

**Carbon Dioxide Capture for Storage  
in Deep Geologic Formations –  
Results from the CO<sub>2</sub>  
Capture Project**

**Geologic Storage of Carbon Dioxide  
with Monitoring and Verification**

*Volume 2*

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# **Carbon Dioxide Capture for Storage in Deep Geologic Formations – Results from the CO<sub>2</sub> Capture Project**

**Geologic Storage of Carbon Dioxide  
with Monitoring and Verification**

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## Chapter 18

# EFFECT OF IMPURITIES ON SUBSURFACE CO<sub>2</sub> STORAGE PROCESSES

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### ABSTRACT

We examine the potential effect of highly reactive impurities (SO<sub>x</sub>, NO<sub>x</sub>) on two important aspects of large-scale geological storage of CO<sub>2</sub>: well injectivity and enhanced oil recovery processes. The primary influence on well injectivity is expected to be geochemical alteration of the near-well formation. Our simulations of a “worst-case” scenario indicate that the net change in mineral volume is likely to be small, even though extensive changes in the type of minerals may occur. Thus, the effect on injectivity is likely to be insignificant. The presence of impurities in their likely concentrations of less than 1 mole% may speed up the reactions, but otherwise should have little incremental effect on the injectivity. The effectiveness of enhanced recovery processes using CO<sub>2</sub> depends on factors such as minimum miscibility pressure (MMP), mobility ratio, and gravity number. Correlations for these factors developed over several decades of field experience in CO<sub>2</sub> flooding indicate that impurities at the levels typical of flue gases are unlikely to affect recovery adversely.

### INTRODUCTION

The CO<sub>2</sub> Capture Project objectives include maximizing safe geologic storage, assessing and mitigating storage risks while minimizing costs. The costs of storing carbon dioxide (CO<sub>2</sub>) captured from typical combustion sources—boilers, turbines, heaters—can be significantly reduced if stored without purification. The effect of impurities, specifically commonly occurring concentrations of sulfur and nitrogen oxides (SO<sub>x</sub>/NO<sub>x</sub>) as found in flue gases is a concern to the injection of CO<sub>2</sub>. Likewise, if the costs of storage are to be offset through enhanced oil recovery (EOR), it could result in a detrimental effect of the SO<sub>x</sub>/NO<sub>x</sub> on the oil-recovery ability of the CO<sub>2</sub>. Our goal is to survey the effect of impurities on such issues.

The work summarized is based on the following two assumptions about impurities in CO<sub>2</sub>:

1. At reservoir/aquifer conditions, the CO<sub>2</sub> to be stored is a super-critical fluid that is as much like a liquid as a gas, compared to CO<sub>2</sub> at standard conditions or even to SO<sub>x</sub>/NO<sub>x</sub> at aquifer/reservoir conditions. Thus, diluting CO<sub>2</sub> with SO<sub>x</sub>/NO<sub>x</sub> will result in a more gas-like mixture than is CO<sub>2</sub> alone. As we will see, such dilution has the effect of making the CO<sub>2</sub> more immiscible with reservoir crude, though this effect on recovery may be offset by other factors.
2. The concentration of SO<sub>x</sub>/NO<sub>x</sub> to be encountered in the stored fluid will be modest, at most around 5 mole%, but usually less. At these concentrations the effect of impurities on density, viscosity and interfacial tension is likely to be small.

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*Abbreviations:* DOE, Department of Energy; EOR, enhanced oil recovery; MME, minimum miscible enrichment; MMP, minimum miscibility pressure; MOC, method of characteristics; SPE, Society of Petroleum Engineers; WAG, water-alternating-gas.

### ***Injectivity and Subsurface Storage***

Many methods proposed for storing CO<sub>2</sub> in subsurface formations (saline formations and hydrocarbon reservoirs) take well injectivity for granted. That is, the injection pressure required to maintain CO<sub>2</sub> flow at a prescribed rate is assumed to remain constant over the course of the injection operation. The geochemical perturbation arising from the dissolution of CO<sub>2</sub> into subsurface brines is a mechanism for altering rock properties. Those alterations in turn have the potential for changing rock permeability and thus injectivity. Even small changes in injectivity could have substantial impact on the economics of storage, including direct costs associated with drilling and completing new wells, well stimulation treatments, and consequent interruptions in the flue gas pipeline operation, and indirect costs, including longer times or higher pressures required to inject the design CO<sub>2</sub> volume.

The rock properties within a few meters of a wellbore typically control injectivity. Because the CO<sub>2</sub> to be stored enters the formation through this small near-wellbore region, the region will be flushed by millions of (local) pore volumes of gas. Thus, even slow incremental geochemical alterations may have a significant cumulative effect over the months or years of the storage operation. The presence of impurities such as NO<sub>x</sub> and SO<sub>x</sub> in the CO<sub>2</sub> stream increases the possibility of rock alteration, since these components are even more reactive than CO<sub>2</sub> when dissolved in brine.

Yet another feedback loop arises when the injected CO<sub>2</sub> is undersaturated with water vapor. Thus, after displacing water to irreducible saturation in the near-wellbore pore-space, the injected CO<sub>2</sub> will gradually dehydrate or dry the near wellbore region. This process will concentrate the dissolved species and increase their reactivity. At the same time, dehydration will reduce the grain surface area in contact with the irreducible water saturation, reducing the reaction rates and hence limiting the extent of the alteration.

The geochemical reactions are likely also to change the surface energies of the water/mineral interface. Feedback, therefore, exists at the grain scale as well, since the contact between irreducible water and the rock grains is controlled by capillary forces. Investigation of this phenomenon is beyond the scope of the project proposed here. For the purpose of our study, we will assume geochemical reactions are unaffected by capillary forces.

Injectivity losses have been reported in EOR field projects in which CO<sub>2</sub> and water are injected alternately (Patel [1]; also see Grigg, this volume). The most likely explanation for these observations involved multiphase flow behavior, rather than geochemical alteration. There is little information currently available to answer the question of how injecting only CO<sub>2</sub> would affect injectivity. In the latter case, the extent of mineral dissolution and the extent of precipitation of new minerals are the most important factors. These will be the focus of this study.

### ***CO<sub>2</sub> Storage and Enhanced Oil Recovery***

The revenue from oil produced miscibly or near-miscibly by injected CO<sub>2</sub> has the potential offset to the cost of CO<sub>2</sub> storage. Determining whether impurities would adversely or positively affect the MMP of CO<sub>2</sub>/crude mixtures and consequently, oil recovery is of significance.

