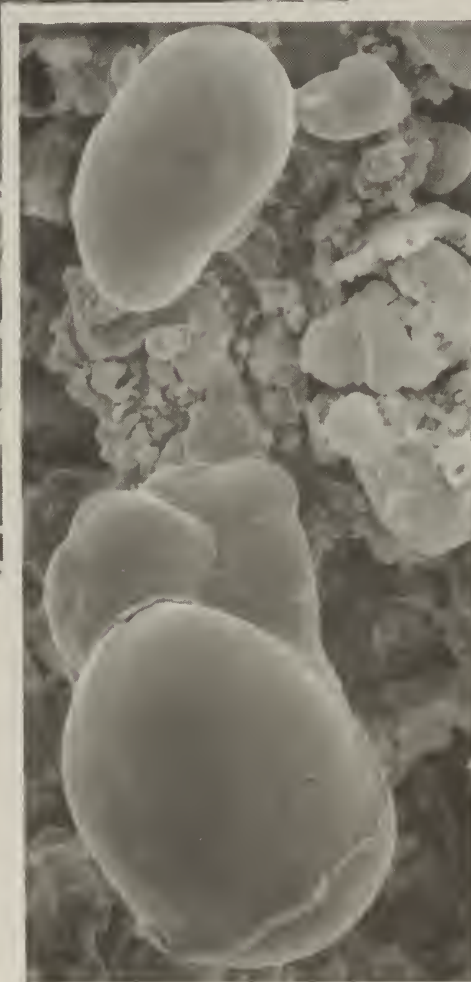
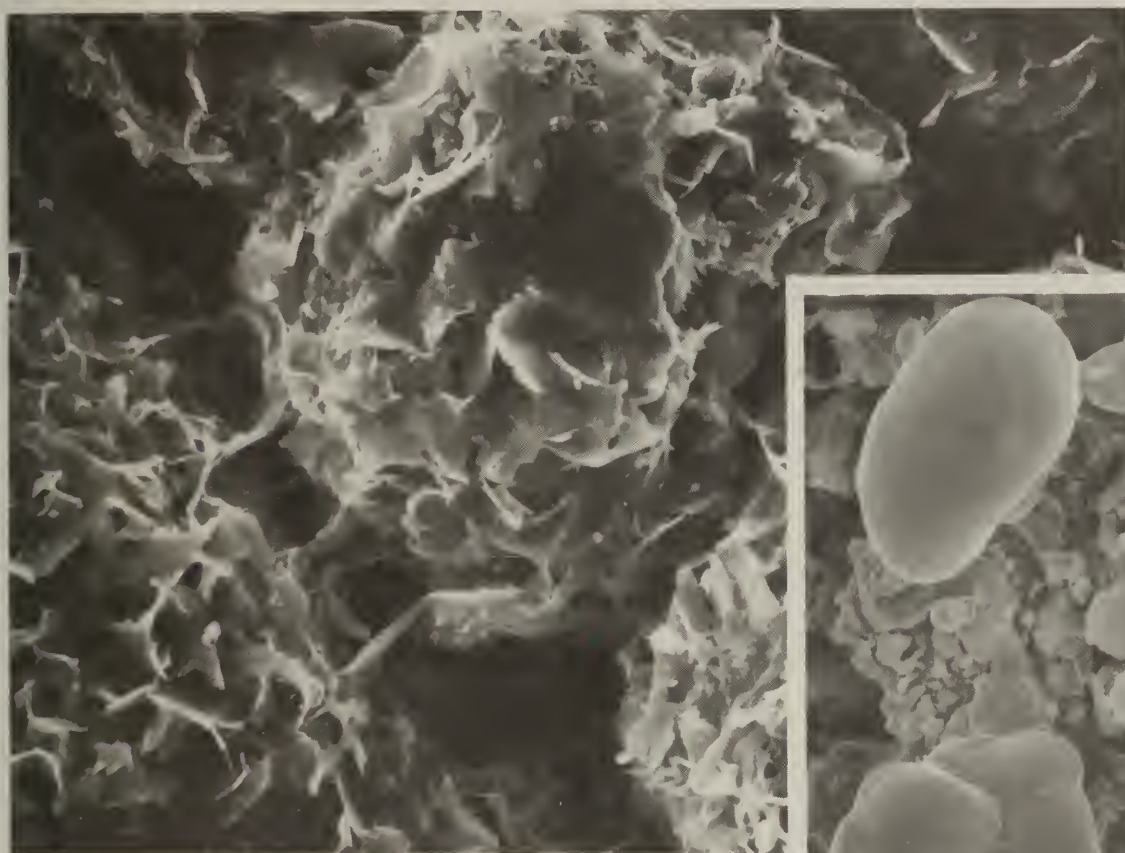


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Investigation of Formation Damage from Mud Cleanout Acids and Injection Waters in Aux Vases Sandstone Reservoirs

Dennis J. Haggerty and Beverly Seyler



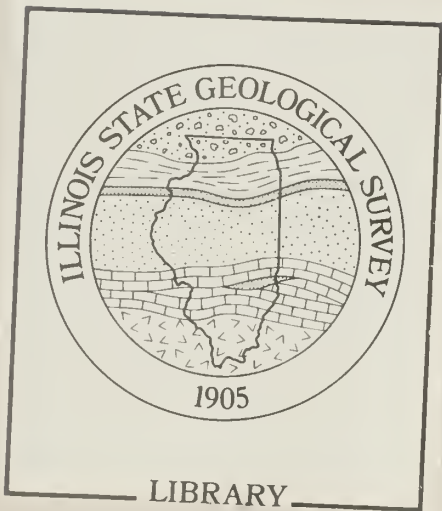
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Illinois Petroleum 152
1997

Illinois State Geological Survey
William W. Shilts, Chief
615 East Peabody Drive
Champaign, IL 61820-6964
(217) 333-4747

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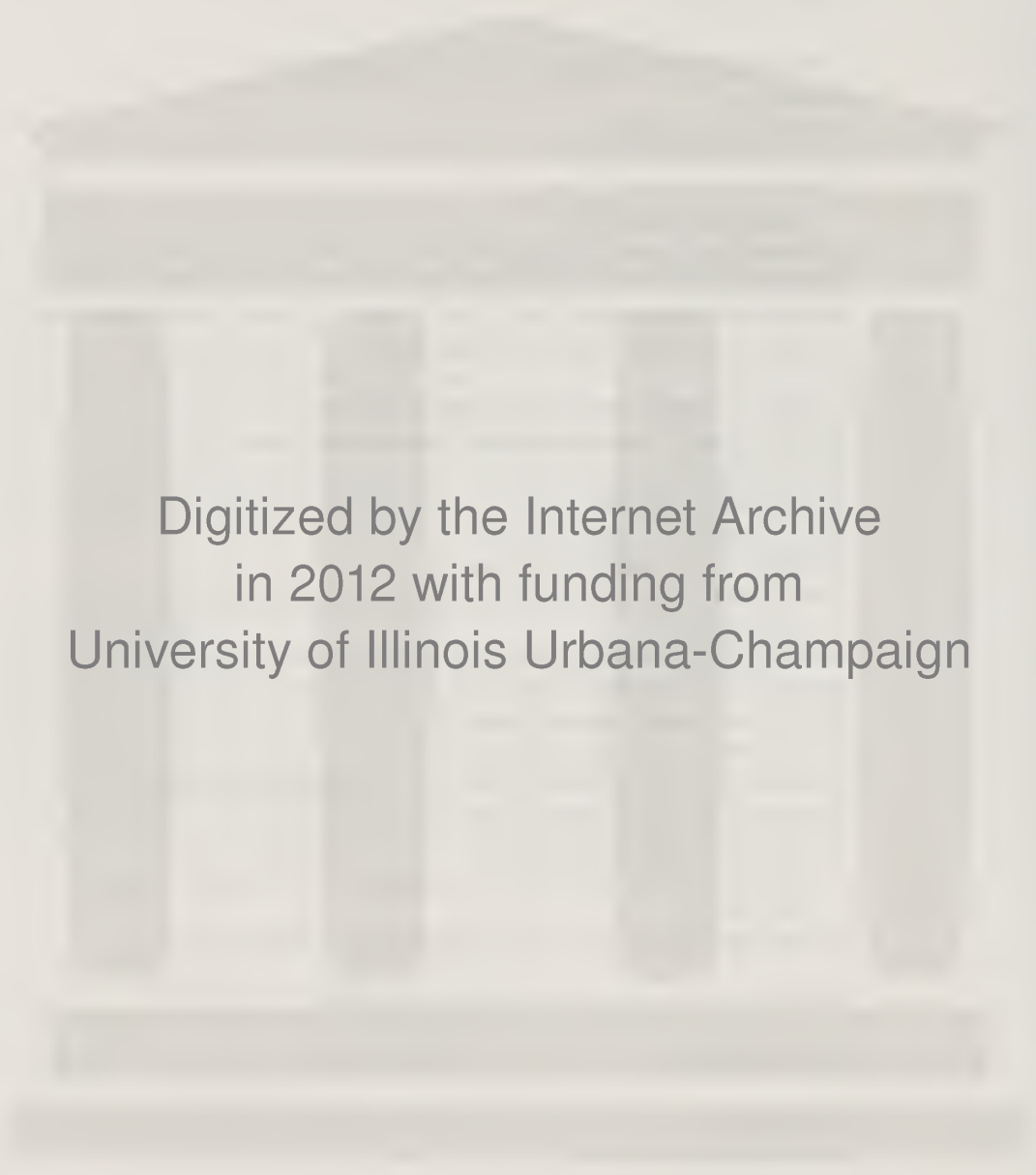
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ABSTRACT

Diagenetic clay minerals line almost every pore of the Aux Vases Sandstone reservoirs in the Illinois Basin. Pore-filling calcite occurs locally. Fluids introduced during drilling, completion, and waterflooding may preferentially react with the clay or other minerals such as calcite cement in the pores, thus damaging the formation and reducing oil recovery.

