of NaCl , MgCl_2 , and of NaCl-MgCl_2 mixture of approximately the same mol ratio as sea water. The values obtained in "synthetic sea water" correspond to those observed in actual sea water.

The data for CO_3^{--} are interpreted in terms of two complexes. The calculations show that of the total CO_3^{--} in sea water, as determined by titration and not including HCO_3^- , about 75 percent is MgCO_3 , 15 percent NaCO_3 , and 10 percent free CO_3^{--} .

The data for HCO_3^- also indicate the presence of complexes of Na^+ and Mg^{++} , but these are less strongly associated, and are not fully characterized.

It is shown that the concentration of Ca^{++} , in equilibrium with calcite, is greater in "synthetic sea water" than in Mg-free NaCl solutions. The observed apparent supersaturation of sea water in calcite is not fully explained here. Although the total concentration of CO_3^{--} in sea water can be predicted from these data, that of Ca^{++} cannot.

86. Garrels, R. M. and Thompson, M. E.: "A Chemical Model for Sea Water at 25°C and One Atmosphere Total Pressure", Am. J. Sci., Vol. 260, (1962), pp. 57-66.

Abstract

Dissociation constants involving Ca^{++} , Mg^{++} , Na^+ , K^+ , SO_4^{--} , HCO_3^- and CO_3^{--} ions, and individual ion activity coefficients have been used to calculate the distribution of dissolved species in sea water at 25° C and one atmosphere total pressure. The distributions obtained for sea water of chlorinity 19% and pH 8.1 are:

Ion	Molality (Total)	% Free Ion	% Me- SO_4 pair ⁴	% Me- HCO_3 pair ³	% Me- CO_3 pair ³
Ca^{++}	0.0104	91	8	1	0.2
Mg^{++}	0.0540	87	11	1	0.3
Na^+	0.4752	99	1.2	0.01	-
K^+	0.0100	99	1	-	-

Ion	Molality (total)	% Free Ion	% Ca-anion pair	% Mg-anion pair	% Na-anion pair	% K-anion pair
SO_4^{--}	0.0284	54	3	21.5	21	0.5
HCO_3^-	0.00238	69	4	19	8	-
CO_3^{--}	0.000269	9	7	67	17	-

The activities calculated for free ions are: 0.00264 for Ca^{++} , 0.0169 for Mg^{++} , 0.0356 for Na^+ , 0.0063 for K^+ , 4.7×10^{-6} for CO_3^{--} , 9.75×10^{-4} for HCO_3^- , 1.79×10^{-3} for SO_4^{--} .

87. Dickson, F. W., Blount, C. W., and Tunell, G.: "Use of Hydrothermal Solution Equipment to Determine the Solubility of Anhydrite in Water from 100°C to 275°C and from 1 Bar to 1000 Bars Pressure", Am. J. of Science, Vol. 261, (1963) pp. 61-78.

Abstract

Specially designed "hydrothermal solution" equipment was used to determine the solubility of anhydrite in H₂O from 100°C to 275°C and from 1 bar to 1000 bars. The solubility of anhydrite decreases with increasing temperature and increases with increasing pressure.

The hydrothermal solution equipment consists of a deformable Teflon sample cell held in a stainless steel pressure vessel and sealed in such a way as to prevent interchange of material between the sample cell and the steel bomb. Separate pressure lines leading to the sample cell and to the steel bomb allow liquid to be pumped into or taken out of each container independently. Liquid and solid phases may be allowed to come to equilibrium in the Teflon cell at constant temperature and pressure. The experimental mixtures are stirred by means of a Teflon-coated bar magnet turned by an externally applied pulsating magnetic field. An internally filtered liquid sample can be withdrawn without significant disturbance of the equilibrium temperature and pressure, by pumping liquid into the steel vessel at the same rate that saturated solution is removed from the Teflon cell.