MMP is defined as the pressure at which CO<sub>2</sub> develops miscibility with oil. Miscibility means that there is no interface (zero interfacial tension) between oil and an enriched CO<sub>2</sub> mixture. The miscibility suppresses capillary forces allowing excellent oil recovery efficiency on the pore scale. CO<sub>2</sub> EOR is complex because miscibility often develops when CO<sub>2</sub> extracts intermediate components from the crude into the CO<sub>2</sub>-rich phase even under circumstances where CO<sub>2</sub> alone is not miscible with the oil. The rate of extraction depends on the purity of the solvent. CO<sub>2</sub>-N<sub>2</sub> mixtures are poorer extractors than CO<sub>2</sub> alone, whereas CO<sub>2</sub>-H<sub>2</sub>S mixtures are better extractors. MMP decreases as the solvent becomes more "oil-like", supporting the conclusion that impurities in a CO<sub>2</sub> stream that are more like the oil than CO<sub>2</sub> will decrease the MMP while impurities that are less like the oil will increase the MMP.

CO<sub>2</sub> has been used as an EOR agent since the early 1970s, and research on this technology predates this by nearly 20 years. More than 50 CO<sub>2</sub> field floods have been conducted, primarily in West Texas,

with a corresponding accumulation of field experience and production data out of which has grown a large technology base for the process. The dependency of MMP upon oil composition was addressed most definitively by Holm [2]. Most of the data on MMP has been captured as statistical correlations. Correlations dealing with CO<sub>2</sub> stream impurity also exist. In Ref. [3], the authors account for the influence of any component in the CO<sub>2</sub> on MMP by means of the critical temperature for that component. The Holm [2] and Sebastian [3] correlations account for the major influences on MMP.

## EXPERIMENTAL/APPROACH

Many numerical simulators of flow accompanied by transport and chemical reactions have been developed, with varying capabilities and sophistication [4]. In this study, we have chosen to use a relatively simple simulator. The concept of *fronts* (also referred to as *waves*) propagating through a porous medium is a powerful method for understanding behavior. A front separates regions of different chemical (and in this context mineral) composition and moves at some fraction of the fluid velocity. When the reactions are fast relative to the flow rate, the fronts can be determined analytically.

Our study considers the following idealizations aimed at producing a “worst-case” scenario where the maximum conceivable mineralogical alteration occurs. Specifically, we consider 1D flow with intra-aqueous reactions (e.g. dissociation of dissolved CO<sub>2</sub> into bicarbonate anion and hydronium cations) in local equilibrium with a few simple minerals.

## RESULTS AND DISCUSSION

### *Enhanced Oil Recovery*

In most projects, the CO<sub>2</sub> injected for EOR is nearly pure. A notable exception was the Slaughter Estate Unit (SAU) in which a mixture of 21 mole% H<sub>2</sub>S and 79% CO<sub>2</sub> was injected, to apparent beneficial effect [6]. The ultimate recovery of oil by CO<sub>2</sub> injection depends on many things including: operating strategy, reservoir pressure, reservoir temperature, solvent purity, well spacing, well conditions, and reservoir heterogeneity. Many factors actually operate in opposing fashion [7]. Thus, it is impossible to estimate ultimate recovery except through an involved calculation that accounts for all these factors. Numerical simulators to do this are in common use. It is possible, however, to qualitatively assess the effect of impurities through the use of dimensionless groups (scale factors) that generally influence ultimate EOR recovery. These groups are the capillary number, the mobility ratio, the gravity number, and the continuity number. Injectivity is also important, and this will be addressed as a separate matter in the second half of this report. The following is a summary of effects and tendencies taken from Ref. [5] that are specific to the issue of CO<sub>2</sub> storage in oil reservoirs. The CO<sub>2</sub>-rich injectant here will be called a “solvent”.

*Capillary Number:* The capillary number expresses the ratio of capillary forces to viscous forces. It is usually defined as [5]

$$N_c = \frac{\text{viscous}}{\text{capillary}} = \frac{\mu u}{\sigma} \quad (1)$$

where  $\mu$  is the solvent viscosity [ = ] F - t/L<sup>2</sup>;  $u$ , superficial velocity of the flood [ = ] L/t and  $\sigma$  is the interfacial tension between solvent and oil [ = ] F/L. (In this equation and those following [ = ] means “has units of”. F is force, L length, m mass, and t time.) Statistical correlations have shown that oil recovery increases as the capillary number ( $N_c$ ) increases [8–11]. Thus, if impurities increase  $N_c$ , the ultimate oil recovery on a small scale (displacement efficiency) will increase. Conversely, if the  $N_c$  is lowered by impurities, recovery will decrease.

Though there are three quantities in Eq. (1), in practice only the interfacial tension can be practically changed sufficiently to be considered significant (the relationship between ultimate recovery and  $N_c$  is logarithmic). If  $N_c$  is very large, the displacement approaches miscibility.

### *Minimum miscibility pressure*

MMP is regarded as one of the primary determinants to the success of an oil-recovering CO<sub>2</sub> flood [12]. If the average reservoir pressure is not greater than the MMP, the flood will be immiscible and expected oil recovery will be much lower.

CO<sub>2</sub> recovers oil by mass transfer and if mass transfer is strong enough, the CO<sub>2</sub> will become miscible with resident crude. The term “mass transfer” means that components transfer from the oil to the solvent or vice versa. For CO<sub>2</sub> injection transfer of intermediates from the oil to the solvent is most important. The mass transfer induces miscibility. Miscibility results in the total suppression of capillary forces (infinite  $N_c$ ) and leads to large displacement efficiency. In most cases the CO<sub>2</sub> will cause intermediate components from the crude to pass into the CO<sub>2</sub>-rich phase creating, after a few contacts, an enriched mixture that is miscible with the crude. In this vaporizing gas drive process, the CO<sub>2</sub>, though initially immiscible with the crude is said to have *developed* miscibility through extraction. The extraction depends strongly on the purity of the solvent; CO<sub>2</sub>-nitrogen mixtures are poorer extractors than CO<sub>2</sub> alone and CO<sub>2</sub>-H<sub>2</sub>S mixtures are better extractors.

A common way to gauge the approach to miscibility is through slim tube experiments. In these experiments a permeable medium is saturated with a crude, and then, at constant temperature, subjected to a succession of CO<sub>2</sub> displacements. Before each displacement the tube is re-saturated with crude and the displacement performed at successively higher pressures. The ultimate oil recovery in these experiments tends to increase with pressure and the recovery tends to level off at a specific threshold pressure. This threshold pressure is defined as the MMP. If attaining miscibility is difficult, the MMP will be large; if easy it will be small. MMP is an analogue quantity for minimum miscible enrichment (MME) previously proposed for miscible gas injection [13].