Coreflood experiments were conducted on 1-inch-diameter core plugs from Boyd, Dale Consolidated, Energy, and Zeigler Fields.

- Prolonged contact (4 hours or more) with 15% hydrochloric acid (HCl) with no additives not only dissolved the calcite, but produced leaching and disintegration of the clay minerals, a closely intergrown mixture of mixed-layered illite/smectite, chlorite, and illite.
- The pure 15% HCl solution also formed sludges when mixed with Aux Vases crude oil. Thus, using 15% HCl without surfactants, clay stabilizers, or de-emulsifiers will contribute to formation damage in Aux Vases Sandstone reservoirs.
- Injection of water less saline than the formation brine decreased permeability up to 56%, apparently through swelling of mixed-layered illite/smectite and migration of fines. These reductions in permeability could not be reversed by subsequent injection of water with higher salinities.

To avoid impairing permeability in Aux Vases reservoirs, oil field operators should inject wells with waters as saline as the formation brines. Using a properly formulated MCA may also significantly reduce formation damage and enhance oil recovery.

INTRODUCTION

Diagenetic clay minerals and other minerals present in the pores of Valmeyeran (Mississippian) Aux Vases Sandstone reservoirs (fig. 1) are likely to be responsible for many oil-production problems encountered in this formation. The cementation of sand grains in the Aux Vases differs from the cementation of sand grains in the Chesterian and other sandstone reservoirs in the Illinois Basin. As a result, the same drilling, completion, and stimulation practices cannot be used successfully for all formations.

Typical Chesterian reservoirs (fig. 2), for example, are composed of highly lithified sandstones tightly cemented by quartz. Pore linings are dominated by quartz overgrowths and minor amounts of discrete crystallites of diagenetic kaolinite, iron-chlorite, mixed-layered illite/smectite, and illite (fig. 3a).

Typical Aux Vases reservoir rock, however, is a poorly cemented, soft, friable, fine-grained sandstone with pores lined with diagenetic clay minerals (fig. 3b) (Seyler et al. in prep.). The diagenetic clay mineral suite in Aux Vases reservoirs is a closely intergrown mixture of mixed-layered illite/smectite, chlorite, and illite. No kaolinite was found in the Aux Vases reservoir rocks sampled for this study.

Introduced fluids come into contact and primarily react with pore-lining diagenetic clay minerals rather than with the framework grains; therefore, the reservoirs containing diagenetic clay minerals are more likely to react adversely to drilling, completion, and recovery treatments than are the reservoirs with pore systems dominated by quartz, a more stable mineral. For these reasons, Aux Vases Sandstone reservoirs in the Illinois Basin are highly susceptible to formation damage that may decrease the total amount of oil recovered.

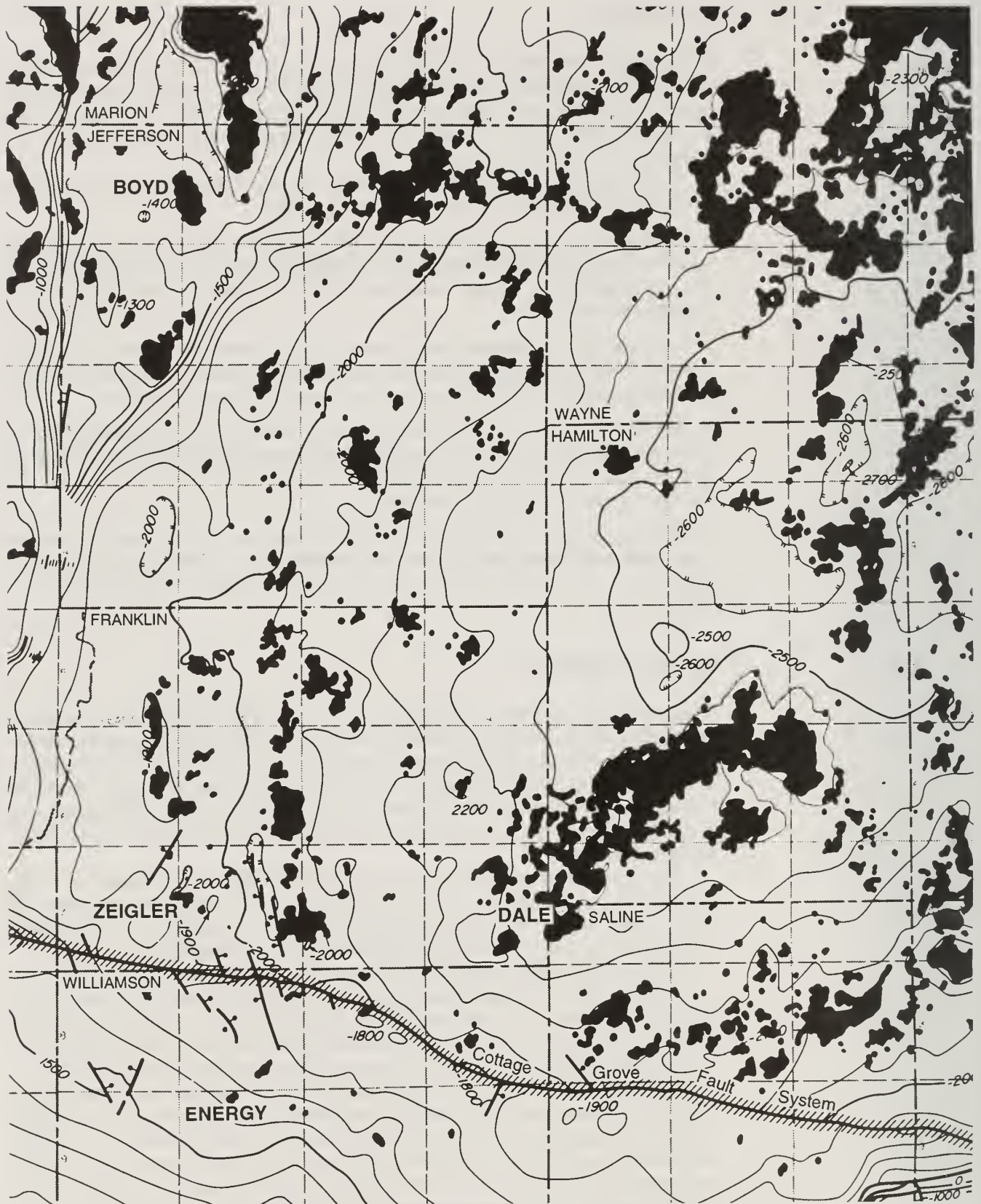


Figure 1 Aux Vases Sandstone oil fields sampled for this study are Boyd, Dale Consolidated, Energy, and Zeigler. Shaded areas show oil fields.

Formation damage, a common problem (Monaghan et al. 1958, Abrams 1977, Krueger 1986, Simon and Anderson 1990, and Civan 1992), can occur at any stage of reservoir development. It results from the reaction of reservoir rocks with fluids introduced into the formation during well drilling, completion, and stimulation.

Development of sandstone reservoirs in the Illinois Basin typically includes these steps:

1. drilling with freshwater mud;
2. perforating the potential reservoir zone, if casing is used, or open hole completions with casing cemented above the producing zone;
3. preflushing with 15% hydrochloric acid (HCl) or mud cleanout acid (MCA) to remove drilling mud;
4. cleaning out perforations or the well bore with MCA;
5. initial swabbing to retrieve stimulation fluids and induce oil flow toward the wellbore;
6. hydraulic fracturing using a freshwater gelled pad and sand proppant;
7. final swabbing during the production test.

Some of these practices enhance the potential for formation damage due to the ubiquitous presence of pore-lining diagenetic minerals in Aux Vases sandstones. A series of bench-scale experiments representing some common practices was conducted to determine the effects on Aux Vases sandstone reservoirs in Boyd, Dale Consolidated, Energy, and Zeigler Fields (fig. 1). Of greatest interest was formation damage that may be caused by contact with fresh water, 15% HCl, and MCA.