From the solubility data obtained the following geologic conclusions can be drawn. Initially saturated solutions of anhydrite in water, migrating toward the Earth's surface, would become undersaturated. The increase in solubility caused by decreased temperature more than compensates for the decrease in solubility caused by decreased pressure. Anhydrite would precipitate from saturated solutions in sediments as burial takes place and the temperature rises, or from ground waters moving downward to regions of higher temperature. Anhydrite would precipitate from saturated solutions moving from a region of high pressure to a region of low pressure, as would be the case in rocks near openings toward which a fluid pressure gradient exists.

88. Nakayama, F. S.: "Calcium Activity, Complex and Ion-Pair in Saturated CaCO_3 Solutions", Soil Science, Vol. 106 (1968) pp. 429-434.

Abstract

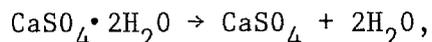
The chemical behavior of all soil-related Ca compounds is of vital interest to soil scientists. This is evidenced in part by the work on determining and explaining the differences in solubility of calcite and aragonite CaCO_3 and on ascertaining the presence and values of stability constants of soil-organic Ca-complexes. One worker, in studying the pH of calcareous soils, noted Ca complexes besides those of sulfate were present, but did not specify their actual forms. In order to describe the correct Ca equilibrium relation of the soil-gypsum and soil-phosphate systems, investigators have used the dissociation constant together with the solubility product constant of CaSO_4 . This procedure is necessary because all of the Ca in solution is not in the ionic form. Workers thus far have not taken into account the possibilities of Ca ion-pairs and Ca complexes in the soil- CaCO_3 system, probably because of the unavailability of appropriate dissociation constants for the different Ca forms in solution. Furthermore, controversy still exists regarding the presence or absence of Ca complex in bicarbonate-carbonate solutions.

This paper reports on the different forms of Ca that may be present in equilibrium with CaCO_3 together with their appropriate dissociation or association constants. A theory is formulated for determining the various Ca species when the necessary H-ion and Ca-ion activity measurements are available.

89. Bock, E.: "On the Solubility of Anhydrous Calcium Sulphate and of Gypsum in Concentrated Solutions of Sodium Chloride at 25°C, 30°C, 40°C, and 50°C", Can. J. Chem. Vol. 39, (1961) pp. 1746-1751.

Abstract

The solubilities of anhydrous CaSO_4 and $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ in concentrated aqueous solutions of NaCl at a series of temperatures (25°C, 30°C, 40°C, and 50°C) have been determined. It was found that the transition temperature for the reaction



which in pure water has a value of 42°C, is shifted progressively to lower temperatures with increasing NaCl concentration. It was also found that the variation of the transition temperature with NaCl concentration could be adequately represented by the equation

$$\Delta G = \Delta H - T\Delta S + 2RT \ln P/P_0,$$

where ΔG , ΔH , and ΔS are the Gibbs free energy, enthalpy, and entropy of the reaction and P_0 and P are the vapor pressures of pure water and the solution, respectively, at the absolute temperature T .

91. Orr, F. M., Jr., Yu, A. D. and Lien, C. L.: "Phase Behavior of CO₂ and Crude Oil in Low Temperature Reservoirs", Soc. of Pet. Eng., Symp. on Enhanced Oil Recovery (April 20-23, 1980) pp. 17-32.

Abstract

Phase behavior of carbon dioxide-crude oil mixtures which exhibit liquid-liquid and liquid-liquid-vapor equilibria is examined. Results of single contact phase behavior experiments for CO₂-separator oil mixtures are reported. Experimental results are interpreted using pseudo-ternary phase diagrams based on a review of phase behavior data for binary and ternary mixtures of CO₂ with alkanes. Implications for the displacement process of liquid-liquid-vapor phase behavior are examined using a one-dimensional, finite-difference simulator. Results of the analysis suggest that liquid-liquid and liquid-liquid-vapor equilibria will occur for CO₂-crude oil mixtures at temperatures below about 50°C (122°F), and that development of miscibility occurs by extraction of hydrocarbons from the oil into a CO₂-rich liquid phase in such systems.

