

How Pressure and CO₂ Affect Reservoirs and Influence the Selection of Scale Control Treatments

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ABSTRACT

This paper gives quantitative calculations of the effects of Carbon Dioxide and pressure on the solubilities of formation minerals in a West Texas brine. Increased pressure makes anhydrite and gypsum significantly more soluble. The solubilities of carbonate minerals are increased to a lesser extent.

The presence of Carbon Dioxide causes large increases in the solubilities of carbonate minerals, thus exacerbating the scale problem. Carbon Dioxide will greatly reduce the pH of injected or connate water, but this undesirable effect is reduced by the buffering action of carbonate minerals. Because of this buffering action, common mineral scale inhibitors can be used in CO₂ floods. Increased dosage may be required because of the potential for more scale.

INTRODUCTION

When an oil well produces only petroleum there are relatively few problems. Problems multiply when water is produced with the petroleum. Some of these problems occur because reservoir minerals are slightly soluble in water. Their solubilities change with temperature, pressure, and other factors. In a reservoir the minerals are generally in equilibrium with the water in the reservoir. The equilibrium process may require days, weeks, or months to be completed, but equilibrium is established over times that are short compared to the times that the water typically has been in contact with the minerals. When a well begins to produce fluids the equilibrium is disturbed due to changes in temperature and pressure. These changes can cause problems. Problems also occur when waters from different zones are mixed. Injecting incompatible waters similarly cause serious problems. When water injection is combined with CO₂ flooding the equilibria are further disturbed by large changes in pH. This is particularly worrisome in carbonate reservoirs.

Because of these changing solubilities portions of the reservoir rocks can dissolve and redeposit in the production tubing as mineral scale. The resulting problems may be mitigated if not eliminated if the engineer has a proper understanding of their causes. It is important to understand the relative solubilities of common reservoir minerals, what factors affect mineral solubility, and how to control scale formation. In what follows I will present quantitative calculations of some of these effects. But first I will present some chemical concepts behind these calculations.

SOLUBILITY CONCEPTS

General Solubility

All substances have some solubility in water. In some cases the solubility may be so slight that the substance is generally considered insoluble. When large amounts of water are considered, however, enough of the substance may be dissolved to be noticed. In this way large caverns are excavated from relatively insoluble limestone.

The solubilities of some substances can be expressed as simple constants. Sugar is an example of such a substance. Its solubility can be expressed as a simple constant because it maintains its chemical identity even when dissolved in water. It is a non-ionic substance.

Most minerals in contrast are ionic substances. They consist of one or a few cations (positively charged ions) and one or a few anions (negatively charged ions) arranged in a particular geometric order. When minerals dissolve in water they dissociate into independent ions. Once in solution the ions lose all memory of where they came from. Ordinary salt is an example of an ionic substance, sodium chloride. When it dissolves it decomposes into sodium ions and chloride ions. It no longer exists as "salt". The same solution could be prepared by dissolving appropriate amounts of sodium hydroxide and hydrochloric acid in water. When the water is evaporated salt crystals form no matter how the solution is made.

Solubility of Minerals

Solubility Product Constant

The solubility of a mineral cannot be expressed as a simple constant. Instead the solubility is expressed as a number called the thermodynamic solubility product constant, K_{sp} . The K_{sp} of salt, for instance, is $K_{sp} = \{Na^+\} \times \{Cl^-\}$. The curly brackets refer to the activities of the Sodium and Chloride ions. In pure water the activities are the same as the concentrations. In a brine the activities are equal to the concentrations times a number known as the activity coefficient. The activity coefficient is near one in dilute solutions, but in high brines it is much less than one. The solubility product constant for limestone, Calcium Carbonate, is $K_{sp} = \{Ca^{2+}\} \times \{CO_3^{2-}\}$. For gypsum, calcium sulfate dihydrate, it is $K_{sp} = \{Ca^{2+}\} \times \{SO_4^{2-}\} \times \{H_2O\} \times \{H_2O\}$. In every case the solubility product constant is just the product of the activities of the constituent species.

Common Ion Effect

It is obvious from the K_{sp} expression that if two minerals have some ion in common, then the solubility of one will be depressed if some of the other has already been dissolved. Thus the solubility of calcite (limestone) will be depressed if some gypsum has been dissolved. This is because both contain calcium ion. This is termed the common ion effect.

Temperature, Pressure and Ionic Strength

The common ion effect is just one complicating factor in calculating the solubilities of minerals in an oil-field brine. The amount of mineral soluble in a given water also depends on the temperature, pressure, and the ionic strength (salinity) of the water. The solubility product constant is defined so that it depends only on temperature. Pressure and ionic strength exert their influence on the activities of ions in solution. Increasing pressure and ionic strength decrease the activities; that is the ions act as if less were there than the actual amount. This results in more mineral being soluble. There are well established ways handling these activity changes. These methods will not be discussed in this paper. There are many articles and books on this subject^{1,2}.

Effects of Specific Ions

pH Effects

Specific substances in solution may influence concentrations and, thereby, activities of other substances. The effects of specific substances may be conveniently broken down into three categories. These are pH ($-\log_{10}\{H^+\}$) effects, chelating effects, and ion pairing effects. These effects are all the result of the ions undergoing further reaction in solution.