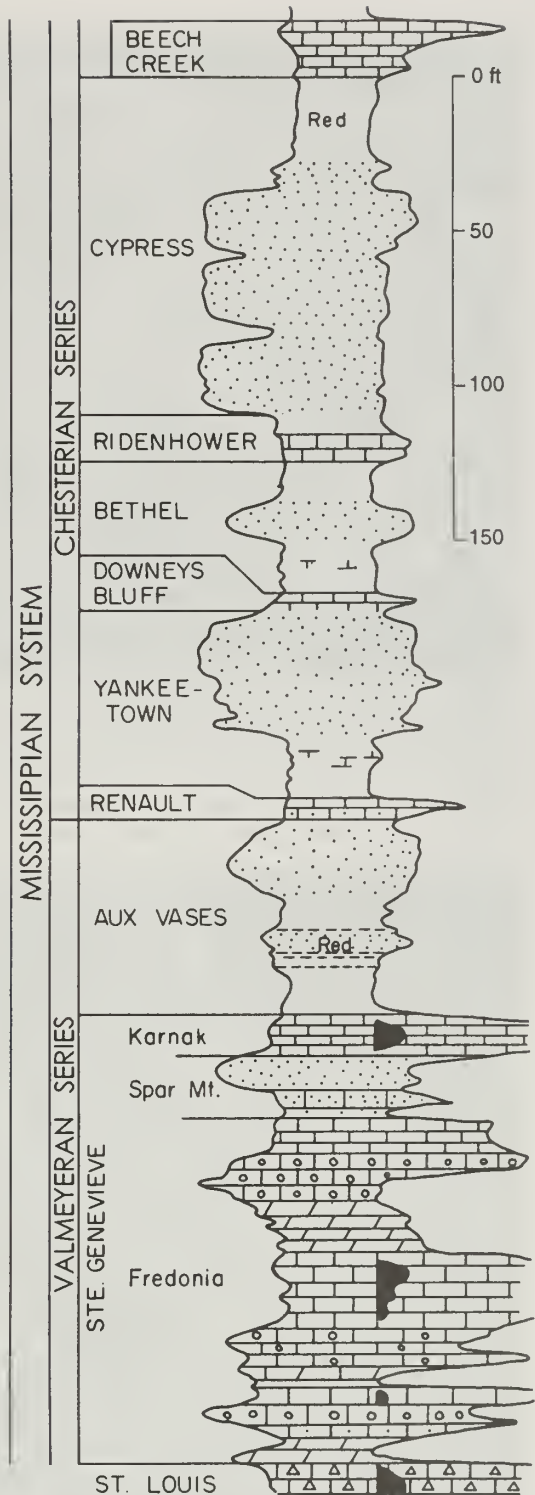


Figure 2 Aux Vases Sandstone forms the transition from predominantly carbonate rocks of the Middle Mississippian Valmeyeran series to predominantly siliciclastic rocks of the Upper Mississippian Chesterian series.

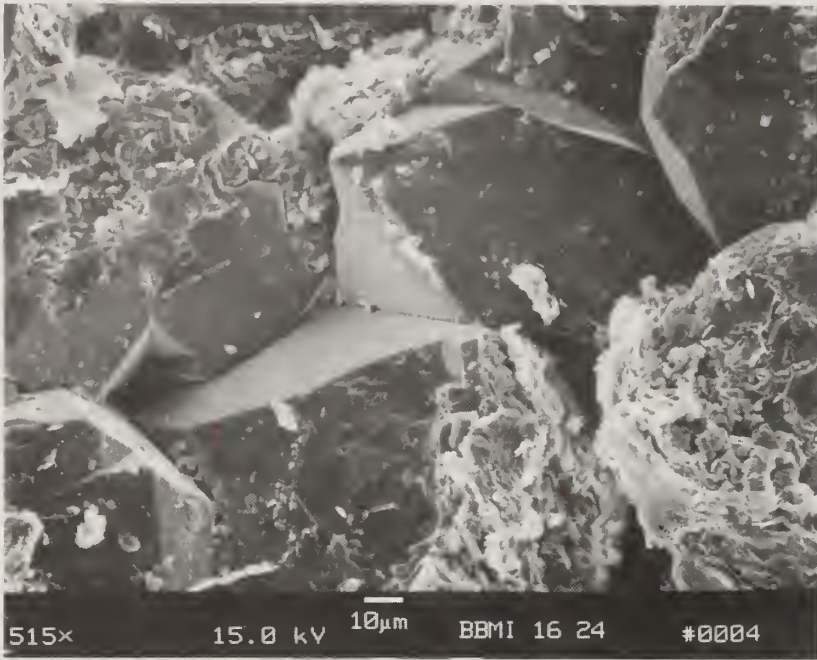


Figure 3a Scanning electron microphotograph (SEM) of sample from a typical Chesterian Cypress Sandstone reservoir (1,324-ft depth, Marathon Oil MI-16 Isaac Boyd, Lawrence Field) shows quartz overgrowths as the predominant cementing agent and pore-lining mineral. Diagenetic clay minerals are iron-rich chlorite, kaolinite, and fibrous illite.

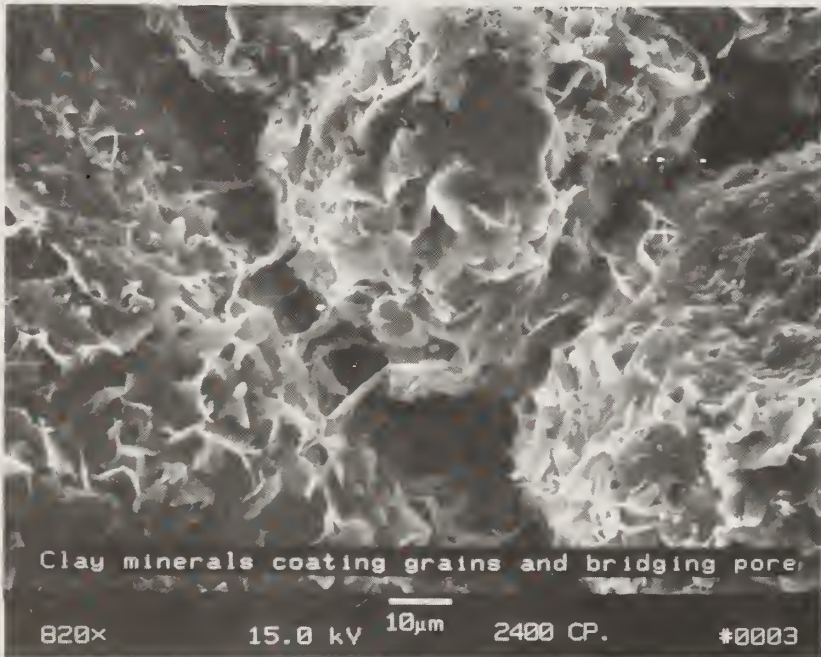


Figure 3b SEM of a critical-point-dried sample from a typical Aux Vases reservoir (2,400-ft depth, Budmark 3 Burr Oak, Energy Field) shows pore-lining and -bridging diagenetic clay minerals (closely intergrown mixed-layered illite/smectite, chlorite, and illite) and no quartz overgrowths.

A common deviation from these practices is incomplete swabbing in the final stages of well completion. When circumstances are ideal, almost all stimulation fluids are retrieved from the reservoir during final swabbing. When this is not possible, however, stimulation fluids may be left in the reservoir overnight—or indefinitely. Therefore, acid-soaking experiments were conducted to represent some conditions that may result from incomplete swabbing.

The experiments focused on five objectives:

1. determine how MCA containing 15% HCl with additives, typically used during completion and/or stimulation, affects pore-lining minerals and the permeability of Aux Vases reservoir rocks by conducting dynamic, constant rate injection coreflood experiments;
2. investigate how 15% HCl and MCA affects crude oil from Aux Vases reservoirs by conducting compatibility experiments;
3. examine how exposure to fluids of various salinities affects permeability in samples of Aux Vases reservoirs by conducting coreflood experiments;
4. investigate the effects of long-term contact of 15% HCl and MCA with pore-lining minerals in reservoir samples by conducting static soak experiments;
5. compare XRD analyses of the bulk mineralogy and SEM/EDX analyses of pore-lining minerals with flood results to identify minerals that would be most affected by fluids commonly used during drilling, completion, and stimulation of Aux Vases reservoirs.

EXPERIMENTAL OVERVIEW

Five sets of bench experiments were conducted to attain the study's objectives (table 1). The first set compared the compatibility of crude oil with 15% hydrochloric acid (HCl) versus its compatibility with mud cleanout acid (MCA). These direct contact experiments demonstrated the changes in physical properties of crude oil when mixed with the acids.

Three coreflood experiments were performed to determine the effects on permeability and pore-lining minerals of continuously injecting MCA and 15% HCl at a constant rate. MCA was injected into two core plugs, one from the 2,392.1-foot depth in the Budmark no. 2 Morgan Coal well at Energy Field, and the other from the 2,627-foot depth in the Gallagher Drilling Company no. 2 Mack well at Zeigler Field. HCl was injected into one sample from the 2,303.5-foot depth in the Budmark no. 2 Morgan Coal well at Energy Field. Fluid was injected continuously to observe changes in permeability.

In two coreflood experiments, the injection of MCA was interrupted several times. One sample was from the 3,198.7-foot depth in the Farrar no. 1 McCreery well at Dale Consolidated Field; the second sample was from the 2,391.1-foot depth in the Budmark no. 2 Morgan Coal well at Energy Field. These interrupted coreflood experiments were conducted to determine the effects of stopping injection and soaking the samples in injection fluids for a few hours to a few days. One or more shut-in periods are common during conventional well treatments with MCA. Interrupted coreflood experiments represented shut-in periods during well stimulation.

The sensitivity of reservoir samples to water of different salinities was tested in interrupted injection experiments on one core plug from each of three fields, Boyd, Dale Consolidated, and Zeigler, and three core plugs from Energy Field.

Static soak experiments were conducted to compare changes in pore-lining minerals in samples soaked in 15% HCl versus those soaked in MCA. For samples,

wafers were sliced from two core plugs from the Budmark no. 2 Morgan Coal well; wafers from a depth of 2,392.8 feet were soaked in 15% HCl, and wafers from a depth of 2,393 feet were soaked in MCA. The soak experiments represent conditions of incomplete swabbing where acids used for drilling and stimulation cannot be retrieved, or retrieval is delayed for a long time.