92. Stalkup, F. L. "Carbon Dioxide Miscible Flooding: Past, Present, and Outlook for the Future", Fifth Symposium on Improved Methods for Oil Recovery of the Society of Petroleum Engineers of AIME, Tulsa, Oklahoma (April 16-19), pp. 39-50.

Abstract

This paper gives an overview of the carbon dioxide miscible-flooding process. It contains a review of current technology, a discussion of past and current field testing, and an assessment of the state-of-the-art. The discussion in one section identifies and evaluates carbon dioxide sources. This is followed by projections of potential oil recovery and producing rate along with an opinion of the near-future outlook. Several areas are identified where improvements in technology and additional laboratory research and field testing are needed.

93. Pilat, S. and Godlewicz, M., "Method of Treating Mineral Oils",
U.S. Patent 2,315,131 (Jan. 30, 1934).

Abstract

This patent describes a method for separating mineral oils into fractions of different physical and chemical properties, and is particularly concerned with the treatment of relatively viscous mineral oils, petroleum residues, and other hydrocarbon mixtures, using gases under pressure. Auxiliary solvents and deasphaltizing agents may be used.

Briefly, the invention consists of introducing into a mineral oil a gas under pressure until a concentration is reached at which the oil separates into two phases. Relative quantities and compositions of the oil portions in the phases are regulated by maintaining suitable temperatures and pressures, as well as by selection of the gaseous treating agent. The gaseous treating agent may be methane, ethane, carbon dioxide, hydrogen or any other substance or mixture of substances, which is gaseous at the temperature and pressure employed and which is capable, on being introduced in the gaseous state under pressure, of making the oil separate into phases. The two phases can then be easily separated.

94. Pilat, S. and Godlewicz, M.: "Method of Separating High Molecular Mixtures", U.S. Patent 2,188,013 (April 27, 1936).

Abstract

This patent describes a method for separating mixtures of high molecular weight substances into two or more fractions by injecting carbon dioxide under high pressure into the mixture. This patent is a continuation-in-part of patent no. 2,315,131 (see reference 93).

Briefly, the invention consists of introducing carbon dioxide under pressure (but below its condensation pressure) into a high molecular weight oil until a concentration is reached at which the oil separates into two phases. Relative quantities and compositions of the oil portions in the phases are regulated by maintaining suitable temperatures and pressures, as well as by using appropriate solvents and deasphalting agents. A separation of higher-molecular-weight components from lower-molecular-weight components can be accomplished by physically separating the different phases.

95. Simon, R., Rasman, A. and Zana, E., "Phase-Behavior Properties of CO₂-Reservoir Oil Systems", Soc. of Pet. Eng. J. (Feb., 1978), pp. 20-26.

Abstract

This paper presents experimental phase behavior data on two CO₂-reservoir oil systems at reservoir pressures and temperatures.

The data include (1) pressure-composition diagrams with bubble points, dew points and critical points; (2) vapor-liquid equilibrium compositions and related K values; (3) vapor and liquid densities compared with values calculated by the Redlich-Kwong equation of state; (4) vapor and liquid viscosities compared with predictions by the Lohrenz-Bray-Clark correlation; and (5) interfacial tensions for six vapor-liquid mixtures compared with values calculated by the Weinaug-Katz parachor equation.

These and other published data contribute to development of the generalized correlations needed by reservoir and production engineers for evaluating, designing, and efficiently operating CO₂-injection projects.

96. Shelton, J. L. and Yarborough, L., "Multiple Phase Behavior in Porous Media During CO₂ or Rich Gas Flooding", J. of Pet. Tech. (Sept. 1977), pp. 1171-1178.

Abstract

Mixing oil with high-ethane-content hydrocarbon gases or CO₂ can produce multiple liquid phases and an asphaltic precipitate in low-temperature reservoirs. The residual saturation that occurs in a reservoir displacement is not significant from a recovery standpoint, but may produce three-phase relative permeability effects that reduce injectivity and, thus, oil recovery rate during alternate gas-water injection.

97. Reed, M.G., "Formation Permeability Damage by Mica Alteration and Carbonate Dissolution", Journal of Petroleum Technology (Sept. 1977), pp. 1056-1060.