The pH effect is particularly pronounced for ions that can react to form weak acids like carbonic acid. Thus when limestone dissolves in water at near neutral pH, the resulting carbonate ion reacts with hydrogen ion to form bicarbonate ion by the reaction $H^+ + CO_3^{2-} \rightleftharpoons HCO_3^-$. This reaction has an equilibrium constant associated with it, $K_{A2} = \{H^+\} \times \{CO_3^{2-}\} / \{HCO_3^-\}$. Similarly there is another expression that relates bicarbonate ion to carbonic acid, $K_{A1} = \{H^+\} \times \{HCO_3^-\} / \{H_2CO_3\}$. Thus carbonate ion, bicarbonate ion, carbonic acid and also the partial pressure of CO_2 in equilibrium with the water are all linked through the pH.

Figure 1 shows the relative amounts of the various carbonate species in pure water as a function of pH. At pH's below 11 the solubilities of carbonate minerals are greatly influenced by the pH because an appreciable amount of carbonate ion reacts to form bicarbonate ion or, at much lower pH's, carbonic acid. Conversely dissolving carbonate minerals in water raises the pH of the water. This is because hydrogen ion is "used up" as carbonate ions form bicarbonate ions. At very low pH the solubility of sulfate minerals can be similarly influenced by the reaction $H^+ + SO_4^{2-} \rightleftharpoons HSO_4^-$.

Chelation

Chelators can decrease the concentrations of certain ions through reactions like $ION + CHELATOR \rightleftharpoons COMPLEX$. Chelators usually are not present in solution unless specifically added, so these reactions need not concern us. Chelators can greatly increase the solubility of minerals if used in sufficient concentration. Scale inhibitors show some chelating ability, but they are usually used at such low concentrations that the chelation tendency is not important.

Ion Pairing

The pH and chelation effects are special cases of a general phenomenon known as ion pairing. Any two ions may react in solution. For instance calcium may react with chloride, $Ca^{2+} + Cl^- \rightleftharpoons CaCl^+$. Reactions like these are usually significant only when the activity of at least one of the ions is high.

The pH and chelating effects are exceptions to this rule. Those reactions can be significant even when concentrations are low. That is why they are generally considered separately. Ion pairing reactions are important in oil-field brines with their high concentrations of sodium, chloride ions and other ions. Any realistic calculation account for ion pairing.

Calculations of Solubility

For any realistically complex oil-field water there are many interrelated equations that must be solved. The above discussion is really just the tip of the iceberg. Before computers were available it was extremely tedious, nearly impossible, to solve these equations with reasonable accuracy, and certainly not in a reasonable amount of time. Consequently various approximations and simplifications were used. Such approximations took all of the activity coefficient and ion pairing effects and transferred them to the other side of the equation where they were rolled into an "effective" solubility product. This solubility product depended on the salinity as well as temperature. It was assumed that all solutions of the same salinity (or ionic strength) had the same effect on the activity coefficients and ion pair formations of the relevant ions. This is not necessarily true.

Some approximations, like the Skillman, McDonald, Stiff method for Calcium Sulfate³, yield the amount of mineral that can dissolve in the water. Others, like the Langelier⁴ or Stiff and Davis⁵ index for calcium carbonate, give a saturation index. Saturation indexes are base ten logarithms of the product of the ion activities divided by the solubility product constant. A saturation index is positive for a water that can precipitate mineral and negative for a water that can dissolve mineral. The value tells nothing about how much mineral can precipitate or dissolve. In fact the amounts can be vastly different for two waters with identical saturation indexes! Saturation Indexes should be used with caution⁶.

Approximations are adequate in many ordinary situations, but a calculation based on them can give erroneous results when used on inappropriate waters. With the widespread availability of computers it is no longer necessary to settle for calculations with such shortcomings. More reliable computations can be made. These can account for the effects of pressure that earlier methods did not take into account. The calculations that follow were made using an in-house program that was modeled after WATEQ⁷. However it has been upgraded significantly by using the methods of Helgeson⁸ to calculate the activity coefficients over an expanded range of temperatures and to correct for pressure effects.

CALCULATIONS ON A TYPICAL WEST TEXAS WATER

Barite

A typical water from a real West Texas oil field was chosen as the basis for this work. Its composition is given in Table 1. Based on the ions in solution, the solubilities of calcite, gypsum, anhydrite, and celestite must all be considered. There is no barium ion in this water. The absence of barium is not at all unusual in water from a formation that may contain anhydrite stringers. The

sulfate ion resulting from the dissolution of the moderately soluble anhydrite greatly depresses the solubility of the relatively insoluble barite through the common ion effect. The solubility of barite in this brine is shown in Figure 2. Its solubility is insignificant at the 80°C bottom hole temperature. This is a graphic illustration of the common ion effect. This figure does show the great increase in the solubility of barite with increasing temperature, and the solubility increase at high pressure. It is expected that barite scale will be troublesome in deep hot wells.