Coreflood experiments conducted in this study most closely represent the totally flushed zone of a reservoir. Twenty-five to 50 pore volumes of fluid were continuously injected during coreflood experiments. A decrease in porosity or permeability is unlikely to occur in such thoroughly flushed samples because potential precipitates have no time to accumulate; they are removed during mechanical flushing of the core plug. As a result, coreflood experiments do not provide information on conditions in incompletely flushed areas of the reservoir where the effects of fines migrating and minerals precipitating from treatment fluids may be pronounced.

Table 1 Experimental overview

Type of experiment	Fluids	Field, well	Depth <i>ft</i>	To determine
Direct contact: crude oil and acids	Crude oils	Boyd, Baldrige B5 Bizot	2,170	Compatibility of 15% HCl vs MCA
		Dale, Farrar 2 McCullum Community	3,158–3,176	
		Energy, Budmark 2 Morgan Coal	2,385–2,395	
		Zeigler, Gallagher Drilling 1 Alex	2,615–2,630	
Coreflood: continuous injection at a constant rate	MCA	Energy, Budmark 2 Morgan Coal	2,392.1	Effects on permeability and pore-lining minerals
	MCA	Zeigler, Gallagher Drilling 2 Mack	2,627	
	15% HCl	Energy, Budmark 2 Morgan Coal	2,393.5	
Coreflood: interrupted injection, constant rate	MCA	Dale Cons, Farrar 1 McCreery	3,198.7	Effects of interrupting injection and soaking sample in MCA; simulates potential damage after injection and before swabbing
	MCA	Energy, Budmark 2 Morgan Coal	2,391.1	
Core waterflood: interrupted injection, constant rate	Waters, various salinities	Boyd, Superior Oil 9 Sanders	2,163	Sensitivity of rock to injected water of varying salinities; note permeability changes
		Energy, Budmark 2 Morgan Coal	2,390	
		Energy, Budmark 2 Morgan Coal	2,388	
		Zeigler, Gallagher Drilling 2 Mack	2,611	
		Dale Cons., Farrar 1 McCreery	3,200.6	
		Energy, Budmark 2 Morgan Coal	2,388.3	
Acid soak	15% HCl	Energy, Budmark 2 Morgan Coal	2,392.8	Long-term reaction of reservoir rock to MCA and 15% HCl
	MCA	Energy, Budmark 2 Morgan Coal	2,393	

The soak experiments were thus performed to observe reactions in long-term experiments representing reactions in unflushed and incompletely flushed zones.

Mud Cleanout Acids

During drilling, the amount of mud or mud filtrate that invades the formation around the wellbore generally depends on the permeability of the formation. Mud particles in the drilling fluid are designed to form a mudcake or "skin" around the wellbore, thus reducing infiltration into the reservoir. Although the mudcake reduces permeability, some mud particles still move into a porous reservoir.

Filtrates from drilling muds can damage the reservoir by restricting oil flow because of an increase in water saturation due to the relative permeability or viscosity of oil. Emulsions may also form in the region of the wellbore. Clay minerals sensitive to fresh water (Grim 1947) may swell in reaction to mud filtrates low in salinity and further reduce formation permeability.

Mud cleanout acids of 15% HCl mixed with corrosion inhibitors, surfactants, clay stabilizers, and deemulsifiers are routinely used by operators in the Illinois Basin to remove mud and establish commercial oil productivity after drilling. Treatment with 15% iron-sequestering acid also has been reported (Jeff Finnell, Equinox Oil, Crossville, Illinois, pers. comm. 1991). Mud cleanout acids of 3% HF (hydrofluoric acid) combined with 12% HCl are not routinely used in Illinois' Aux Vases reservoirs, probably because HF reacts adversely with the calcite or dolomite cement generally present in reservoir sandstone.

The HCl in mud cleaning acid (MCA) mixtures can react adversely with clay minerals (Ross 1969). Simon and Anderson (1990) demonstrated that HCl can destroy clay minerals, of which chlorite is the most susceptible. Their x-ray diffraction (XRD) studies revealed that HCl attacked chlorite by leaching iron (Fe^{++}) ions from the chlorite, thus causing a breakdown in the crystalline structure. The available evidence indicates that the amorphous residue from this acid-chlorite reaction consists of iron hydroxide gels, which contribute to clogging of pore throats, and significantly impair formation permeability. According to Simon and Anderson (1990), formation damage was less extensive at lower acid concentrations and temperatures, and for shorter durations of exposure to the acid. No work has been published previously on the effects of MCA on reservoirs containing the specific suite of intergrown clay minerals found in the Aux Vases sandstone reservoirs.

Acid treatments may induce the mechanical breakup of sands and clay minerals, particularly where carbonate cements are present, and result in migration of fines that impair permeability or plug perforations. Thus, although dissolution of carbonate cement may improve permeability (Allen and Roberts 1989), it may also dislodge sand grains or other fines held in place by the carbonate.

The effect of poorly formulated MCA on the oleic (oil) phase has been discussed by Allen and Roberts (1989). HCl may become separated from additives in poorly formulated MCA. When HCl reacts with oil, it can form emulsions and cause precipitation of asphaltenes and sludge. When a sludge forms, the reservoir's relative permeability to water increases, thus water production increases. This response may explain the immediate decline in oil production and the increase in water production from some Aux Vases wells after MCA treatments.

Injection Waters

The sensitivity of smectite to fresh water is well known (Vaidya et al. 1957, Mungan 1965, Gray and Rex 1966, Khilar and Fogler 1981). The sensitivity of mixed-layered illite/smectite (I/S) is less well understood because each clay mineral structure within the I/S group/category may respond differently to treatment.

Major waterflooding operations in the Illinois Basin have traditionally drawn injection waters from surface pools or shallow fresh-water aquifers (Huff, ISGS,

pers. comm. 1995). Although some operators have investigated the compatibility of injection water and formation brine, they have rarely considered the impact of injection water on the mineral constituents of the reservoir. The choice of drilling, completion, and injection fluids for the Aux Vases and other formations in the Illinois Basin can be assisted by an understanding of the reservoir's mineral content and chemistry. This study will examine the sensitivity of clay minerals to the saline content of injection waters.

EXPERIMENTAL MATERIALS AND METHODS

Materials

The core samples used in this study were obtained from the ISGS Geologic Samples Library. (Table 2 shows the original sources.) Cores from Aux Vases reservoirs were selected primarily on the basis of their availability.

Plugs 1 inch (2.54 cm) in diameter and as long as possible were drilled from 4-inch-diameter whole cores. They were cleaned at 150°F (66°C) in a CO₂-solvent, core cleaning apparatus. The cleaning solution was high-pressure CO₂ gas and a solvent mixture of 60% toluene, 25% hexane, and 15% methanol. This cleaning process, as shown by Seyler (unpublished 1992), adequately removes oil from plugs without altering the mineral content of the reservoir rock.

Core plugs ranging in length from 1 inch (2.54 cm) to 2.5 inch (6.35 cm) were used for the coreflood experiments. Variations in length did not affect results because the measurements of each core plug were used for calculations. Eight core plug wafers 1.0 inches in diameter and 0.25 inches (0.635 cm) thick were used in the MCA and HCl soak experiments.

The MCA solution used in this work was supplied by Halliburton, Inc., and contained 15% HCl in a proprietary formulation of surfactants, suspending agents, anti-sludge agents, clay mineral stabilizers, iron-sequestering agents, and corrosion inhibitors. (A proprietary agreement with Halliburton prohibits our performing or publishing chemical analyses of this MCA.)

Table 2 Samples used for the experiments and methods used to describe them

Field, well and well ID	Depth <i>ft</i>	SEM/EDX	XRD	Thin section
Energy	2,393.5	Yes	No	No
2 Morgan Coal	2,388.3	Yes	Yes	Yes
1219923465	2,391.1	Yes	No	No
	2,390	No	Yes	Yes
	2,388	No	No	No
	2,393	Yes	No	No
	2,392.8	Yes	Yes	Yes
Dale	3,198.7	Yes	No	Yes
1 McCreery	3,200.6	No	No	No
1205523456				
Zeigler	2,611	Yes	Yes	Yes
2 Mack	2,627	Yes	Yes	Yes
1205523750				
Boyd	2,163	No	No	No
9 Sanders				
1208102628				

Produced Aux Vases formation brine, collected from the Budmark no. 3 Morgan Coal lease (2,389 ft subsurface) in Energy Field and containing 126,000 parts per million (ppm) total dissolved solids (TDS), was used as the formation water in these experiments. The TDS content of Aux Vases brines generally ranges from 120,000 to 140,000 ppm (Demir 1995); therefore, the TDS content of the Energy Field brine is typical of Aux Vases brines. A synthetic fresh-water mixture was prepared to match the 1,200 ppm TDS composition of the fresh-water supply from a pond at Energy Field (table 3).

The Aux Vases brine from Energy Field was filtered and used to flood core samples from the Boyd Dale Consolidated, Energy, and Zeigler Fields. Varying proportions of this brine and the synthetic freshwater supply were also injected into the core plugs. The resistivities of these mixtures were determined with a resistivity meter. Their salinities were calculated from the TDS–resistivity relationship established by Demir (1995) for Aux Vases brines:

$$\text{TDS(ppm)} = \frac{6786.09}{(R_w)^{1.2853} \cdot 1.022^T}$$

where

R_w = resistivity of water in Ω -m,
 T = water temperature, °F.