Abstract

This article proposes two mechanisms to account for at least some of the permeability damage observed in some friable micaceous sands. The two mechanisms are supported by present laboratory and field data which are shown in the report.

98. Holm, L. W., "Carbon Dioxide Solvent Flooding for Increased Oil Recovery", Pet. Trans., Vol. 216 (1959), pp. 225-231.

Abstract

Laboratory flooding experiments on linear-flow systems indicated that high oil displacement, approaching that obtained from completely miscible solvents, can be attained by injecting a small slug of carbon dioxide into a reservoir and driving it with plain or carbonated water. Data are presented in this paper which show the results of laboratory work designed to evaluate this oil recovery process, particularly at reservoir temperatures above 100°F and in the pressure range of 600 to 2,600 psi.

99. Nathan, C., 'Vaterite in Lake Water', Nature Physical Science, Vol. 231, No. 24 (June 14, 1971), p. 158.

Abstract

During tests of scale inhibitors, two types of calcium carbonate crystals were observed. One type was vaterite, which is extremely rare in nature.

100. Le Grand, H. E. and Stringfield, V. T., "Differential Erosion of Carbonate-Rock Terrances", Southeast Geol., Vol. 13, No. 1 (1971), pp. 1-17.

Abstract

The topography of carbonate-rock terranes takes on many different forms. These forms can be explained in terms of "differential erosion" of the terrane. The factors involved in "differential erosion" include amount of cover over the carbonate-rock formation, purity of the carbonate rock, topographic relief, and precipitation. This article looks at some of the categories of topography found in carbonate-rock terranes and discusses the conditions involved in their formation.

101. Tate, J.F., Venable, R.L. and Nathan, C.C.: "The Solubility of Gypsum in Oil Field Brines," ACS National Meeting (1964).

Abstract

The solubility of gypsum was determined under conditions simulating compositions and temperatures of oil field brines at 30-100° C. The effects of sodium ion, magnesium ion, and sulfate ion were determined in solutions containing up to 200 g NaCl, 15 g Na₂SO₄, and 10 g Mg(NO₃)₂ per 1000 g of water. It was found that the effects of temperature, common ions, and inert ions are not independent; the reduction of solubility effected by temperature or common ions being proportionally less at higher than at lower salinities.

Inert ions such as sodium or magnesium are equivalent in their ability to raise the solubility of gypsum when they are compared at equal ionic strengths up to values of about 0.1. At higher values of μ , magnesium gives solubilities about 10-15% greater than does sodium. At low values of μ , the behavior is in qualitative agreement with predictions of the Debye-Huckel theory, but the agreement is considerably poorer than with the less soluble BaSO₄. At higher values of μ , the basic theory must be modified to obtain an explanation of the observed behavior. The constants in the modified theory and equations are of the correct order of magnitude, but must be determined empirically from solubility data. Further work is required before solubilities in these systems can be calculated from fundamental concepts.

102. Nathan, C.C., "Solubility Studies on High Molecular Weight Paraffin Hydrocarbons Obtained From Petroleum Rod Waxes", Petroleum Transactions AIME, Vol. 204 (1955), pp. 151-155.

Abstract

Data are presented on the physical properties of five waxes obtained from fields in Texas and Louisiana in which "paraffin" troubles were being experienced. The crude paraffin was fractionated into three components, soluble in cold acetone soluble in boiling acetone, and insoluble in boiling acetone. The acetone insoluble fraction was found to consist essentially of straight chain paraffin hydrocarbons in the molecular weight range 525 to 700.

Solubilities of the purified high-molecular-weight paraffins were determined in a number of solvents. It was found that in hydrocarbon solvents, including crude oil, solubilities could be calculated satisfactorily by use of ideal solubility relations. In chlorinated and oxygenated solvents, large deviations from ideal behavior were observed. These deviations could be partially correlated with the internal pressure of the solvent.

103. Nixon, R. A., "Differences in Incongruent Weathering of Plagioclase and Microcline-Cation Leaching Versus Precipitates", Geology, Vol. 7, (1979), pp. 221-224.