Gypsum and Anhydrite

Solubility Curves

The calculated effect of temperature on the solubilities of gypsum and anhydrite in this brine is shown in Figure 3. These two minerals yield the same two ions when dissolved, calcium and sulfate. An amount of gypsum weighs more than the same amount of anhydrite (i.e., same amount of calcium and sulphate) because gypsum contains water in the crystal. The ions are also arranged differently in gypsum. This mass difference is reflected in the different scales on the graph's y-axes. At the point where the two curves cross the two minerals are in equilibrium with each other. At other temperatures only one is stable; the more soluble form will tend to dissolve and to reprecipitate as the less soluble form. Gypsum is the low temperature form and anhydrite is the high temperature form. Transforming anhydrite into gypsum will cause an increase in the volume of solids because gypsum is less dense and weighs more than an equivalent amount of anhydrite. Kinetics, which are not addressed by these calculations, determine whether this transformation takes place.

Anhydrite Saturation Temperature

This oil-field brine is supersaturated with respect to anhydrite above about 120°C (248°F). Thus if there are anhydrite stringers in the reservoir, and if this is a good water sample, and if the pressure is zero, we can conclude that the reservoir temperature is 120°C. A calculation of this type can serve as a check on the analysis of this water and the calculation. The actual bottom hole temperature is about 80°C. This suggests that there probably was some precipitation of gypsum from the cooled brine before the analyses were done.

Pressure Effects

Figure 4 shows how a pressure of 69,000kPa (10,000psi) affects these solubility curves. This figure is drawn to the same scale as Figure 3. Note that the solubilities of both forms increase substantially. This is the major effect. The curves, however, are not shifted to the same extent by pressure. This is because gypsum contains water and its activity is also affected by pressure. The intersection point and therefore the equilibrium temperature of the two forms is shifted to a higher temperature. The equilibrium temperature of the brine with anhydrite has now been shifted to 155°C. This is a significant increase and illustrates the importance of taking pressure into account.

A comparison of Figure 3 with Figure 4 shows how much more soluble gypsum and anhydrite are at 69,000kPa (10,000psi) than they are near zero pressure. Note the magnitude of the change, up to 5000mg per thousand grams of water. For comparison 3000mg per thousand grams of water corresponds to about a pound of scale per barrel of water. That's a lot of scale. Note too that the

solubility of gypsum is changed little by temperature. Gypsum is unusual in this property; most mineral solubilities are greatly affected by temperature. It is seen that pressure drops are more likely to cause gypsum scale problems than are temperature changes. Mixing of different waters, of course, also may cause gypsum problems.

Carbonate Minerals

Calcite

The calcite curve is shown in Figure 5. First observe that this water has "negative solubility" for calcite. This means that calcite will precipitate from this water. Note too the significant effect of temperature, similar in shape to the anhydrite curve. Observe that increasing pressure also increases the solubility of this mineral. The magnitude of the solubility increase, however, is only about one hundredth of the increase for anhydrite or gypsum. This implies that a pressure drop should result in very little calcite scale forming! But how can this be? "Everybody" knows that calcite occurs routinely in troublesome quantities where there are pressure drops. This is an example of a little knowledge being a dangerous thing, i.e., it leads to a false conclusion. To explain why calcite forms at pressure drops it is necessary to examine other factors that affect the solubility of calcite and other carbonate minerals.

pH effect on Calcite and Dolomite

Because the solubilities of carbonate minerals depend on the activities (or concentration) of carbonate ion, anything that affects the activity of that ion will affect the solubilities of the minerals. We showed earlier that pH has a powerful effect on the concentration of carbonate ion. The pH, then, may be the factor we have failed to consider. Figure 6 shows the effect of pH on the saturation indexes of calcite and dolomite. The saturation index is a nearly linear function of pH. Most simplified approaches assume it is an exactly linear function of pH. Clearly carbonates are more soluble at low pH.

Carbon Dioxide Exchange

pH Shift

As was mentioned earlier, saturation indexes must be interpreted with caution. The saturation index does not tell you how much more mineral will dissolve at the lower pH. To do the calculation of either the amount or the saturation index, the manner in which the pH is lowered must first be specified. The curves shown in Figure 6 are based on the assumption that the bicarbonate ion concentration is the same at every pH. This is true when the pH is shifted by the exchange of carbon dioxide between the gas and aqueous phases. This is the most common way that pH is shifted at a pressure drop. Carbon dioxide exchange affects the pH through the reaction $\text{CO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{HCO}_3^-$. For a typical concentration of bicarbonate ion at a typical pH, the amount of bicarbonate ion produced by this reaction is insignificant. The pH change, however, is very significant.

Figure 7 shows the same data as Figure 1 presented differently. It shows that the ratios of carbonic acid to bicarbonate ion and carbonate ion to bicarbonate ion in pure water change exponentially with

pH. There is a linear relationship between the amount of carbonic acid in solution and the partial pressure of carbon dioxide in the gas phase. Therefore there is an exponential relationship between the equilibrium partial pressure of carbon dioxide above the solution and the pH when the bicarbonate ion is held constant.

Pressure and Amount of Carbon Dioxide

Figure 8 shows the pH that would be measured at 25°C (77°F) if our selected oil-field water were in equilibrium with various partial pressures of CO₂ at 80°C (176°F). This curve is specific for this brine. The logarithm of the carbon dioxide pressure is seen to be a nearly linear function of the pH. There is close to one pH unit change for each factor of ten change in the carbon dioxide partial pressure above about 5kPa (0.7psia). Quite high partial pressures of carbon dioxide are required to push the pH below 4.