Interestingly, though MMP is defined in terms of oil recovery in a flowing medium, it is also associated with the phase behavior of CO<sub>2</sub>-crude mixtures. This means that MMP has a thermodynamic basis in that the mass transfer is that which occurs after repeated contacts in which equilibrium is successively established.

There are three ways to estimate MMP:

1. *Experimental.* Within this category are
  - (a) The slim tube experiment discussed above. This is the most common way.
  - (b) The rising bubble apparatus [14]. This technique estimates miscibility as the height in a column of crude at which a bubble of CO<sub>2</sub> disappears under gravity rise. The height can be translated into a pressure and thence to MMP. This technique is offered as a commercial service but is much less used than the slim tube experiment.
  - (c) Vanishing interfacial tension. This technique is based on the direct correspondence between miscibility and non-zero interfacial tension [15]. The extrapolation of IFT to zero with increasing pressure determines the MMP. This technique, being much newer than the others, is the least used of all [16].
2. *Theoretical.* Because of the thermodynamic basis of MMP, it can be estimated by calculation. There are two categories for this
  - (a) Mixing cell models. These are calculations in which solvent is mixed with crude in a succession of well-mixed cells. The solvent-crude mixtures come to equilibrium after each mixing and the equilibrated gaseous phase (solvent plus extracted intermediate components) pass to another cell for further equilibration. There are specialized simulators for this, but the calculation can be done with any commercial compositional simulator.
  - (b) Method of characteristics (MOC) models. In the limit of zero dispersion—which all mixing cell models possess to some degree—the MOC provides a direct measure of the MMP through quasi-analytic calculation. This procedure has been developed by the Stanford group [17–19].
3. *Correlation.* Because of the expense of making site-specific MMP measurements, much of the slim tube data has been captured through correlation. There are two types:
  - (a) Neural networks. The complexity of the dependencies of MMP has led some to exploit artificial neural networks for correlation [20]. The success of this has been good in matching data but a neural network is not easy to use for prediction.



- (b) Statistical correlation. By far the most common type of correlation has been statistical correlation and this, along with the MOC approach above, would be the recommended approach for subsequent estimation. Before reviewing these, we review some of the qualitative trends of MMP with other quantities.

That the composition of crude oils is highly variable accounts for the complexity of MMP correlations. General trends are

- (i) MMP should increase with temperature. That is, it should be more difficult to develop miscibility at high temperatures than at low.
- (ii) MMP should decrease with increases in the intermediate content in the crude. This is a logical consequence of the development of miscibility depending on the extraction of intermediates. There is, unfortunately, no simple way of simply characterizing the intermediate content in crude.
- (iii) MMP should decrease as the solvent becomes more "oil-like". This means that impurities in a CO<sub>2</sub> stream that are more like the oil than CO<sub>2</sub> will decrease the MMP. Impurities that are less like the oil will increase the MMP. Figure 16 in Ref. [20] gives a good summary of this effect. See also Refs. [21–23]. The "oil-like" nature of the solvent will figure into other effects as they are covered.

We now turn, in conclusion, to the more significant MMP correlations. Yellig [24] gave one of the earliest correlations. This correlation was only for West Texas crude and did not contain a composition dependence. The compositional dependency was addressed by Johnson [21] and, most significantly, by Holm [2, 25–27]. Correlations dealing with CO<sub>2</sub> stream impurity also exist. Perhaps the best of these is by Sebastian [3] who attempted to correlate deviations away from the pure CO<sub>2</sub> critical temperature.

$$\frac{P_{MM}}{(P_{MM})_{CO_2}} = 1.0 - (2.13 \times 10^{-2})(T_{pc} - T_c) + (2.51 \times 10^{-4})(T_{pc} - T_c)^2 - (2.35 \times 10^{-7})(T_{pc} - T_c)^3 \quad (2)$$

where  $P_{MM}$  is the MMP of a solvent against a particular crude [ = ] F/L<sup>2</sup>;  $(P_{MM})_{CO_2}$ , the MMP of a pure CO<sub>2</sub> solvent as from, for example, the Holm [2] correlation [ = ] F/L<sup>2</sup>;  $T_c$ , critical temperature of CO<sub>2</sub> [ = ] degrees Rankine and  $T_{pc}$  is the pseudocritical temperature of a multicomponent solvent [ = ] R, where

$$T_{pc} = \sum_{i=1}^{i=N} y_i T_{ci}$$

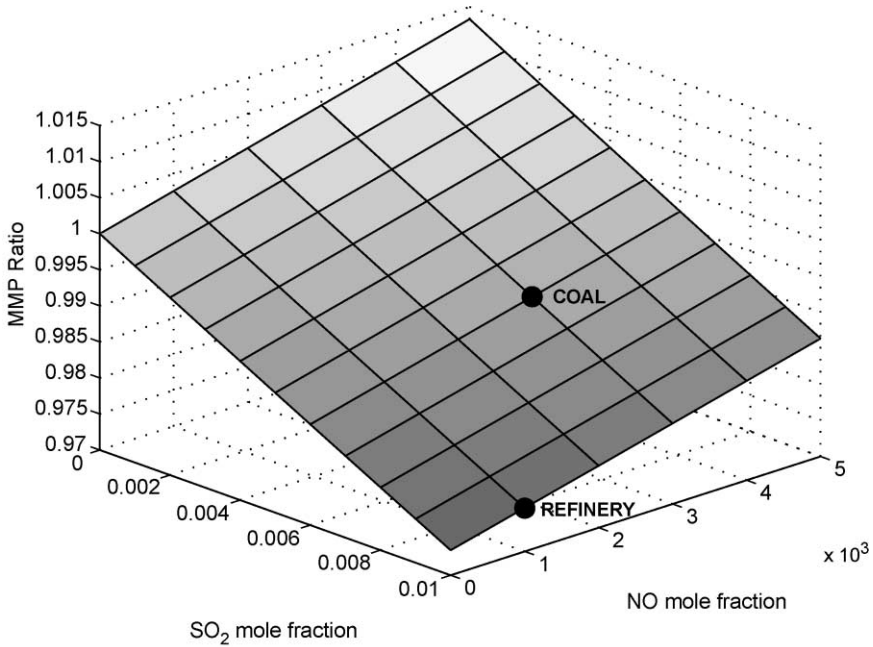
and  $y_i$  is the mole fraction of component  $i$  in the solvent.

The combination of Eq. (2) and Sebastian [3] correlations gives the combined effects of temperature, oil composition, and the characteristics of the solvent. The accuracy is within about 50 psia, which should be sufficient for screening.