Abstract

Comparisons of plagioclase and microcline taken from different weathering environments show that the mechanisms of feldspar dissolution are independent of the weathering environment. However, microcline and plagioclase do not weather by identical mechanisms. Calcium and sodium can be removed from the plagioclase lattice to depths greater than one or two unit cells, which implies that the "leached layer" may form on weathering plagioclase grains. The larger potassium ions cannot be removed from the microcline lattice deeper than one or two unit cells unless the anionic lattice is distorted or disrupted. Macroscopic solution features on plagioclase parallel the arrangement of calcium and sodium ions within the crystal. Solution features that develop on microcline may begin at dislocations on the crystal surface, or they may be located at inclusions of plagioclase. Scanning electron microscopy of microcline indicates that a precipitate as thick as 1 μm may form at the surface of the mineral. The rate of dissolution of microcline may be related to the cation exchange capacity of this layer and by reactions within the layer.

104. Rodgers, G. P. and Holland, H. D., "Weathering Products within Microcracks in Feldspars", Geology, Vol. 7 (1979) pp. 278-280.

Abstract

Tonalite cobbles from moraines in the Tobacco Root Mountains, Montana, have weathering rinds in which the feldspars are altered to clays along microcracks. Energy-dispersive X-ray and X-ray diffraction analyses have shown that microcracks in orthoclase contain only kaolinite, but that microcracks in oligoclase contain a central zone of kaolinite surrounded by a zone of smectite. These observations are in accord with predictions based on activity diagrams for the appropriate chemical systems. Feldspar dissolution was probably the rate-determining step in the development of the microcracks and their clay fillings.

105. Huang, W. H. and Kiang, W. C., "Laboratory Dissolution of Plagioclase Feldspars in Water and Organic Acids at Room Temperature", American Mineralogist, Vol. 57 (1972) pp. 1849-1859

Abstract

Freshly-fractured albite, oligoclase, labradorite, bytownite, anorthite, and a high-K variety of plagioclase in particle sizes between 44 μm and 150 μm were dissolved at room temperature in deionized water, 0.01 M acetic and aspartic acids (weakly complexing), and salicylic and citric acids (strongly complexing). Solutes of centrifuged solution were analyzed for pH, and for Si, Al, Fe, Mg, Ca, Na, and K.

Ca-rich plagioclases dissolved in organic acids more readily than did Na-rich plagioclases; whereas, Na-rich plagioclases were the more soluble in deionized water. Al was preferentially dissolved over Si, in particular from Ca-rich plagioclase in complexing acids. Ca was relatively more soluble than was Na in both organic acids and water.

The organic solvents, in order of increasing effect of dissolution, were acetic, aspartic, salicylic, and citric acids, which is the order of complexing capacities. Citric acid was more effective than other acids in extracting Al and Ca, particularly from Ca-rich plagioclases, presumably because of the formation of Al- and Ca-complexes.

106. Chafetz, H. S., "Surface Diagenesis of Limestone", J. of Sed. Pet., Vol. 42 (1972) pp. 325-329.

Abstract

Surface diagenesis of the Morgan Creek Limestone has resulted in dedolomitization, silicification, and aggradational recrystallization. Horizons displaying similar diagenetic properties in subsurface carbonate data are indicative of superjacent unconformities.

107. Nooner, D. W., Oro, J., Gilbert, J. M., Ray, V. L. and Mann, J. E., "Ubiquity of Hydrocarbons in Nature: Aliphatic Hydrocarbons in Weathered Limestone", Geochim. Cosmochim. Acta, Vol. 36 (1972) pp. 953-959.

Abstract

The aliphatic hydrocarbons in two specimens of limestone (one from Texas and the other from Italy) which were weathered in place as parts of building structures have been investigated using gas chromatography and gas chromatography-mass spectrometry. The hydrocarbons in the limestone from Texas and the algae cultured from this limestone have similar distributions, i.e., the predominating hydrocarbon in both cases is n-C₁₇, thus indicating that most of the aliphatic hydrocarbons in the limestone may be derived from recent algal growth. The hydrocarbons in the limestone from Italy, in which n-C₁₇, is a maximum but which also include relatively large amounts of pristane, phytane and other aliphatic hydrocarbons, appear to be a mixture of in situ, biogenically derived hydrocarbons and extraneously derived fossil hydrocarbons.