A certain amount of gas must dissolve in the water to lower the pH. Figure 9 shows how much is required. The amount, like the pressure, is a nearly linear function of pH. This implies a linear relationship between the amount dissolved and the partial pressure. This is a normal gas solubility relationship and is not a surprise. For this water, large amounts of CO₂ are required to lower the pH below about 4. Volumes of this magnitude are likely to be found only in a CO₂ flood.

Dolomite Solubility

When the pH is lowered by CO₂ exchange, much more calcite or dolomite can dissolve in the brine. Figure 10 shows how much more dolomite can dissolve. Calcite gives a similar curve. The partial pressure of CO₂ operating through its effect on the pH is an important factor to consider as far as the solubility of carbonate minerals in water is concerned. We can now explain why calcite formation is so often observed at a pressure drop. It is because CO₂ comes out of solution at the pressure drop. This results in a pH jump and a corresponding increase in the saturation index of calcite. If the system contains only the brine phase, we also can predict that CO₂ cannot come out of solution until the pressure drops below the partial pressure of CO₂ in equilibrium with the water, i.e., the bubble point of CO₂. This commonly occurs on the intake side of pumps and calcite scale is often found there.

Buffering by Carbonate Minerals

It was mentioned earlier that carbonates dissolving in water affect the pH of the water. The effect is clearly seen when Figure 11 is compared with Figure 8. Instead of a change of one pH unit for each factor of ten change in carbon dioxide partial pressure, there is only a change of about 0.5 unit. This buffering of the pH by the dissolution of carbonate minerals means that very low pH's (below 4) will virtually never be found in waters from carbonate formations, even those under CO₂ flood. This is good news because later we will show that scale inhibitors of all types lose effectiveness at low pH.

Figure 12 shows how much CO₂ must be dissolved in the brine when it is also in equilibrium with dolomite to produce a given partial pressure of CO₂. This curve turns out to be about the same whether or not the dissolution of carbonate minerals is buffering the pH. The resulting pH, however,

is very different. This is not too surprising if you study Figure 1 or 7. Below about pH 6 most of the carbonate species are in the form of carbonic acid. It is the carbonic acid that is in equilibrium with the carbon dioxide. The pH is irrelevant as long as it is below about 6. This argument also explains why Figures 8 and 9 lose linearity above pH 6; the concentration of bicarbonate ion becomes important. Considering how much carbon dioxide dissolves in the water, it is unlikely that high partial pressures of CO_2 could be achieved at equilibrium in a realistic situation. This is particularly true when it is remembered that CO_2 is more soluble in oil than in water. The oil is a significant competitive sink for CO_2 .

Summary

In summary, the solubilities of minerals are increased by increasing salinity, increasing pressure, the presence of chelators and other specific ions. These are the most important factors affecting the solubilities of sulfate minerals. The solubilities of carbonate minerals are most influenced by pH. The partial pressure of carbon dioxide has the greatest influence on the pH in normal oil-field operations. The effect of temperature varies from one mineral to another. The solubilities of anhydrite, dolomite, and calcite decrease with increasing temperature. Therefore none of these should present a scale problem because of decreasing temperature alone, as might occur during production from an oil well. The solubility of barite increases significantly with increasing temperature, so it is most likely to be formed in the cooler parts of the system. Barite is unlikely to be found in water from a reservoir that contains anhydrite stringers and is not too hot. This is because of the common ion effect. The solubility of gypsum is not strongly influenced by temperature, but since it is so soluble, even a small percentage change in solubility can result in a large amount of scale. Pressure does cause a significant percentage change in mineral solubilities.

KINETICS

The earlier discussion in this paper dealt with thermodynamics. Thermodynamics tells what will happen given enough time, but not the rate at which it will happen. All other things being equal, however, a greater thermodynamic driving force, such as that expressed by the saturation index, will result in a greater rate.

Scale will not form spontaneously in a liquid unless the saturation index is extremely high. It will, however, readily form on surfaces even at low supersaturations. Any type of surface may serve as an initial growth site, even the surface of a bubble. This is yet another reason that calcite forms so readily at pump intakes. When the intake pressure drops below the bubble point of carbon dioxide, the pH is raised while simultaneously a nucleation surface is created. Many solid surfaces also can nucleate scale. The more similar the surface is to the scale, the more effective it is at nucleating growth. Corrosion products are more effective at starting scale growth than are clean metal walls. The most effective surface is the surface of the same kind of scale. Thus once scale starts it can grow rapidly, and if not completely removed it can reform faster than it did the first time.

SCALE CONTROL

Methods

It is often impossible to avoid pressure drops or mixing of incompatible waters. Coating tubing with coatings that do not nucleate scale growth only works for a short time. Scale often must be handled in some other manner. One method is to let scale form and then remove it. Although calcite and gypsum sometimes can be removed as long as tubing is not completely obstructed, it is not the recommended procedure. The acids used with calcite removers and some gypsum converters will cause increased corrosion. The chelators used in gypsum removers also contribute to corrosion. No truly effective removal method exists for barite. It is much better to prevent the scale in the first place. The use of scale inhibitors is usually the preferred method. Scale inhibitors do not change the thermodynamics of the situation, instead they drastically affect the rate at which the system attains equilibrium. The rate of scale formation can often be slowed to the point where it is insignificant until after the water is reinjected or disposed of in another manner. From an operating viewpoint this is as good as stopping it forever.