We apply this correlation with SO<sub>2</sub> and NO as representative impurities. The critical temperatures of SO<sub>2</sub> and NO are 430.5 and 180 K, respectively. The critical temperature of CO<sub>2</sub> is 304 K. Thus, the pseudocritical temperature can be written as

$$T_{pc} = 304y_{CO_2} + 430.5y_{SO_2} + 180y_{NO}$$

Inspection of the MMP correlation shows that SO<sub>2</sub> will decrease the MMP relative to the pure CO<sub>2</sub> value, while NO will increase it. Because the coefficients in the correlation are small and because the expected values of SO<sub>2</sub> and NO mole fractions are small, the effect on MMP is also small, as illustrated in Figure 1.



**Figure 1:** Effect of impurities on MMP ratio calculated from Eq. (2).

Concentrations typical of coal combustion flue gas and a refinery fuel flue gas are plotted; the basis for determining the composition neglects water vapor and nitrogen. The changes in MMP over this range of impurities (less than 1% for SO<sub>2</sub>, less than 0.5% for NO) are less than 2%. Thus, we expect little overall effect on MMP. In other words, a candidate flood that would nominally be miscible with pure CO<sub>2</sub> would also be miscible with a diluted solvent.

*Factors influencing immiscible and miscible displacements*

Several factors affect the efficiency of displacement processes, whether the process is carried out above the MMP or below. Factors that can be affected by the presence of impurities include mobility ratio and gravity number. The subsequent discussion applies to immiscible floods and to miscible floods alike; for these purposes both types can be regarded as EOR.

*Mobility ratio (M).* While the capillary number and MMP are indicators of ultimate oil recovery on a small scale, the mobility ratio indicates the ability of a solvent to contact volumes of a reservoir, a quantity usually known as volumetric sweep efficiency. *M* is the ratio of the mobility of the displacing fluid to that of the displaced fluid.

$$M = \frac{(k_r/\mu)_{\text{displacing}}}{(k_r/\mu)_{\text{displaced}}} \approx \frac{\mu_{\text{displaced}}}{\mu_{\text{displacing}}} \tag{3}$$

where *k<sub>r</sub>* is the relative permeability.

As Eq. (3) indicates, *M* is strongly affected by the viscosities of the fluids. The connection between ultimate recovery and *M* is complicated but there is a universal tendency that applies to both miscible and immiscible floods. As *M* increases—displacing fluid become more mobile—volumetric sweep decreases because the displacing fluid now has a greater tendency to bypass the resident or displaced fluid. The more SO<sub>*x*</sub>/NO<sub>*x*</sub>

there is in a CO<sub>2</sub>-rich solvent (the more gas-like it becomes), the smaller its viscosity, the larger the  $M$  and the smaller the ultimate oil recovery. Unlike the MMP issue, impurities here decrease ultimate oil recovery. However, the concentration of SO<sub>x</sub>/NO<sub>x</sub> being considered is small enough to make this effect small.

*Gravity number* ( $N_g$ ). The gravity number is a dimensionless ratio of gravity (buoyancy) forces to viscous forces. The usual definition is

$$N_g = \frac{\text{buoyancy}}{\text{viscous}} = \frac{kk_r}{\mu u} \Delta \rho g \quad (4)$$

where  $k$  is the permeability [=] L<sup>2</sup>;  $g$ , gravitational acceleration constant [=] L/t<sup>2</sup> and  $\Delta \rho = \rho_{\text{displacing}} - \rho_{\text{displaced}}$  is the density difference [=] m/L<sup>3</sup>.

This number was derived in Ref. [28].  $N_g$  expresses the propensity for a solvent to segregate within a reservoir. For  $\Delta \rho > 0$  the solvent would fall to the bottom of a reservoir; for  $\Delta \rho < 0$ , the normal case in solvent flooding, the solvent would move to the top of the reservoir causing overriding. Either type of segregation would result in poor volumetric sweep and small ultimate oil recovery.

As Eq. (4) shows, five quantities normally determine the magnitude of  $N_g$ ; however, the permeability seems to have the most influence. Large  $k$  reservoirs inevitably show extensive segregation. The principal effect of solvent impurities would be to decrease  $\rho_{\text{displaced}}$  (increase  $\Delta \rho$ ) thereby increasing segregation to the result that ultimate oil recovery would be decreased. However, as in the case of the mobility ratio, the decreases are not likely to be significant at the concentrations envisioned.

*Vertical communication.* The relationships between ultimate recovery and the quantities discussed above are complicated. Some of this complication can be conveyed through an effective aspect ratio  $R_L$  that, which of itself being of little importance to ultimate recovery, is a determinant of the strength of the relationships we have been discussing. The effective aspect ratio is

$$R_L = \frac{L}{H} \sqrt{\frac{k_v}{k_h}} \quad (5)$$

where  $L$  is the length of the reservoir (usually the well spacing) [=] L;  $H$ , the thickness of the reservoir [=] L;  $k_v$ , the harmonic average vertical permeability [=] L<sup>2</sup> and  $k_h$  is the arithmetic average horizontal (lateral) permeability [=] L<sup>2</sup>.

The relationship between volumetric sweep efficiency  $E_v$  and the above three quantities can be written as

$$E_v = f(M, N_g, R_L). \quad (6)$$

When  $R_L$  is small the relationship between  $E_v$  and  $N_g$  is weak; when it is large, the relationship is strong. Sometimes the two effects—buoyancy and vertical communication—are combined into a single group as

$$N'_g = \frac{k_v k_r L}{\mu u H} \Delta \rho g. \quad (7)$$

Finally, comments about the effect of buoyancy on solvent floods must be tempered by a consideration of the dip of the reservoir. In a steeply dipping reservoir, the buoyancy effects can be used to increase the ultimate recovery of oil by injecting the light fluid at the top of a structure. Indeed, some of the largest ultimate recoveries reported in injection process have been by displacements that are made to be gravity stable even sometimes at the expenses of miscibility. In these cases, a large  $N_g$  would increase ultimate oil recovery, meaning that impurities would be beneficial.

Factors particular to immiscible displacement include changes in oil properties (swelling, viscosity alteration, etc.). These arise because of mass transfer between the CO<sub>2</sub> and oil. SO<sub>x</sub>/NO<sub>x</sub> impurities are more “gas-like” than “oil-like”. The mass transfer that occurs in immiscible floods is not large enough to cause miscibility. Thus, the incremental changes in oil properties caused by the presence of these impurities

are anticipated to be small. It is unlikely that the behavior of an immiscible displacement would be noticeably different than that of a pure CO<sub>2</sub> flood.

### **Injection Rate**

The fluid velocity appeared in the above groups involving viscous forces. The superficial velocity  $u$  is directly proportional to the ability to inject fluid into a reservoir, a large injection rate means a large  $u$ . But the effect on  $N_c$  and  $N_g$  on injection rate is secondary given the sensitivities of the other quantities in the groups. Injection rate is far more important, however, than these groups indicate because it is the major determinant of how many wells are needed for a storage project. Because most of these remarks would apply equally well to storage in a saline formation as to an oil reservoir, we refer to the CO<sub>2</sub>-rich injectant as simply the "injectant".