A degassed crude oil mixture from the Budmark no. 2 Morgan Coal well in Energy Field was used in some of the experiments. The crude oil mixture has a density of 0.85 gm/cc (35° API gravity) and a viscosity of 6.57 cp at 77° F (25°C).

Petrographic Analyses

Petrographic analyses were performed on samples from Aux Vases reservoirs studied for the enhanced and improved oil recovery project cosponsored by the U.S. Department of Energy and State of Illinois. More than 150 thin sections from Aux Vases reservoirs were made and studied during this project (Seyler et al. in prep.). In addition, several samples were collected from rocks adjacent to those supplying the core plugs used in coreflood experiments to compare untreated with treated reservoir rocks in Boyd, Dale Consolidated, Energy, and Zeigler Fields.

These analyses included standard optical microscopy with thin sections, x-ray diffraction analysis (XRD), and scanning electron microscopy (SEM) with energy

Table 3 Characteristics of water mixtures

Type	Ionic composition meq/l						Cl ⁻	SO ₄ ²⁻	HCO ₃ ⁻	pH	R _w Ω-m	TDS %
	Ca ²⁺	Na ⁺	Ba ²⁺	Fe ³⁺	Mg ²⁺							
Formation brine	341	1883	0.0	0.4	173	2394	1.0	1.7	6.1	0.063	13.7	
Supply water	16	14	0.1	0.0	13	28.2	13.5	1.5	5.3	0.433	1.2	
95%(1) – 5%*										0.064	13.5	
90%(1) – 10%										0.068	12.4	
75%(1) – 25%										0.076	10.5	
50%(1) – 50%										0.124	5.95	

* 95% (by volume) of formation brine and 5% (by volume) of the supply water.
 meq/l = mole wt/charge per liter

dispersive x-ray microbeam (EDX) analysis. Experimental details of thin section, SEM/EDX, and XRD analyses are discussed in Appendix I. Thin sections were used to characterize petrographic relationships, including framework grain composition, cementing agents, grain size, porosity types, and reservoir quality. SEM/EDX analyses identify the pore-lining constituents that will interact directly with fluids contacting the formation; whereas XRD analyses provide the type and amount of all minerals present.

Critical point drying was used, whenever possible, to observe the morphology of potentially hydrated clay minerals coating the framework grains and to ensure that air-drying of cores used in this study did not alter the clay minerals (Seyler et al. in prep.). Fresh cores suitable for critical point drying were limited to two wells in fields sampled for this study. Examples of critical point drying are included in this study to illustrate typical untreated samples.

Coreflood Experiments

Coreflood experiments were performed with a TEMCO™ integrated coreflood apparatus (described in Appendix II). Each core plug was cleaned in a CO₂/solvent core cleaner and vacuum-dried. The porosity of each core plug sample was determined at room temperature and atmospheric pressure by the saturation method, and its permeability to nitrogen gas was determined at atmospheric ambient confining pressure prior to the coreflood experiments (Tiab 1985). Standard operating and quality control procedures for permeability and porosity measurements and other analytical methods used in this paper are on file (ISGS Oil and Gas Section 1993).

For baseline liquid permeability determination, brine was continuously injected into a core sample at a rate of 1.5 cm³/min. This process resaturates samples that were previously dry or contained an irreducible water saturation. This rate, which corresponds to a commonly observed reservoir flow velocity of 14 feet per day (ft/day) and 68.6 barrels per day in a 10-foot pay, was determined according to the scaling coefficient of Kyte and Rapoport (1958). The scaling coefficient of unity (LVμ_w = 1) corresponding to oil recovery of 65% at water breakthrough was used (Delclaud 1991). No fines migration was observed in the core plugs when nonreactive liquid (brine) was injected at this rate. The pressure drop across the core sample was continuously monitored and recorded directly by desktop computer. The effective permeability of the liquid at any time was determined from Darcy's equation by measuring the pressure drop across the core:

$$K(md) = \frac{1000\mu QL}{A\Delta P}$$

where

μ = viscosity of flowing liquid (in centipoise)

L = core length (cm)

A = core cross-sectional area (cm²)

Q = liquid throughput (cm³/sec)

ΔP = pressure drop across core (atm)

Coreflood experiments were performed at a confining pressure of 1,000 psig (6895 KPa) and a temperature of 75°F (24°C). The core samples were mounted in a conventional Hassler-type coreholder. Inside the coreholder, the core was inserted into a rubber (viton) sleeve of slightly larger diameter. Metal end pieces and spacers, which compensate for various core lengths, filled the remainder of the sleeve. The

space outside of the sleeve and inside the coreholder was filled with hydraulic fluid to provide an even confining pressure on the sample. This procedure ensures that fluid injected into the end-piece ports flows through, not around, the core sample, and that no mixing of the confining pressure fluid and the injection fluid can occur. The differential pressure across the core plug at a flow rate of 14 ft/day ranged from 10 to 50 psi (69.8–345 KPa). A back pressure of 50 to 75 psi (345–517 KPa) was required to prevent gas bubbles and maintain single phase flow. Higher backpressures were attempted to more closely simulate reservoir conditions. Using higher backpressures resulted in regulator malfunction due to the generation of CO₂ gas, which caused erratic fluctuations in pressure and led to erratic permeability calculations.

The flow rate was selected because the average net pay of Aux Vases reservoirs is 10 feet and wellbores are commonly 4 to 6 inches in diameter. Initial production rates from Aux Vases reservoirs can exceed 200 barrels of oil per day (BOPD) but average less than 100 BOPD; these rates usually decline rapidly because these reservoirs have a solution-gas-drive mechanism. Experimental injection rates of 14 ft/day (1.5 cc/min) through the 1-inch-diameter plugs (equivalent to 68.6 BOPD from an Aux Vases well) were selected, using the above parameters as a guide. This rate was also chosen because of the limits of the available pressure transducers.

Coreflood experiments were conducted at constant rates of injection, rather than constant pressures. Some core plugs were continuously injected and permeability calculated at a constant rate. Other experiments used discontinuous, constant rate injection during which permeability was measured after each injection pulse.

Aux Vases reservoirs in this study occur between 2,100 and 3,200 feet below the surface. A gradient of 1 psi/ft was used to estimate the overburden pressure. This gradient, a typical sedimentary basin value (Levenson 1967), results in overburden pressures ranging from 2,100 to 3,200 psi. In addition, the average initial bottom-hole pressure of the reservoirs sampled for this study is approximately 1,200 psi, as measured by drill stem tests. Hydrostatic pore pressure has a gradient of approximately 0.45 psi/ft, therefore 1,200 psi is normal. Because reservoir conditions are in flux once production is initiated, matching of exact reservoir conditions during experiments is extremely difficult. At reservoir pressures lower than 3200 psi, coreflow experimental results are not significantly different from those obtained at atmospheric pressures (Amyx et al. 1960).

Bottom-hole temperatures measured during logging in these reservoirs range from 24° to 36°C (75° to 98°F). Experiments run at room temperature are only 4° to 10°C (8° to 20°F) lower than the highest bottom-hole temperatures. Because the temperature difference between Aux Vases wells and the laboratory is less than 10°C (20°F), the net effect of the temperature differences is negligible (Eickmeier and Raimey 1970, Amyx et al. 1960).

One of the inherent limitations in using core plugs for experimentation is that their small size represents a very small percentage of the total reservoir; therefore, the entire range of effects that introduced fluids may have on reservoir behavior cannot be fully determined. Nevertheless, the coreflood experiments conducted for this study will enable a better understanding of the reaction of pore-lining minerals with fluids introduced during the drilling, completion, or stimulation phase of an Aux Vase reservoir at temperature and pressure conditions that approximate those found in reservoirs. Another limitation in using coreflood techniques to simulate reservoir conditions in this study is that each experiment represents a discrete phase of the drilling, completion, or stimulation process. Determination of the cumulative effects of fluid reactions on reservoir samples was beyond the scope of this study but is recommended for future work.

Coreflood Tests with Acids

The effects of the MCA and 15% HCl on permeabilities of Aux Vases core samples were examined under laboratory conditions. Coreflood tests with MCA were performed on samples from Energy, Dale Consolidated, and Zeigler Fields (tables 1 and 2). The 15% HCl solution without additives was only injected through one sample from Energy Field. Ten pore volumes of test fluid, driven through core plugs during each experiment, ensured that the samples were completely flushed. Therefore, coreflooded samples represent the invaded portion of the reservoir around the perimeter of the well bore. This invaded zone usually is totally flushed during well stimulation, then swabbed to retrieve almost all the spent and unreacted fluids. All effluents were collected, including migrated fines from these experiments.

Interrupted coreflood In the first test, MCA was injected into a dry core sample from the Dale Consolidated Field; there was no oil or water in the sample. This particular test was used as a benchmark to isolate the short- and long-term effects of the MCA solution on the rock from effects due to other fluid saturations.

The permeability of the sample to MCA was determined at hourly intervals from hours 1 to 6, then at hours 50 and 74. This was an interrupted coreflood because permeability was measured after a set time, once equilibrium was reached. At this time fluid injection was stopped, and the coreflood apparatus was closed-in for a permeability measurement, then it was restarted. The SEM/EDX analysis of the sample was performed after completion of the entire coreflood. While such prolonged exposure to MCA is rarely a planned part of the drilling and stimulation process, it could occur if problems are encountered during mud cleanout and acidizing operations.