Scale Inhibitors

Functioning

Scale inhibitors work by adsorbing on the solid surface and making it ineffective at supporting further scale growth. Scale inhibitors often need to cover only one or two percent of the solid surface to do this. This is because scale grows at only a few active growth sites on the solid, not on the whole solid surface. All currently known commercial and biological scale inhibitors contain weak acid groups. Some of these must be ionized in order for the inhibitor to function. At very low pH the acid groups become protonated and the inhibitors fail. This is why it is fortunate that very low pH's are very difficult to attain, and are virtually impossible to attain in combination with positive calcite saturation indexes.

Inhibitor Families

Virtually all commercial scale inhibitors belong to one of three different chemical families. These are phosphate esters, phosphonates, and carboxylic acid containing polymers. Differences within families determine which particular inhibitor should be used in a particular situation. The families have certain characteristics. The phosphate esters usually combine excellent performance and with excellent solubility. They are, however, the least thermally stable type of inhibitor; they should not be used above 70 to 90°C depending on the application. They also are a poor choice for squeezing because they do not stick in the formation. Phosphonates usually have a good balance of properties. They typically are stable up to 175°C or more and are widely used for squeezing. Polymers allow for a large range of different structures. They usually are thermally stable to 200°C or more, but are more prone to microbial attack. They also are more likely to have solubility problems. Many are less effective at controlling gypsum scale than the other scale inhibitor types. There are exceptions to these general rules. In addition new inhibitors are being constantly discovered, some of which are in new chemical families and some are crossbreeds of the above families.

Squeeze Treatment

Application Method

Scale inhibitors may be applied in one of several ways. A squeeze treatment is often recommended because it protects the near well-bore area as well as the production tubing. In this method a slug of inhibitor is squeezed into the formation. It may be preceded by a pre-flush to prepare the reservoir rock to receive the inhibitor. The squeeze is followed by an over-flush to force it back into the formation and to expose more of the rock surface to the inhibitor. The inhibitor either precipitates, is reversibly adsorbed onto the rock surface, or is trapped in vugs in the formation. The exact mechanism depends on the nature of the formation, the scale inhibitor and the squeeze procedure. When the well is put back onto production, the inhibitor gradually enters back into the water by dissolution, desorption or diffusion. From the point where it enters the water the inhibitor prevents scale formation. This includes the near well-bore area and the production tubing. While highly recommended, this method is an inefficient use of chemical. This is because some of it comes back too early at higher than necessary levels and some returns too late at too low a concentration to be effective. As a rule of thumb, only about one third of the chemical is usefully employed. Fortunately only low levels are generally required, so the waste is not too expensive.

Monitoring of Squeezes

To make sure that enough is coming back it is necessary that there be some method of monitoring the chemical return. This is easily done with phosphorus containing scale inhibitors, since there are well established, sensitive, interference resistant methods for determining phosphorus. Polymers can sometimes be detected, but the detection methods suffer from a lack of sensitivity and the tests are subject to many interferences from materials in a typical oil-well water.

Continuous Treatment

Scale inhibitors also may be applied continuously. This often requires that a capillary be run down the back side of the well. Inhibitor is then continuously pumped down the capillary. This is a more efficient use of chemical and does not require a monitoring method. But it does not protect the formation, it does not provide automatic fail-safe protection, and there are higher initial capital costs and continuing operation and maintenance concerns. Still it is effective when it is not considered necessary to protect the formation. It may not be necessary to protect the formation when the scale formation is due to the mixing of incompatible waters from different zones in the well bore. Or it may not be necessary when calcite is the potential scale and the pressure does not drop below the bubble point of carbon dioxide until after the water is in the production tubing. In these cases there is no potential for scale formation within the rock itself.

Final Decision

Often the data does not exist to decide if it is safe to use continuous treatment. That is why squeeze treatment is usually recommended. The cost of the extra chemical is cheap insurance to prevent the loss of a well. The final decision must be made by the engineer in charge after a careful consideration of all the factors involved. I hope that this paper has deepened his understanding and not just added to his decision making burden.

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Table 1
Representative West Texas Brine

ANIONS	mg/L	CATIONS	mg/L
B(OH) ₄ ⁻	66	Na ⁺	15550
HCO ₃ ⁻	240	K ⁺	100
SO ₄ ²⁻	700	Mg ²⁺	700
Cl ⁻	29990	Ca ²⁺	2500
		Sr ²⁺	150
			-
pH	7.7	TDS	50000