The injectivity of a well is defined as

$$J = \frac{q}{\Delta p} \left[ \frac{L^5}{t - F} \right] \quad (8)$$

The usual oilfield units for  $J$  are barrel/(day-psi). Other terms in Eq. (8) are  $q$  is the injection rate [ = ] L<sup>3</sup>/t and  $\Delta p = p_{wf} - \bar{p}$  is the pressure difference [ = ] F/L<sup>2</sup>, where  $p_{wf}$  is the bottom hole flowing well pressure [ = ] F/L<sup>2</sup>;  $\bar{p}$  is the volumetrically average reservoir pressure [ = ] F/L<sup>2</sup>.

Other definitions for injectivity are possible [29] but all lead to the same conclusion that the larger the  $J$ , the greater the injection rate for a given pressure difference.

We now turn to a discussion of factors that could cause injectivity changes. An expression for  $J$  that is consistent with the injectivity definition is

$$J = \frac{4\pi k k_r H}{\mu \left( \ln \left( \frac{4A}{1.781 C_A r_w^2} \right) + 2s \right)} \quad (9)$$

where  $A$  is the area being flooded by the well [ = ] L<sup>2</sup>;  $r_w$ , well radius [ = ] L;  $C_A$ , a shape factor and  $s$  is the skin factor.

Eq. (9) is the injectivity of a vertical well in a region having flooded area  $A$ . The shape factor can be picked to express the geometry of the flooded area, the tilt of the well, the existence of partially perforated intervals, or even, with suitable adjustment, vertical wells. The skin factor  $s$  represents "damage" to the well caused by impairment in the well itself, or in the immediate vicinity of the well. One immediately apparent effect of CO<sub>2</sub> impurities would be to increase injectivity through a lessened viscosity, the injectant now being more gas-like.

Injectivity in CO<sub>2</sub> oil recovery floods has long been recognized as a factor that is important to economic success [30,31]. The seminal reference on this subject is by Patel [1] who noted that CO<sub>2</sub> injectivity was unexpectedly smaller than what was estimated. Patel [1] attributed this to one of three causes:

1. Interactions between the CO<sub>2</sub> and crude oil that resulted in solids precipitation. This would increase  $s$  in Eq. (9).
2. Mineralization induced by reactions between CO<sub>2</sub>-saturated water and host minerals. This would lower  $k$  in Eq. (9).
3. Relative permeability hysteresis caused by decreasing the oil saturation (in a preceding waterflood) and then increasing it in a banked up oil zone. This would cause a small  $k_r$  in Eq. (9).

Patel [1] concluded that the third effect was the most significant, even though all effects could be present. The first effect would only be present for storage in oil reservoirs, but the other two effects could be important. The following discusses the second and third effects. Interestingly, the two effects combined seem to shed the most insight into predicted behavior.

### Mineralization

Water saturated with  $\text{CO}_2$  is slightly acidic with pHs in the range of 3–6 depending on the partial pressure of the  $\text{CO}_2$ -rich phase with which it is in equilibrium. Such lowered pHs can increase the solubility of resident minerals, especially carbonates and some clay minerals. This would increase  $J$  by increasing  $k$  through enlargements of the pore space as a result of mineral dissolution.

However, the possibility exists that ions liberated from the dissolution of the primary mineral can combine with ions in the water to form a secondary mineral. The secondary precipitation can decrease  $J$  by decreasing  $k$ . Indeed, calculations based on sea water injection show that it is possible for the volume of secondary minerals and yet-undissolved primary minerals can be greater than the volume of the initial mineral assemblage [32]. Secondary mineralization can also be beneficial because the secondary mineral can be a carbon-storing mineral. Indeed co-injection of the  $\text{CO}_2$  with water may be a way to induce such storage.

To investigate these effects, we performed calculations of mineralization in one-dimensional media undergoing inorganic reactions in local equilibrium with a flowing solution, as described in Ref. [4]. Assuming local equilibrium, the specific velocity of a component in single-phase flow is

$$v_{\Delta C_i} = \frac{1}{1 + D_i} \quad (10)$$

where  $D_i$  is the dimensionless retardation factor for component  $i$  and  $v_{\Delta C_i}$  is the specific velocity relative to water velocity.

Here and elsewhere retardation factors are always positive. Our calculations were based on three base components, carbon, calcium and sulfur, for which the primary mineral was  $\text{CaSO}_4$ , which dissolution could result in precipitation of the secondary mineral calcite  $\text{CaCO}_3$ . The aqueous phase was everywhere in local equilibrium with a gaseous injectant that was mainly  $\text{CO}_2$ , which also could contain varying amounts of  $\text{SO}_2$ . The reason for this is discussed below. The  $\text{SO}_2$  is a surrogate for the  $\text{SO}_x/\text{NO}_x$  impurities.

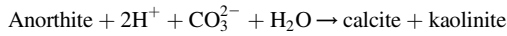
Ideal chemistry (speciation and dissociation reactions involving aqueous phase components) was simulated. Repeating simulations with corrections for non-ideal solutions (activity coefficients) made little difference. The continuous flow of the saturated brine provides an overestimate of the extent of dissolution and precipitation. In practice brine will flow for a relatively short time in the near-well region.

The model formation contains a mineral that dissolves when contacted by the acidic brine. Both equilibrium and rate limited dissolution were modeled. Though unlikely to be attained under realistic field conditions, the equilibrium assumption establishes a worst case (maximum possible mineral dissolution and precipitation). The dissolved mineral releases divalent cation into the  $\text{CO}_2$ -saturated brine, causing the precipitation of a carbonate mineral. This is the simplest model that captures two key features: mineral precipitation, which is the only geochemical mechanism likely to cause injectivity loss, and supplying divalent cations for precipitation by dissolving in situ minerals. A more complicated suite of precipitation/dissolution reactions can occur in the field, but their unfavorable influence on injectivity depends only on the extent of precipitation. Thus for the limited purposes of this study, this simplified model was used.