Continuous acid corefloods Continuous coreflood experiments were conducted to represent flushed, completely swabbed reservoir rock. In these and subsequent MCA and HCl coreflood tests, core plugs were restored to their native saturation states; saturation with formation brine was followed by displacement with degassed crude oil until irreducible water saturation was attained. Core plugs were then soaked in degassed crude oil for 48 hours to attain oil–water equilibrium (Anderson 1987). Mobile oil in the continuous acid coreflood experiments was displaced with brine, then the brine was displaced with either MCA or a 15% HCl solution. All movable brine was effectively flushed out using about 400 mL or 10 pore volumes of the acid solutions for about 30 minutes. Effective permeabilities of core plugs to acid solutions were continuously measured until equilibrium was attained, usually in about 1 hour at the set flow rate.

Water Sensitivity Coreflood Experiments

Brines of different salinities were injected into core plugs from Boyd, Dale Consolidated, Energy, and Zeigler Fields (table 1). Two water sensitivity tests were performed.

The first tested the effect of slowly decreasing water salinities on the permeability of Aux Vases sandstone. The purpose of this test was to determine the lowest level of salinity that would not significantly reduce the permeability of the sample. It was not necessary to conduct this particular test for every Aux Vases sample because a common trend of decreasing permeability with increasing exposure to fresh water was observed in samples from all fields in the study. A core plug from the 2,388-foot depth of the Budmark no. 2 Morgan Coal well in Energy Field was selected because of its typical mineralogy, porosity, and permeability. The water injection sequence was filtered formation brine, followed by a sequence of mixtures of formation brine (TDS = 120,000 ppm) and deionized water (TDS = 0.0) with progressively lower salinities.

The objectives of the second test were to examine the effect of fresh water on Aux Vases permeability and to investigate whether subsequent injection of brines with higher salinities could restore permeability already impaired by fresh water. Core plugs from Aux Vases reservoirs in Boyd, Dale Consolidated, Energy, and Zeigler were used in these experiments. The sequence of injection in this test was formation brine, fresh water, then mixtures of formation brine and fresh water with progressively lower concentrations of the formation brine. Mixtures were changed without removing the plug and permeabilities were measured after equilibrium was reached following injection of mixture.

Acid Soak Experiments

In some Illinois Aux Vases fields, a 15% HCl solution rather than MCA is used for well cleanup, as a cost saving measure. Poorly formulated MCA may be inadvertently used where 15% HCl does not remain in solution, but separates from other ingredients in the MCA. Static soak tests at ambient room temperatures and atmospheric pressures were conducted to examine the changes in pore-lining minerals in reservoirs. These experiments represent reservoir zones where stimulation acids are not recovered during swabbing but remain in the reservoir until they are spent. These underflushed zones are generally located away from the well bore, but may occur near the well bore when cleanup acids are allowed to remain in the borehole for more than a few hours.

Two separate soak experiments were performed, one with MCA and the other with a 15% HCl solution. In each test, eight 1.0-inch (2.5-cm) diameter and 0.25-inch (0.625-cm) thick core wafers of an Aux Vases core plug from the 2,393-foot depth in the Budmark no. 2 Morgan Coal well in Energy Field were soaked in an acid solution for intervals, each increasing by ½ hour (e.g., ½, 1, 1½, 2, 2½...), ranging from 30 minutes to 7 hours. The samples were immediately placed under vacuum and coated with gold and palladium in preparation for SEM/EDX analysis. The effects of the acid solutions on the pore minerals of Aux Vases sandstone reservoirs were investigated using SEM/EDX analyses before and after soaking for 30 minutes in the acid solutions. Permeability measurements were not possible before or after these experiments.

Crude Oil–Acid Compatibility Experiments

Simple compatibility experiments were conducted to determine the effects of both the 15% HCl solution and MCA on four crude oils produced from the Aux Vases Sandstone at Boyd, Dale, Energy, and Zeigler Fields. These experiments were conducted to simulate the acid preflush step of the well completion and stimulation process. The common industry practice of using atmospheric pressure and normal room temperature 75°F (24°C) for shallow, normally pressured reservoirs was used in these tests (Bradley 1987). Five mL of oil was poured slowly, without mixing into 25 × 125 mm glass test tubes containing 5 mL of the acid solution (MCA or 15% HCl). The mixture was inspected after remaining undisturbed at laboratory room conditions for several hours.

INITIAL RESERVOIR ROCK COMPOSITION

Bulk Mineralogy of Selected Aux Vases Sandstone Reservoirs

Aux Vases reservoir samples generally consisted of 65–90% quartz, 3–15% feldspar, 0–15% calcite and 2–7% clay minerals (table 4). Siliciclastic framework grains in Aux Vases reservoirs generally include, in descending order of relative abundance, undulose quartz, non-undulose quartz, polycrystalline quartz, K-feldspar (orthoclase and microcline), plagioclase feldspar, and chert. Carbonate framework

Table 4 Aux Vases samples: bulk weight percentage of clay minerals; absolute percentage of other minerals

Depth ft	Perm. md	Porosity %	I %	I/S %	C %	BC %	Q %	Kf %	Pf %	Cc %	D %
Farrar 1 McCreery, Dale Consolidated Field — API 1205523456											
3,190.5	49.0	20.4	3.2	1.4	0.7	5.3	84.5	1.3	2.5	6.4	0.0
3,191.5	81.5	23.4	2.8	1.5	0.7	5	81.6	1.7	3.2	8.6	0.0
3,192.7	106.0	25.6	2.5	1.1	0.6	4.3	84.9	1.5	3.7	5.6	0.0
3,194.0	116.0	23.6	3.4	2.5	0.9	6.8	79.5	1.2	4.3	8.1	0.0
3,195.7	55.8	19.8	2.6	1.5	0.7	4.8	88.0	0.0	1.9	3.2	2.0
3,197.9	56.8	24.8	3.1	1.7	0.8	5.6	80.7	2.6	2.6	8.5	0.0
3,199.4	41.9	24.3	2.1	1.5	0.6	4.2	82.5	2.7	3.7	6.8	0.0
3,201.0	35.5	21.4	3.1	2.3	0.9	6.3	82.3	2.6	3.3	5.5	0.0
3,203.3	27.9	18.6	2.1	2.1	0.4	4.6	77.8	1.5	1.9	14.2	0.0
3,205.8	15.8	21.4	2.4	2.1	0.5	5.1	83.7	1.2	2.4	7.6	0.0
3,207.1	1.8	14.6	3.1	4.2	0.7	8	67.8	0.8	1.5	21.8	0.0
3,208.4	2.5	13.1	1.7	1.9	0.5	4.1	82.9	1.7	2.8	8.4	0.0
3,209.9	-0.1	0.7	5.2	4.7	1.9	11.8	68.4	1.2	1.8	16.8	0.0
3,212.7	NA	NA	2.7	3.7	0.0	6.4	2.4	0.0	0.0	91.2	0.0
3,216.7	NA	NA	1.5	2.0	0.0	3.5	2.9	0.0	0.0	93.6	0.0
3,219.2	NA	NA	4.6	4.4	0.1	9.1	3.4	0.0	0.0	71.8	15.6
Gallagher Drilling Company 2 Mack, Zeigler Field — API 1205523750											
2,605.5	24.9	14.4	5.5	2.7	1.1	9.4	69.2	0.0	2.9	18.5	0.0
2,606.5	216.0	25.1	3.7	2.7	2.2	8.7	64.2	3.0	7.4	16.7	0.0
2,608.5	49.0	22.1	2.9	1.2	1.9	6	85.0	1.1	3.9	3.9	0.1
2,610.5	64.0	22.1	2.4	1.4	2.2	6	86.4	0.6	4.0	2.9	0.0
2,611.5	124.0	24.1	1.7	0.8	1.9	4.3	86.2	0.4	4.9	3.9	0.3
2,612.5	152.0	25.5	4.2	1.9	3.3	9.4	72.1	8.9	6.1	3.4	0.0
2,614.5	35.6	23.6	2.3	1.2	3.7	7.1	77.9	2.3	9.0	3.7	0.0
2,617.5	89.5	24.5	0.5	0.3	1.5	2.3	91.4	0.0	4.4	1.9	0.0
2,618.5	47.8	24.8	1.2	0.6	4.3	6.2	82.7	0.2	7.1	3.8	0.0
2,620.5	47.8	23.5	2.0	2.1	6.0	10.1	61.8	20.5	4.3	3.3	0.0
2,621.5	56.0	23.8	2.2	0.7	7.2	10.1	78.8	0.6	6.4	4.2	0.0
2,623.7	NA	NA	2.4	2.1	5.2	9.7	72.7	0.2	2.2	15.2	0.0
2,623.8	-0.1	8.8	2.5	1.9	5.3	9.7	80.3	5.0	3.1	1.9	0.0
2,625.5	-0.1	17.0	2.5	2.5	4.9	9.9	84.5	0.5	3.7	1.5	0.0
2,629	-0.1	11.0	1.0	1.1	3.0	5.1	90.6	0.4	3.9	0.0	0.0
Budmark 2 Morgan Coal, Energy Field — API 1219923465											
2,387.6	184.0	21.3	1.6	0.9	2.4	5	80.8	0.0	8.2	6.0	0.0
2,388.4	246.0	21.7	1.2	1.1	1.9	4.2	56.5	0.2	8.2	30.9	0.0
2,390.1	69.0	23.6	1.4	0.7	2.5	4.7	85.4	0.6	2.6	6.7	0.0
2,392.7	85.0	23.3	0.8	0.3	1.7	2.7	72.7	0.2	7.8	16.6	0.0
2,394.7	69.0	20.6	1.0	0.5	3.0	4.5	76.3	0.4	6.3	12.5	0.0
2,395.2	4.3	13.6	1.6	0.9	4.1	6.6	63.5	0.0	2.5	27.5	0.0
Superior Oil Company 1 Price, Boyd Field — API 1208101972											
2,129.0	0.0	7.3	1.2	0.9	0.5	2.6	93.7	2.0	1.0	0.5	0.2
2,131.0	1.7	17.7	0.8	0.6	1.5	2.9	90.7	3.3	2.3	0.5	0.3
2,133.0	118.0	15.1	0.5	0.3	0.7	1.5	88.3	1.3	0.5	8.1	0.2
2,134.0	81.0	11.4	3.7	2.6	2.5	8.8	80.6	1.2	0.8	8.4	0.2
2,135.0	0.0	7.0	0.4	0.3	1.1	1.8	67.6	1.2	0.8	28.5	0.1
Superior Oil Company 7 Sanders, Boyd Field — API 1208101950											
2,141.0	42.0	21.6	1.1	0.8	0.7	2.6	80.9	2.5	0.7	12.9	0.5
2,144.0	362.0	24.2	0.4	0.3	0.7	1.5	84.2	2.6	1.3	10.1	0.4
2,151.0	140.0	21.5	1.4	1.0	1.6	4.1	84.9	3.2	1.6	6.0	0.3
2,155.0	58.0	19.5	0.6	0.5	1.3	2.4	88.3	2.9	1.1	4.7	0.5