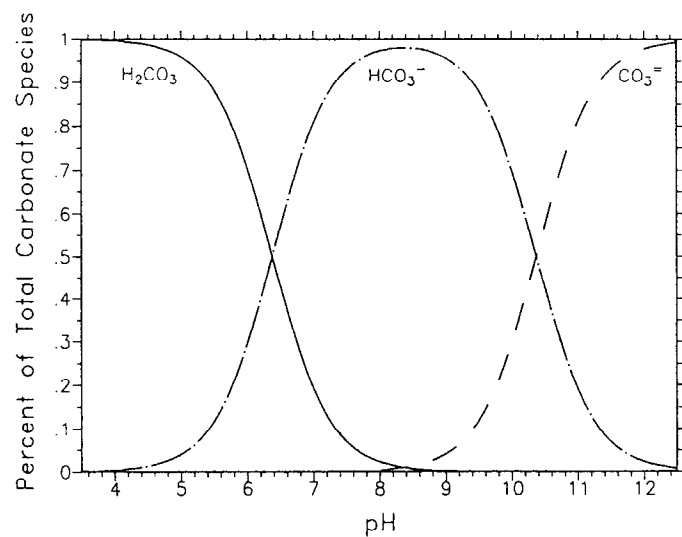


Figure 1 - The effect of pH on carbonate species distribution

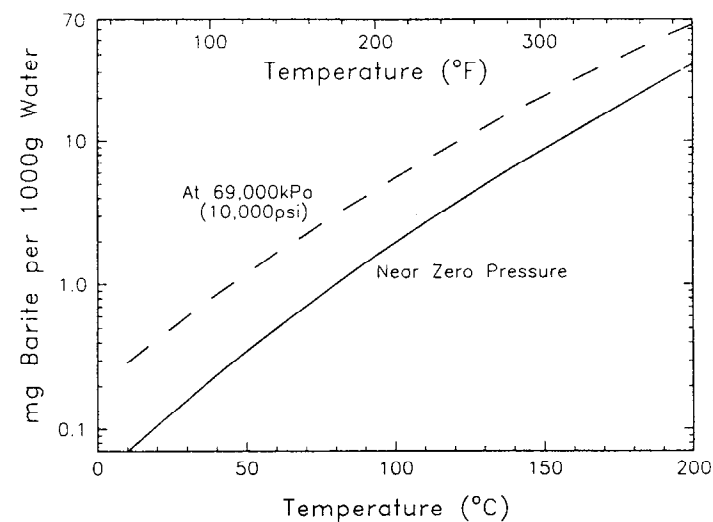


Figure 2 - Solubility of barite in an oilfield brine

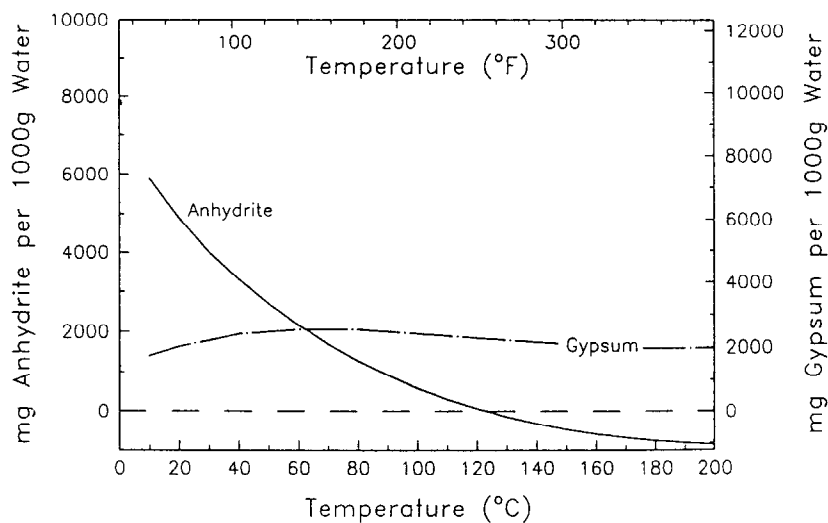


Figure 3 - Solubility of gypsum and anhydrite in an oilfield brine near zero pressure