Results show a  $\text{SO}_2$ -free injectant will indeed dissolve the primary mineral and precipitate a secondary mineral. Typical retardation factors for the first dissolution are 2–3 for  $\text{CaSO}_4$  and 5–6 for  $\text{CaCO}_3$ . The replacement of  $\text{CaSO}_4$  by  $\text{CaCO}_3$  was on an equal molar basis or less. This means that total mineral concentration, the sum of  $\text{CaSO}_4$  and  $\text{CaCO}_3$ , nowhere exceeded the initial  $\text{CaSO}_4$  concentration. Results with an injectant that contained  $\text{SO}_2$  showed that even modest concentrations of  $\text{SO}_2$  reduce the pH of the water even further, down to 1–2 compared to 5–6 for the  $\text{SO}_2$ -free injectant. This decrease has two causes:  $\text{SO}_2$  is more soluble in water than is  $\text{CO}_2$ , and the acid formed by  $\text{SO}_2$  in water, sulfurous acid or  $\text{H}_2\text{SO}_3$ , is a far stronger acid than the carbonic acid  $\text{H}_2\text{CO}_3$  formed by  $\text{CO}_2$ . The lowered pH has two effects on the flow: the primary mineral is dissolved much faster, and a secondary mineral never precipitates. The presence of impurities in this regard is entirely beneficial to good injectivity.

Other simulations indicate that the *net change* in mineral volume is likely to be small, even when extensive changes in mineral state may occur. The physical reason is simple: the injected fluids contain no cations, and thus

any mineral that precipitates *must* use cations released from dissolution of existing minerals. For example, the carbonic acid-driven attack of a calcium feldspar, anorthite, leads to precipitation of calcite and kaolinite.



The increase in mineral volume associated with this reaction going to completion is 20%. If anorthite occupies 10% of the bulk volume of a formation, this reaction would reduce the porosity by 2%. Even with a strong dependence of permeability on porosity the effect on injectivity is likely to be relatively small regardless of the initial mineral state. This assumes that the precipitated minerals are distributed uniformly within the pore space. Current understanding offers little insight into the likelihood of non-uniform precipitation, but it should be noted that preferential precipitation in pore throats would cause a much larger reduction in permeability.

*Relative permeability effects*

We consider only the injection of a CO<sub>2</sub>-rich injectant into a one-dimensional aquifer here. Initially the gas saturation in the aquifer is zero and the injectant displaces water immiscibly. If the initial water is free of CO<sub>2</sub>, a portion of the leading edge of the CO<sub>2</sub> front dissolves into the water resulting in a shock. If the injectant is free of water (dry) eventually, all of the water dissolves in the CO<sub>2</sub>, leaving a completely dry region in the vicinity of the injection well. Schematically the sequence is

$$\left\{ \begin{array}{l} \text{Inlet, } J \\ f_g = S_g = 1 \end{array} \right\} \xrightarrow{\text{slow(trailing)shock}} \left\{ \begin{array}{l} f_g \text{ varies} \\ C \text{ constant} \end{array} \right\} \xrightarrow{\text{fast(leading)shock}} \left\{ \begin{array}{l} \text{Initial, } I \\ f_g = S_g = 0 \end{array} \right\}$$

Here *I* and *J* refer to initial and inlet (injected) fluids. The specific velocity of the fast (leading) shock, the CO<sub>2</sub> dissolution shock, is

$$v_{\text{leading}} = \frac{f_g^- + \frac{C_{\text{CO}_2}^a}{(C_{\text{CO}_2}^g - C_{\text{CO}_2}^a)}}{S_g^- + \frac{C_{\text{CO}_2}^a}{(C_{\text{CO}_2}^g - C_{\text{CO}_2}^a)}} \tag{11}$$

where  $f_g^-$  is the fractional flow of gas just upstream (toward *J*) of the leading shock;  $S_g^-$ , the gas saturation just upstream of the leading shock;  $C_{\text{CO}_2}^a$  and  $C_{\text{CO}_2}^g$ , concentrations of CO<sub>2</sub> in the aqueous and gas phases in the region between the leading and trailing shocks.

The latter concentrations are set by the partial pressure in the injectant. The specific velocity of the trailing or drying shock is

$$v_{\text{trailing}} = \frac{f_g^+ - \frac{C_J^g - C_{\text{CO}_2}^a}{C_{\text{CO}_2}^g - C_{\text{CO}_2}^a}}{S_g^+ - \frac{C_J^g - C_{\text{CO}_2}^a}{C_{\text{CO}_2}^g - C_{\text{CO}_2}^a}} \tag{12}$$

where  $f_g^+$  is the fractional flow of gas just downstream (toward *I*) of the trailing shock;  $S_g^+$ , the gas saturation just downstream of the trailing shock and  $C_J^g$ , the inlet or injected CO<sub>2</sub> concentration.

Between these two limits the specific velocity of a gas saturation is the well-known Buckley–Leverett velocity

$$v_{S_g} = \frac{df_g}{dS_g} \tag{13}$$

Eq. (13) assumes that the phase concentrations do not change in the region between the leading and trailing shocks. Setting Eq. (11) equal to Eq. (13) defines the downstream shock saturation, the relationship  $f_g = f_g(S_g)$  being known and independent of phase concentrations. Setting Eq. (12) equal to Eq. (13) defines

the upstream shock saturation. These equations admit to a graphical solution [5]. Eqs. (11) and (12) are of the form

$$v = \frac{f_g + D}{S_g + D}. \tag{14}$$

The retardation factors for both the leading and trailing waves are small; for the leading shock it is about 0.05 and substantially less for the trailing shock.

For a reacting component in the aqueous phase the specific velocity is

$$v_{\Delta C_i} = \frac{f_w}{S_w + D_i} = \frac{f_g - 1}{S_g - (1 + D_i)} \tag{15}$$

where  $f_w$  is the fractional flow of aqueous phase and  $S_w$  is the saturation of aqueous phase.

Eq. (15) is the generalization of Eq. (10) to two-phase flow.

Now for mineralization in two-phase flow to occur we must have

$$v_{\Delta C_i} > v_{\text{trailing}}.$$

This inequality means that mineralization can only occur when water is present. If the inequality is satisfied, the mineralization occurs where there is remaining water. Substituting from Eqs. (10) and (12) gives

$$\frac{f_g - 1}{S_g - (1 + D_i)} > \frac{f_g - \frac{C_J^g - C_{CO_2}^a}{C_{CO_2}^g - C_{CO_2}^a}}{S_g - \frac{C_J^g - C_{CO_2}^a}{C_{CO_2}^g - C_{CO_2}^a}}. \tag{16}$$

The ratios of concentration differences on the right side of Eq. (16) are close to one; hence, the only way for this inequality to hold is if  $D_i < 0$ , which is a physical impossibility. Mineralization cannot occur during the injectant cycle because the  $CO_2$  dries out the medium before this can happen [34]. Stated differently, the trailing (drying) shock is the mineralization wave. This wave is very slow and, in any event, precipitates only the minerals that are dissolved in the water when dried. This amount is too small to cause damage because, once again, there is insufficient supply of minerals.