108. Perkins, A. T.: "Decomposition of Silicate Minerals by Acid Extractions - Chemical Composition and Exchange Capacity", Transactions of the Kans. Academy of Sci. Vol. 67, (1964) pp. 486-495.

Abstract

A 100-day citric-phosphoric extraction of California bentonite (Filtrol) and vermiculite, minerals with high cation-exchange capacities, dissolved, respectively, about 37% and 49% of the minerals by weight, and removed about 75% of the R_2O_3 group of each mineral and only 10% and 13% of the SiO_2 . The loss of exchange capacity paralleled the loss of the R_2O_3 group.

A similar extraction of muscovite and kaolinite, minerals with low exchange capacities, dissolved little, if any, of the minerals and did not change their chemical composition.

109. Petrovic, R., Berner, R. A., and Goldhaber, M. B., "Rate Control in Dissolution of Alkali Feldspars - I. Study of Residual Feldspar Grains by X-ray Photoelectron Spectroscopy", Geochim. Cosmochim. Acta, Vol. 40, (1976) pp. 537-548.

Abstract

Sanidine grains (100-600 μm in diameter) were subjected to dissolution at 82°C in aqueous electrolyte solutions of pH ranging from 4 to 8 for 293 or 377 hr. Dissolution, equivalent to the removal of silica from the outer 300-900 Å of these grains, was accomplished. The shallow subsurfaces of feldspar grains were then analyzed for K, Al, and Si by X-ray photoelectron spectroscopy. The results rule out any continuous precipitate layer; if an alkali-depleted subsurface zone (leached layer) was present in the feldspar, the thickness of such a zone, approximated by linear increase of alkali concentration with depth, was not more than about 17 Å.

It is concluded that in the absence of a compact precipitate layer, dissolution of feldspars in the temperature range corresponding to deep diagenesis is controlled by the processes at the feldspar-solution interface, and a leached layer more than one feldspar unit cell thick does not form. Whether the same applies at the temperatures of shallow diagenesis and weathering cannot be judged with certainty, but parallels with leached layers on alkali silicate glasses suggest that it does.

110. Busenburg, E.: "The Products of the Interaction of Feldspars with Aqueous Solutions at 25°C", Geochim. Cosmochim. Acta, Vol. 42, (1978) pp. 1679-1686.

Abstract

Chemical analyses of 300 solutions produced by the artificial weathering of eight different feldspars in fourteen experiments of up to 1200 hr duration were used to study the evolution of water during weathering. The range of pH was between 4 and 5.5. Within 4 hr of dissolution, the activity of Al was controlled by the pH and the solubility of microcrystalline gibbsite. After 100 hr of dissolution, the pH and microcrystalline halloysite controlled the activities of Al and silicic acid in all of the solutions.

Microcrystalline halloysite was the only phase identified in the weathering of plagioclases in distilled water and 1 atm CO₂ partial pressure. Montmorillonites, halloysite and other clay minerals were produced from oligoclase in aqueous solutions containing high initial concentrations of Ca, Mg, K and SiO₂.

The experimentally determined solubility product of microcrystalline gibbsite, log K, was -32.78 ± 0.04 , and log K for the hydrolysis of microcrystalline halloysite was 11.58 ± 0.05 . The results suggest that very poorly crystalline, metastable phases may control the initial compositions of some waters in contact with rocks containing feldspar minerals.

111. Nancollas, G.H. and Sawada, K.: "The Formation of Scales of Calcium Carbonate Polymorphs. The Influence of Magnesium Ion and Inhibitors", SPE 9992, SPE Fifth International Symposium on Oilfield and Geothermal Chemistry, Stanford, California, pp. 167-177.