Perm. = permeability, D = dolomite, Cc = calcite, C = chlorite, I = illite, I/S = illite/smectite, BC = bulk content, KF = K-feldspar (microcline or orthoclase), PF = plagioclase feldspar, Q = quartz

grains are common in some reservoirs such as Dale Consolidated and Energy Fields. These carbonate grains include micritized pelloids, ooids, and marine fossil fragments such as echinoderms, bryozoans, and brachiopods. Pore-filling halite, observed in some samples from Zeigler Field, was not quantified during XRD analyses because it was presumed to be precipitated from brine. Heavy minerals are very rare in the Aux Vases, although trace amounts of zircon, anatase, and pyrite were observed in thin sections.

Although the mineral compositions of Aux Vases reservoir samples were generally similar, relative mineral abundances differed significantly from one sample depth to another within the same reservoir and from one reservoir to another. Mixed-layered illite/smectite, chlorite, and illite, in an intimately intergrown mixture, were the only clay minerals detected in these samples.

Pore-Filling Mineral—Calcite

Three types of calcite were observed in Aux Vases samples. In relative order of abundance, they are (1) patchy cement filling intergranular porosity (fig. 4c); (2) framework grains such as marine fossil fragments, ooids, and pelloids; and (3) minute, late-stage euhedral crystals (fig. 4a) on diagenetic clay minerals that coat framework grains and line pores. When thin sections are stained with a mixture of alizarin red and potassium ferricyanide, the primary calcite becomes red and a secondary ferroan variety appears violet.

Calcite cement is the most abundant form of calcite and its dissolution by acid can significantly alter reservoir properties. Whether primary or secondary, it is locally abundant in Aux Vases reservoirs. It may either occur as nodules or patchy intergranular cement aligned along bedding planes in coarser grained laminae (Seyler et al. in prep.).

A core sample from the 2,631-foot depth in the Gallagher Drilling Company no. 1 Mack well in Zeigler Field (fig. 5a) illustrates a tidally deposited, bidirectionally crossbedded sandstone typical of most high-quality Aux Vases reservoirs. The coarser grained, porous laminae alternating with finer grained, less porous laminae, as shown in thin section (fig. 5b), may cause a high degree of horizontal permeability, which in turn, may lead to channeling. Because the coarser grained laminae were originally more porous than the more clay-rich, finer grained laminae, they were more favorable sites for precipitation of calcite cement. In some instances, coarser grained laminae contain carbonate framework grains that serve as nucleation sites for calcite precipitation. Therefore, much of the calcite in reservoir sandstones is concentrated along coarser grained laminae. Dissolution of primary calcite cement by acid may produce high permeability channels oriented along the strike of crossbedding laminae. In contrast, the dissolving of nodules develops isolated pores for only a marginal increase in permeability.

Pore-Lining Minerals

Pore-lining minerals in Aux Vases Sandstone reservoirs are, in descending order of abundance, dominantly diagenetic clay minerals, calcite, partially dissolved feldspars, solid hydrocarbons, anatase, barium-rich celestite, and traces of dolomite (Seyler et al. in prep.). Aux Vases reservoir sandstones rarely contain individual crystallites of diagenetic clay minerals that are easily identified using SEM/EDX; therefore, XRD analyses were used to identify the clay mineral suite.

Pores in Aux Vases sandstone reservoirs are lined with and may be bridged by diagenetic clay minerals that consist of an intimately intergrown mixture of mixed-layered illite/smectite, chlorite, and illite (fig. 6). Although clay minerals constitute only 2–7% of the bulk mineral content, SEM analysis indicates that clay minerals coat more than 95% of pore surfaces; they are the first materials exposed to MCA or HCl when it is used to drill or stimulate a well. Therefore, an understanding of the

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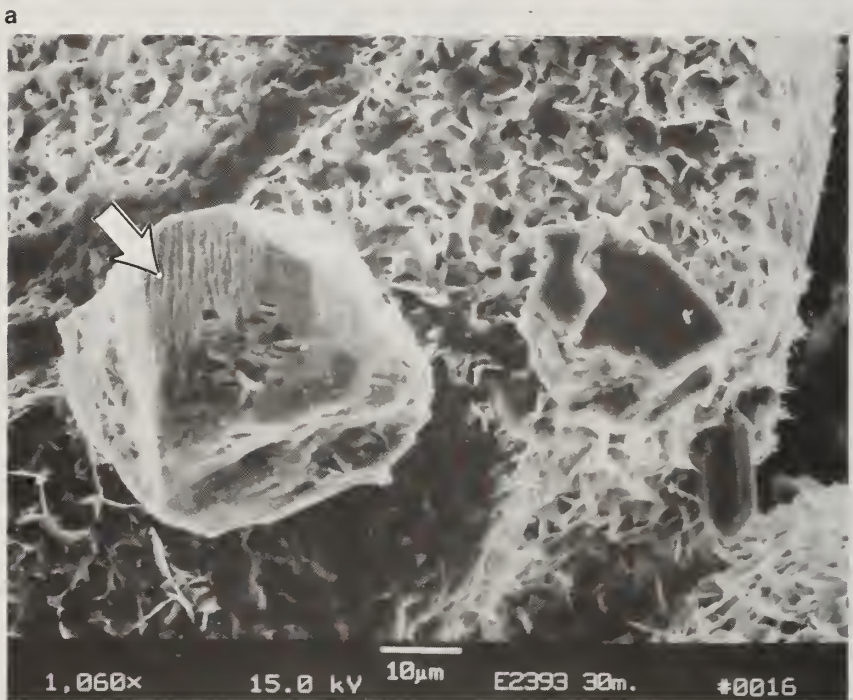
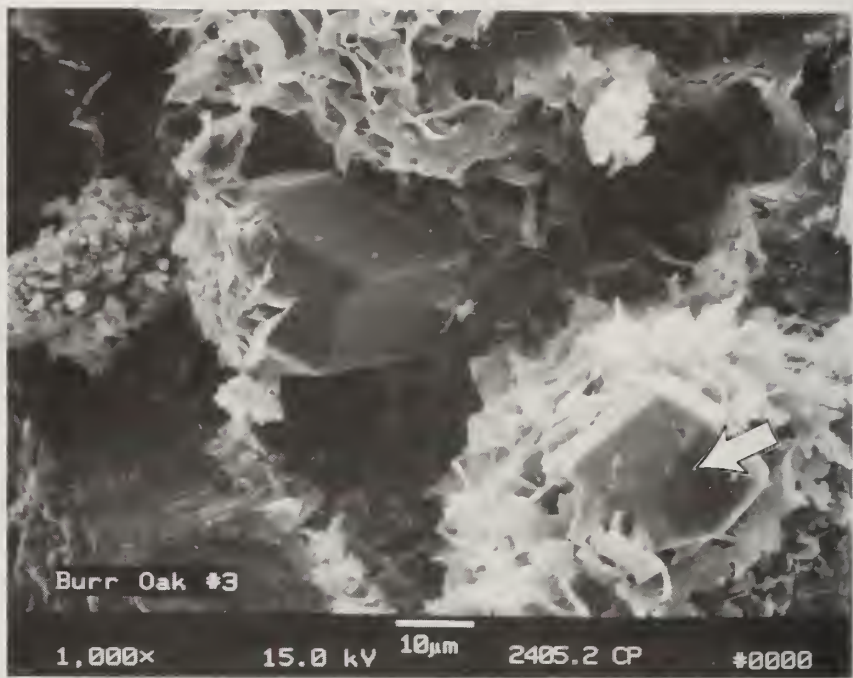