Injectivity may actually increase because of the drying in the near-wellbore region. If the residual water saturation is large, the end-point relative permeability to the injectant can be small. When the residual water is removed, this injectant relative permeability increases, possibly by a large amount.

After injection, the  $CO_2$  slug may be driven with additional water injection, or natural water flow may displace the  $CO_2$ .

$$\left\{ \begin{array}{l} \text{Inlet, } K \\ f_g = S_g = 0 \end{array} \right\} \xrightarrow{\text{slow(trailing)shock}} \left\{ \begin{array}{l} f_g \text{ varies} \\ C \text{ constant} \end{array} \right\} \xrightarrow{\text{fast(leading)shock}} \left\{ \begin{array}{l} \text{Initial, } J \\ f_g = S_g = 1 \end{array} \right\}.$$

Here  $J$  and  $K$  refer to initial and inlet (injected) fluids after  $CO_2$  injection has ended. Water displacing a  $CO_2$ -rich injectant is described by the same equations as above, Eqs. (10)–(12), except that the fractional flow function, being hysteretic, now follows a different path. The principal effect of hysteresis is that there is now a residual gas phase that is removed by dissolution in water. The specific velocity of this wave is given

by Eq. (11) now written as

$$v_{\text{trailing}} = \frac{0 + \frac{C_{\text{CO}_2}^a}{(C_{\text{CO}_2}^g - C_{\text{CO}_2}^a)}}{S_{\text{gr}} + \frac{C_{\text{CO}_2}^a}{(C_{\text{CO}_2}^g - C_{\text{CO}_2}^a)}}. \quad (17)$$

The formerly leading wave now becomes the trailing wave. Mineralization would now occur when

$$v_{\text{trailing}} < v_{\Delta C_i}. \quad (18)$$

Combining Eqs. (10) and (17) shows that it is possible for mineralization to occur according to inequality equation (18) if the water displacing the  $\text{CO}_2$  is saturated with  $\text{CO}_2$ . It therefore appears that mineralization (and well damage if water is being injected) most likely occurs during the water-displacing injection where water is in single-phase flow in the presence of a trapped gas saturation. If the displacing water is free of  $\text{CO}_2$  the trailing wave will be fast and mineralization suppressed. There is anecdotal evidence of diminished water injectivity following a  $\text{CO}_2$  oil recovery flood, though this effect is more likely caused by the trapped gas saturation than mineralization.

The gradual dissolution from the trapped gas saturation provides a  $\text{CO}_2$  source for the water that causes the mineralization. That an excess of  $\text{CO}_2$  was needed for mineralization was why we modeled the mineralization as a single-phase injection of water in the presence of an excess of injectant. As noted before, the effect of the impurities is to suppress secondary precipitates and advance primary mineral dissolution. So the effect of water displacing an impure  $\text{CO}_2$  stream seems unlikely to result in injectivity reduction.

## CONCLUSIONS

The several decades of literature on field and laboratory  $\text{CO}_2$  flooding provide a reasonably sound foundation for estimating the effects of impurities in the  $\text{CO}_2$  phase on EOR behavior. The MMP is a widely used measure of enhanced recovery performance for  $\text{CO}_2$  flooding. The most common and most convenient technique for determining MMP is statistical correlations. We have identified correlations of MMP with solvent composition that allow reasonable estimates of the tradeoff between oil recovery vs. the cost of impurity removal. These indicate that the likely range of impurity concentrations ( $\text{SO}_x$ ,  $\text{NO}_x$  mole fractions of order 1%) will change the MMP only a few percentage points from its pure- $\text{CO}_2$  value.

Several other mechanisms influence the performance of an EOR process. These are applicable to immiscible as well as miscible displacements. The most important effects are captured in two terms, the mobility ratio and the gravity number. Impurities are likely to reduce the viscosity of the solvent, thereby increasing the mobility ratio (ratio of solvent mobility to oil mobility; mobility is phase relative permeability divided by phase viscosity). Impurities are likely to reduce the density of the solvent, thereby decreasing the gravity number (ratio of buoyancy forces to viscous forces). Both these effects will tend to reduce the effectiveness of the process. Factors particular to immiscible displacement include changes in oil properties (swelling, viscosity alteration, etc.). The incremental changes in oil properties due to the presence of these impurities in the displacing gas are anticipated to be small. For the small concentrations of impurities likely to be encountered, all these effects are quite small and should not significantly influence the process.

The injectivity of the disposal well is of primary importance in the logistics and economics of subsurface  $\text{CO}_2$  storage. Geochemical alteration of the formation mineralogy is the main potential influence on well injectivity. In the absence of impurities,  $\text{CO}_2$  injection is unlikely to have a significant deleterious effect on injectivity. The presence of  $\text{SO}_x$  and  $\text{NO}_x$  in the injected stream will significantly increase the acidity of the aqueous phase in the formation. This speeds up dissolution of native minerals, but does not significantly change the ultimate extent of the changes in mineralogy. Thus, these impurities are likely to have little incremental effect on injectivity.



In summary, this study anticipates no substantial disadvantages to injecting an impure CO<sub>2</sub> stream, relative to a purified CO<sub>2</sub> stream. The presence of impurities may even offer slight advantages. Thus, the additional costs required to remove SO<sub>x</sub> or NO<sub>x</sub> impurities, motivated by concerns about storage reservoir performance, are unlikely to be justified.

## RECOMMENDATIONS

1. From the subsurface perspective, impurities can be safely disregarded when developing a storage scheme. But the possible deleterious effects of impurities on surface handling facilities and on the wellbore itself should also be taken into account (cf. Gupta [33] in this volume).
2. Certain waste gases such as hydrogen sulfide may even improve enhanced recovery processes, and the feasibility of co-storage of multiple gas streams should be studied.