Abstract

The crystallization of calcium carbonate on calcite and aragonite has been investigated at 70°C using a highly reproducible seeded-growth technique. In both cases the rates of reaction are proportional to the square of the relative supersaturations and are surface controlled. The presence of low levels of magnesium ion inhibits calcite growth with the formation of magnesian calcite while at higher concentrations the spontaneous precipitation of aragonite takes place. Hydroxyethylidene-1,1-diphosphonic acid, HEDP, a potential scale inhibitor, markedly reduces the growth-rate of both calcite and aragonite but has little effect upon the crystallization of vaterite, the least thermodynamically stable calcium carbonate polymorph. The exclusive growth of vaterite on vaterite seed at 70°C under these conditions strikingly demonstrates the possibility of the formation of intermediate metastable precursors during scale formation.

112. Vetter, O.J. and Kandarpa, V.: "Prediction of CaCO_3 Scale Under Downhole Conditions", SPE 8991, SPE Fifth International Symposium on Oilfield and Geothermal Chemistry, Stanford, California, pp. 155-165.

Abstract

CaCO_3 is one of the most common scales in oilfield and geothermal operations. Various thermodynamic models have been reported in the literature to predict the precipitation of CaCO_3 . Each of these existing models has its limitation when applied to the real situations of the field operations. Some models (e.g., Stiff-Davis Method) ignore many conditions leading to CaCO_3 precipitation.

This paper describes a model to predict CaCO_3 scale formation at any location within the field as a function of water composition, temperature and pressure. This model is based on equilibrium thermodynamics, but uses only the experimentally-measured parameters. The input data for the model are (1) one water analysis, (2) one pH measurement at any location in the field, (3) the temperature at which the only field pH measurement is made, (4) the CO_2 concentration of the gases (if a gas phase exists up-stream or at the point where the liquid sample is taken and the pH is measured), and (5) the amount of flash (if a gas phase exists upstream or at the point of sample collection). The model then takes these measured data and calculates the equilibrium brine composition (including pH) in the reservoir.

The calculated brine composition data can then be used either to predict the CaCO_3 precipitation for any set of prescribed conditions or to predict the CaCO_3 precipitation at various locations within an oilfield or geothermal operation. For a set of temperature and pressure, the model goes through a decision to determine whether a single-phase or two-phase condition exists for the brine.

For the case of the existence of the single-phase brine, the model calculates the amount of CaCO_3 precipitate, taking into account the pertinent chemical reactions involving the various carbonate species.

For the case of the existence of two-phase brine, the model first computes the CO_2 emission and its effect on the pertinent reactions involving the various carbonate species and, hence, calculates the amount of CaCO_3 precipitate.

APPENDIX B DATA BASES

CAS77 and CAS7276

Provides worldwide coverage of the chemical sciences literature from over 12,000 journals, patents from 26 countries, new books, conference proceedings, and government research reports. Coverage corresponds to the printed Chemical Abstracts Condensates, including 80 main subject sections such as biochemistry, organic chemistry, macromolecular chemistry, applied chemistry and chemical engineering, and physical and analytical chemistry. Includes special searching features from Chemical Abstracts Subject Index Alert (e.g., registry numbers, molecular formula fragment).

PREPARED BY: Chemical Abstracts Service

FILE SIZE: CAS77: Approximately 390,000 citations
per year since 1976

CAS7276: Approximately 2,500,000 citations

COVERAGE: CAS77: January 1977 to present

CAS7276: January 1972 to December 1976

UPDATING: CAS77: Bi-weekly, approximately 12,000 citations

CDI

Comprehensive Dissertation Index, containing all dissertations accepted for academic doctoral degrees granted by U.S. educational institutions and over 122 non-U.S. universities. Contents correspond to two printed products: Dissertation Abstracts International (for which full-text) copies are available from UMI) and American Doctoral

Dissertations. Subject coverage is multi-disciplinary, and includes the humanities, social sciences, science, and engineering.