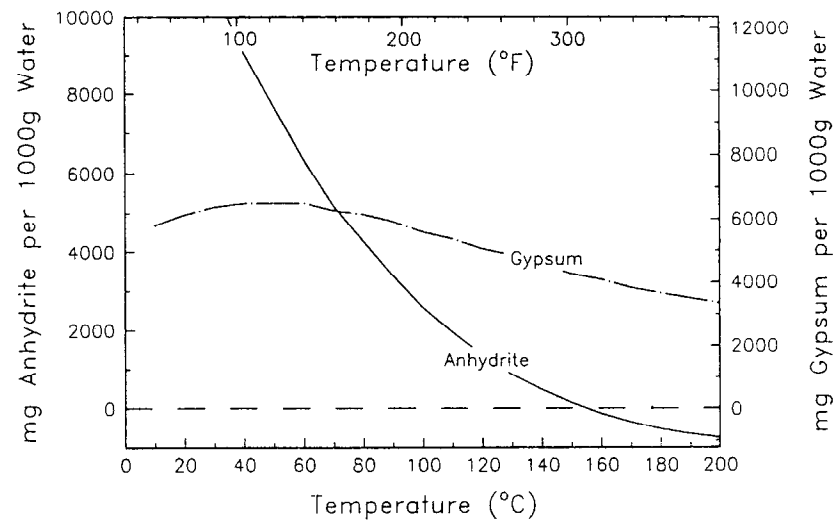


Figure 4 - Solubility of gypsum and anhydrite in an oilfield brine at 10000 psi

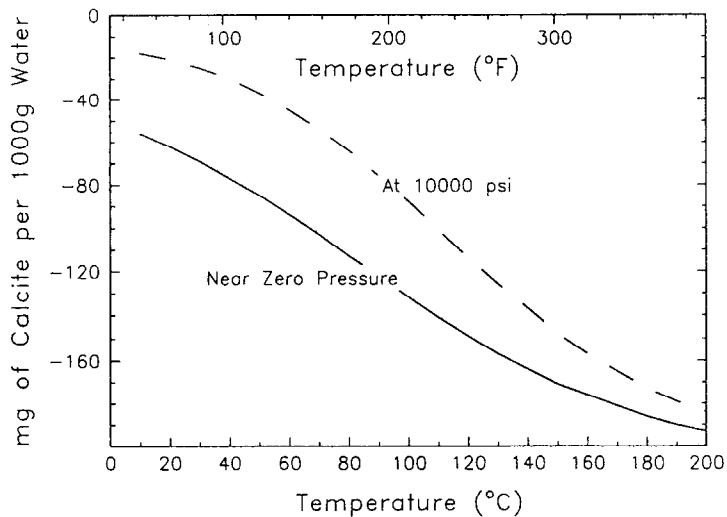


Figure 5 - Solubility of calcite in an oilfield brine

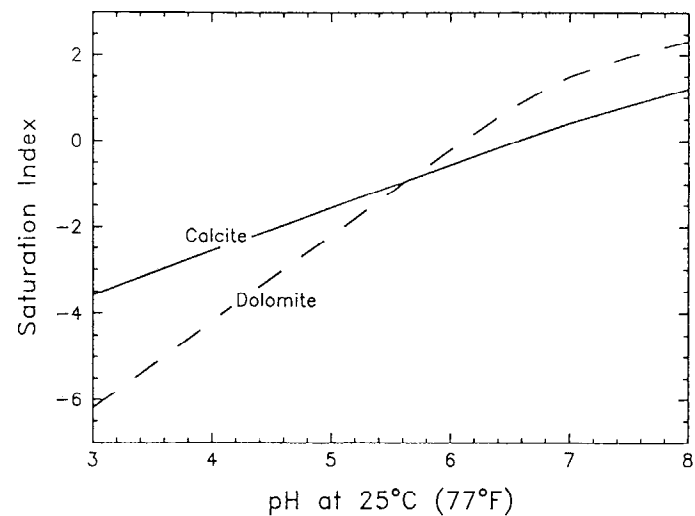


Figure 6 - Effect of pH on the saturation indexes of carbonates in an oilfield brine

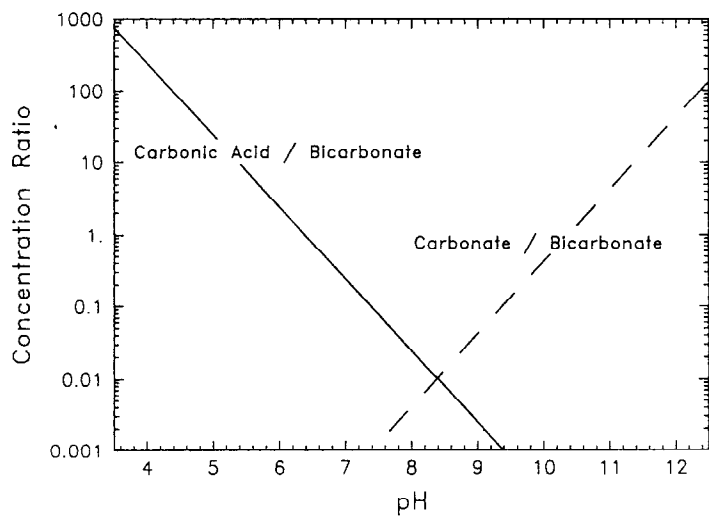


Figure 7 - Ratios of the concentrations of carbonic acid and carbonate ion to bicarbonate ion in water