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## REFERENCES

1. P.D. Patel, R.G. Christman, J.W. Gardner, Investigation of unexpectedly low field-observed fluid mobilities during some CO<sub>2</sub> tertiary floods, *SPE Reservoir Eng.* (1987) 507–513. November.
2. L.W. Holm, V.A. Josendal, Effect of oil composition on miscible-type displacement by carbon dioxide, *Society of Petroleum Engineers Journal* **22** (1982) 87–98.
3. H.M. Sebastian, R.S. Winger, T.A. Renner, Correlation of minimum miscibility pressure for impure CO<sub>2</sub> streams, SPE/DOE 12648, *Presented at the Fourth Joint Society of Petroleum Engineers/Department of Energy Symposium on Enhanced Oil Recovery*, Tulsa, Oklahoma, 1984.
4. L.W. Lake, S.L. Bryant, A.N. Araque-Martinez, *Geochemistry and Fluid Flow*, Elsevier, New York, 2002.
5. L.W. Lake, *Enhanced Oil Recovery*, Prentice-Hall, Englewood Cliffs, NJ, 1989.
6. J.C. Ader, M.H. Stein, Slaughter estate unit CO<sub>2</sub> pilot reservoir description via a black oil model waterflood history match, SPE/DOE 10727, *Presented at the 1982 SPE/DOE Third Joint Symposium on Enhanced Oil Recovery of the Society of Petroleum Engineers*, April 4–7, Tulsa, OK.
7. M.K. Roper, Simulation of tertiary carbon dioxide injectivity, PhD Dissertation at UT, December 1994.
8. M. Delshad, G.A. Pope, K. Sepehrnoori, A compositional simulator for modeling surfactant enhanced aquifer remediation, 1. Formulation, *J. Contam. Hydrol.* **23** (1996) 303–327.
9. K.D. Pennell, G.A. Pope, L.A. Abriola, Influence of viscous and buoyancy forces on the mobilization of residual tetrachloroethylene during surfactant flushing, *Environ. Sci. Technol.* **30** (4) (1996) 1328–1335.
10. G.A. Pope, W. Wu, G. Narayanaswamy, M. Delshad, M.M. Sharma, P. Wang, Modeling relative permeability effects in gas-condensate reservoirs with a new trapping model, *SPE Reservoir Eval. Eng.* **3** (2) (2000).
11. G.W. Paul, L.W. Lake, G.A. Pope, G.B. Young, A simplified predictive model for micellar/polymer flooding, SPE 10733, *Presented at the California Regional Meeting of the Society of Petroleum Engineering*, San Francisco, California, 1982..
12. H. Yuan, Application of miscibility calculations to gas floods, PhD Dissertation, The University of Texas at Austin, August 2003.
13. A.L. Benham, W.E. Dowden, W.J. Kunzman, Miscible fluid displacement—prediction of miscibility, *Trans. Soc. Petrol. Eng. AIME* **219** (1961) 229–237.
14. A.M. Elsharkawy, C.U. Suez, F.H. Poettmann, R.L. Christiansen, Measuring minimum miscibility pressure: slim-tube or rising-bubble method? SPE 24114, *Proceedings of the Society of Petroleum Engineers/Department of Energy Eighth Symposium on Enhanced Oil Recovery*, Tulsa, OK, April 22–24, 1992.
15. D. Rao, A new technique of vanishing interfacial tension for miscibility determination, *Fluid Phase Equilib.* **139** (1997) 311–324.

16. D. Rao, J.I. Lee, Determination of gas–oil miscibility conditions for interfacial tension measurements, *J. Colloid Interface Sci.* **262** (2003) 474–482.
17. Y. Wang, F.M. Orr Jr., Analytical calculation of minimum miscibility pressure, *Fluid Phase Equilib.* **139** (1997) 101–124.
18. Y. Wang, F.M. Orr Jr., Calculation of minimum miscibility pressure, *J. Petrol. Sci. Eng.* **27** (2000) 151–164.
19. B. Dindoruk, F.M. Orr, R.T. Johns, Theory of multicontact miscible displacement with nitrogen, *SPE J.* **2** (1997) 268–279. .
20. Y.F. Huang, G.H. Huang, M.Z. Dong, G.M. Feng, Development of an artificial neural network model for predicting minimum miscibility pressure in CO<sub>2</sub> flooding, *J. Petrol. Sci. Eng.* **37** (2003) 83–95.
21. J.P. Johnson, J.S. Pollin, Measurement and correlation of CO<sub>2</sub> miscibility pressures, SPE/DOE 9790, *Presented at the 1981 Joint SPE/DOE Symposium on Enhanced Oil Recovery*, Tulsa, Oklahoma, 1981.
22. W.R. Whitehead, O.K. Kimbler, R.M. Hoshman, J.R. Hervey, Investigations of Enhance Oil Recovery Through Use of Carbon Dioxide, U.S. Department of Energy Progress Report, DOE/MC/03103-2, U.S. Department of Energy, 1980.
23. R.S. Metcalfe, Effects of impurities on minimum miscibility pressure and minimum enrichment levels for CO<sub>2</sub> and rich-gas displacements, *Soc. Petrol. Eng. J.* **22** (1981) 219–225.
24. W.F. Yellig, R.S. Metcalfe, Determination and predication of CO<sub>2</sub> minimum miscibility pressures, *J. Petrol. Technol.* (1980) 160–168. January.
25. L.W. Holm, A.K. Csaszar, Oil recovery by solvents mutually soluble in oil and water, Society of Petroleum Engineers Reprint Series No. 8, *Miscible Processes*, 1965, pp. 31–38..
26. L.W. Holm, V.A. Josendal, Mechanisms of oil displacement by carbon dioxide, *J. Petrol. Technol.* **26** (1974) 1427–1438.
27. L.W. Holm, A comparison of propane and CO<sub>2</sub> solvent flooding processes, *Am. Inst. Chem. Eng. J.* (1961) 179–184. June.
28. M. Shook, D. Li, L.W. Lake, Scaling immiscible flow through permeable media by inspectional analysis, *In Situ* **16** (4) (1992) 311–349.
29. M.P. Walsh, L.W. Lake, *A Generalized Approach to Primary Hydrocarbon Recovery*, Elsevier, New York, 2003.
30. M.K. Roper Jr., G.A. Pope, K. Sepehrnoori, Analysis of tertiary injectivity of carbon dioxide, SPE 23974, *Presented at the Society of Petroleum Engineers Permian Basin Oil and Gas Recovery Conference*, Midland, TX, March 18–20, 1992a.
31. M.K. Roper Jr., C.T. Cheng, J.E. Varnon, G.A. Pope, K. Sepehrnoori, Interpretation of a CO<sub>2</sub> WAG injectivity test in the San Andres Formation using a compositional simulator, SPE/DOE 24163, *Presented at the Society of Petroleum Engineers/Department of Energy Eighth Symposium on Enhanced Oil Recovery*, Tulsa, OK, April 22–24, 1992b.
32. A. Araque-Martinez, L.W. Lake, A simplified approach to geochemical modeling and its effect on mineral precipitation, *Soc. Petrol. Eng. J.* (2001) 98–107. March.
33. B. Sass, B. Monzyk, S. Ricci, A. Gupta, B. Hindin, N. Gupta, CO<sub>2</sub> purity tradeoff-surface facilities, this volume.
34. M.-Y. Noh, L. Lake, S. Bryant, A. Araque-Martinez, Implications of coupling fractional flow and geochemistry for CO<sub>2</sub> injection in aquifers, SPE89341, *Presented at SPE/DOE 14th Symp. Improved Oil Recovery*, Tulsa, April 17–21, 2004.