PREPARED BY: University Microfilms International (UMI)
FILE SIZE: Approximately 46,000 citations per year
COVERAGE: 1861 to present
UPDATING: Monthly, approximately 3,000 citations

CHEM 7071

Provides the same literature coverage as CAS77 and CAS7276 without the merger of Chemical Abstracts Subject Index Alert.

PREPARED BY: Chemical Abstracts Service
FILE SIZE: Approximately 600,000 citations
COVERAGE: January 1970 to December 1971

COMPENDEX

Corresponds to Engineering Index Monthly. Covers civil-environmental-geological engineering; mining-metals-petroleum-fuel engineering; mechanical-automotive-nuclear-aerospace engineering; electrical-electronics-control engineering; chemical-agricultural-food engineering; and industrial engineering, management, mathematics, physics, and instruments, including approximately 1,500 serials and over 900 monographic publications.

PREPARED BY: Engineering Index, Inc.
FILE SIZE: Approximately 84,000 citations per year
COVERAGE: January 1970 to present
UPDATED: Monthly, approximately 6,000 citations

GeoRef

Geological Reference file, covering geosciences literature from 3,000 journals, plus conferences and major symposia and monographs, in such areas as geology, economic geology, engineering-environment geology, geo-chemistry, geochronology, geomorphology, igneous and metamorphic petrology, solid earth geophysics, and stratigraphy; a total of some 29 different geoscience areas. Includes citations from Bibliography and Index of Geology and more.

PREPARED BY: The American Geological Institute
FILE SIZE: Approximately 36,000 citations per year
COVERAGE: January 1967 to present
UPDATING: Monthly, approximately 4,000 citations

Tulsa

Covers worldwide literature and patents related to oil and natural gas exploration, development, and production in such areas as petroleum geology, exploration geophysics and geochemistry; well drilling; well logging, well completion and servicing; oil and gas production; reservoir studies and recovery methods; pollution; alternative fuels and storage. Corresponds in coverage to Petroleum Abstracts.

PREPARED BY: University of Tulsa
 Information Service Department
FILE SIZE: Approximately 18,000 citations per year
COVERAGE: 1965 to present
UPDATING: Monthly, approximately 1,500 citations

APPENDIX C DESCRIPTORS FOR LITERATURE SEARCH

A. Plugging of Reservoirs

1. OIL AND (ALL RESERVOIR:/IT OR ALL FIELD:/IT OR ALL FORMATION:/IT
OR ALL WELL:/IT OR CRUDE)
2. STIMULATION OR INJECTION
3. ALL FLOOD
4. DAMAGE OR PLUGGING OR ATTACK OR ALL SCAL:/IT OR ALL PRECIPITAT:/IT
5. PERMEABILITY AND (LOSS OR DECREASE)
6. INJECTIVITY AND (LOSS OR DECREASE)
7. PRESSURE AND (DROP OR DECREASE)
8. 4 OR 5 OR 6 OR 7
9. 1 AND 8
10. 1 AND (2 OR 3) AND 8
11. (CARBON DIOXIDE) OR CO₂ OR (CARBONIC ACID) OR (CARBONATED WATER)
OR ORCO
12. 1 AND 8 AND 11
13. TUBING OR PIPES OR LINES
14. 1 AND 8 AND 13

B. Attack on Rocks

15. FELDSPAR OR DOLOMITE OR LIMESTONE OR SILICATE OR CARBONATE OR
SULFATE
16. ATTACK OR ALL DECOMPOS:/IT OR DECAY OR ALL DISOLV:/IT OR ALL
WEATHER:/IT

- 17. 15 AND 16
- 18. 11 AND 17
- 19. 1 AND 11 AND 17
- 20. 1 AND 17

C. Asphaltene Precipitation

- 21. ASPHALTENE OR ALL PRECIPITAT:/IT OR ALL SOLID:/IT
- 22. PRECIPITAT:/IT OR DEPOSITS OR SOLUBILITY OR SCALE
- 23. 11 AND 21
- 24. 1 AND 11 AND 21
- 25. 17 AND 22 AND NOT (CONCRETE OR CORROSION)