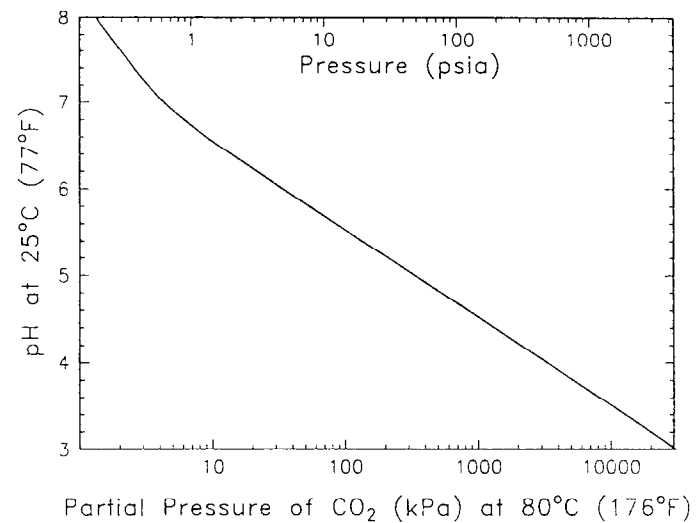


Figure 8 - Effect of the partial pressure of CO₂ on the pH of an oilfield brine

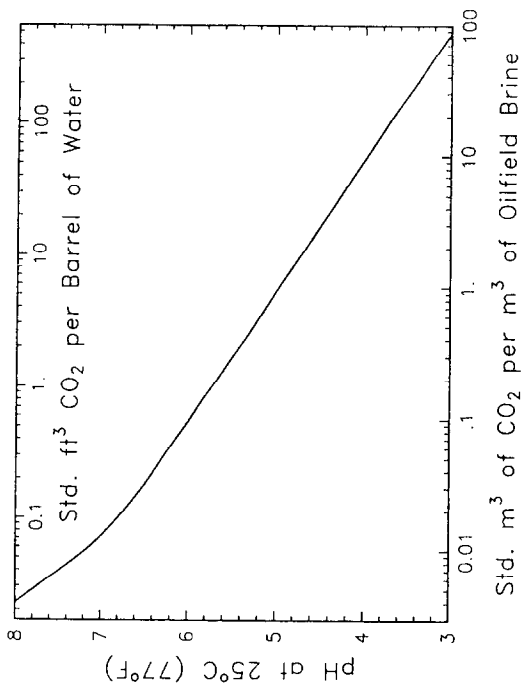


Figure 9 - Amount of CO₂ dissolved in an oilfield brine at different pH's

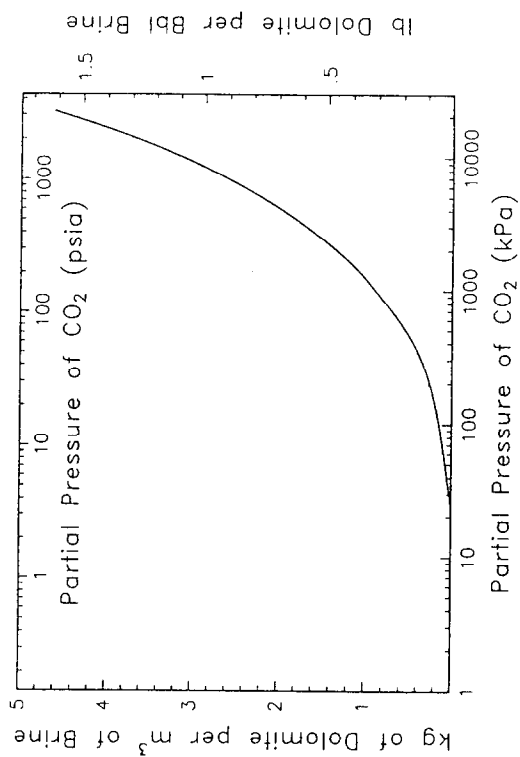


Figure 10 - Amount of dolomite dissolved by CO₂ in oilfield brine at 80°C (176°F)

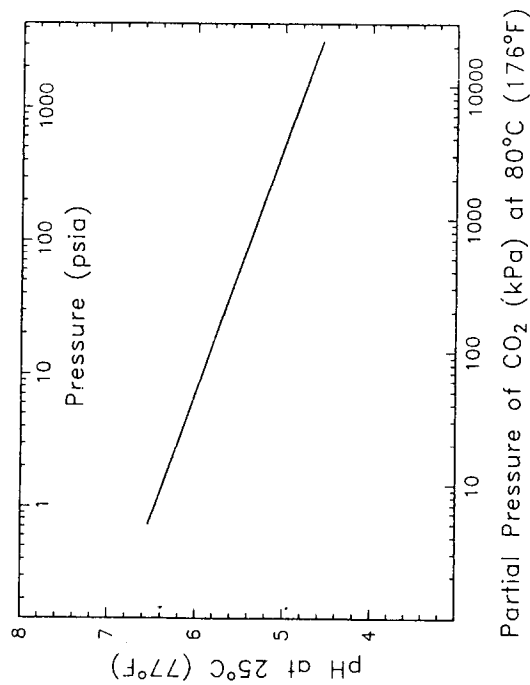


Figure 11 - pH of oilfield brine saturated with CO₂ and dolomite at 80°C (176°F)

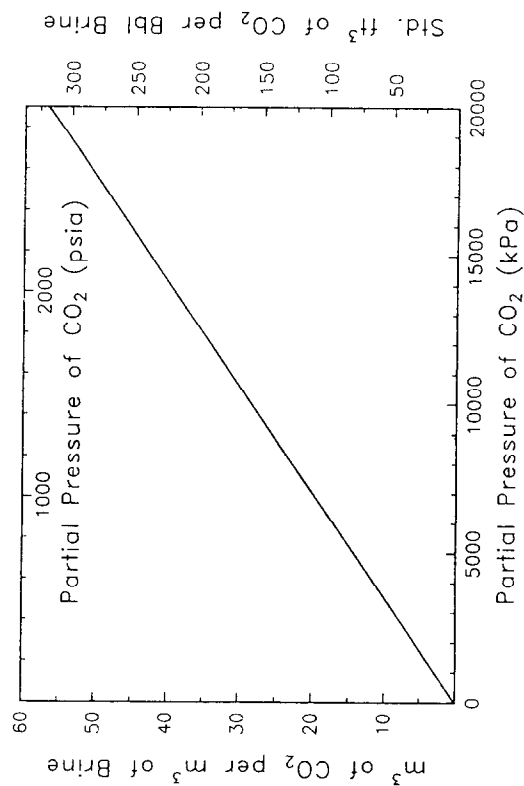


Figure 12 - Amount of CO₂ dissolved in oilfield brine in equilibrium with dolomite at 80°C (176°F)