Figure 4 SEMS comparing acid-soaked with untreated wafers sliced from 1-inch-diameter core plugs from two wells in Energy Field:

a) An untreated, critical-point-dried sample (2,405.2-ft depth, Budmark 3 Burr Oak) shows a late-stage, minute calcite crystal with sharp euhedral edges (arrow) on top of diagenetic clay minerals; its position indicates that it precipitated after the clay minerals. This type of calcite is the first to be affected by exposure to MCA or 15% HCl.

b) A minute calcite crystal (arrow) was etched on this sample (2,393.5-ft depth, Budmark 2 Morgan Coal) after 30 minutes of soaking in MCA. Compare the etched crystal faces with the straight euhedral crystal faces shown in figure 4a; clay minerals do not appear to have been affected.



d

c) An untreated sample (2,393.5-ft depth, Budmark 2 Morgan Coal) shows patchy calcite cement filling pores (arrows). This type of calcite is much more extensive than the minute late-stage crystals shown in figure 4a. Dissolution of this type of calcite would improve porosity and permeability of reservoirs.

d) Partial dissolution of pore-filling calcite cement (arrow) after 30 minutes of soaking the sample (depth 2,393.5-ft, Budmark 2 Morgan Coal) in MCA. Compare this example with the untreated calcite cement shown in 4c. The edges of the calcite are etched and contrast sharply with the flat, smooth cleavage surfaces in the untreated sample. Note that the clay minerals appear to have been unaffected.

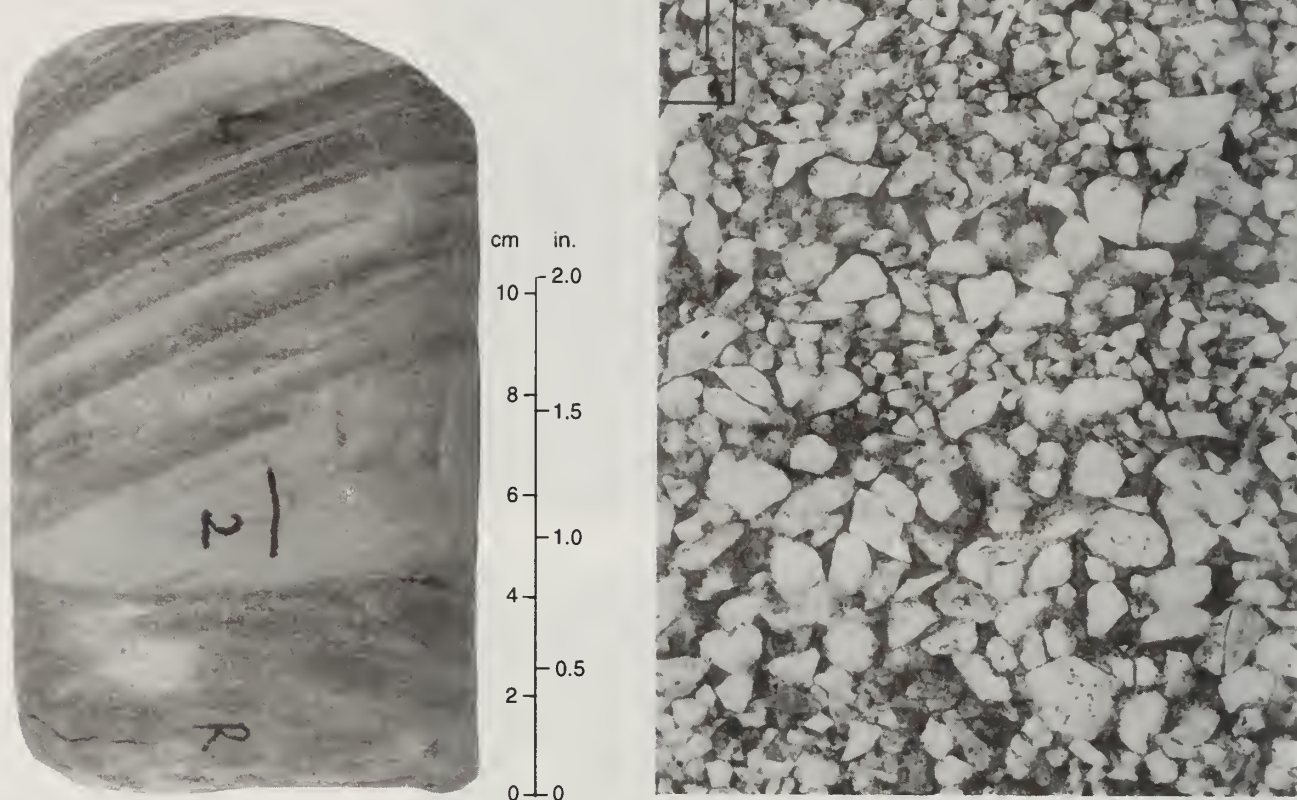


Figure 5 a) Crossbedded sandstone (left), in a sample (2,631-ft depth, Gallagher Drilling Co. 1 Mack, Zeigler Field) of a typical Aux Vases reservoir shows coarser grained, more porous, darker oil-stained laminae that alternate with finer grained, less porous, lighter unstained laminae. b) Thin section photomicrograph (right), of a sample from the same well (2,627-ft depth) shows coarser grained, porous laminae alternating with finer grained, less porous laminae. Early-stage calcite cement may fill pores in some coarser grained laminae. When this occurs, a band of calcite cement forms, aligned with crossbedding. Its dissolution will cause local channelized permeability. Bar scale is 0.25 mm.

composition and response of these diagenetic clay minerals to injected fluids is of utmost importance when selecting drilling muds and stimulation methods.

This composition is unique to the Aux Vases. The clay minerals in the overlying sandstone reservoirs in Chesterian formations contain fibrous illite, kaolinite booklets, and iron-rich chlorite, which are easily identifiable from their unique morphologies and their representative elemental compositions. Because diagenetic clay minerals are different in the overlying Cypress and other Chesterian sandstones than they are in the Aux Vases, the experimental results from Aux Vases samples should not be applied to Cypress sandstones. Chlorite identified by XRD and SEM/EDX analyses in Aux Vases samples is typically not iron-rich, but contains approximately equal amounts of iron and magnesium. Only a minute amount of iron-rich chlorite was observed in two Aux Vases reservoir samples during SEM/EDX examination. Therefore the typical chlorite is rich in aluminum or magnesium, but not in iron.

This distinction is important because some of the literature (Simon and Anderson 1990) suggests that iron-rich chlorite is more soluble than aluminum- or magnesium-rich chlorite. Reservoirs containing chlorite rich in iron may be more

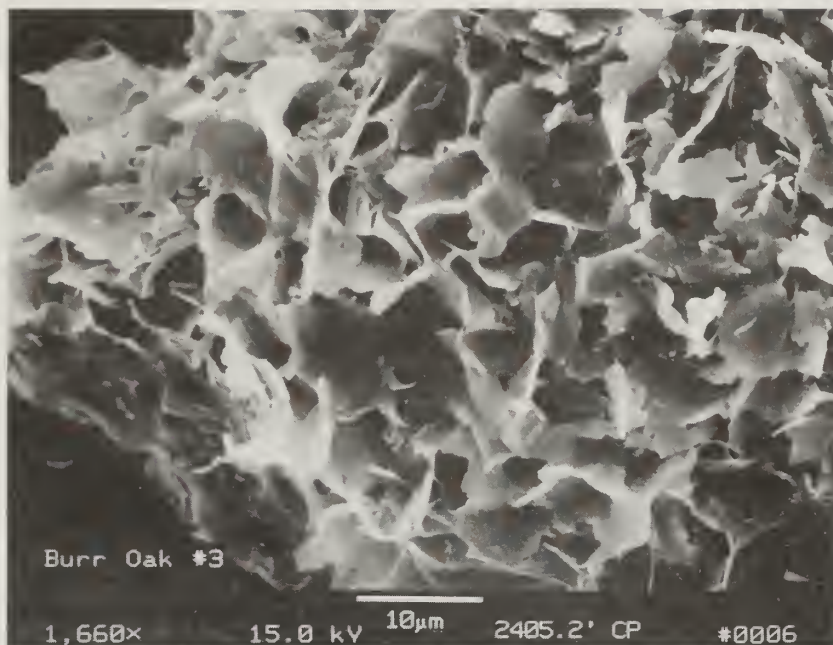


Figure 6 SEM shows a close-up of typical intergrown diagenetic clay minerals coating grains and lining pores in Aux Vases reservoirs. This sample was critical-point-dried to preserve the morphology of hydrated clay minerals composed of intimately intergrown mixed-layered illite/smectite, chlorite, and illite. Fresh cores with preserved fluids needed for critical point drying were available from only two wells. This sample (2,405-ft depth, Budmark 3 Burr Oak, Energy Field) was chosen because the well is near the Budmark 2 Morgan Coal well sampled for this study.

susceptible to formation damage than those containing other varieties of chlorite because they may form insoluble iron oxides or iron hydroxides.

Expandable clay minerals, present in mixed-layered illite/smectite in all Aux Vases samples, are discussed later in the section on water sensitivity.

RESULTS AND IMPLICATIONS

Effect of MCA on Aux Vases Samples: Calcite Dissolution in Coreflood Experiments

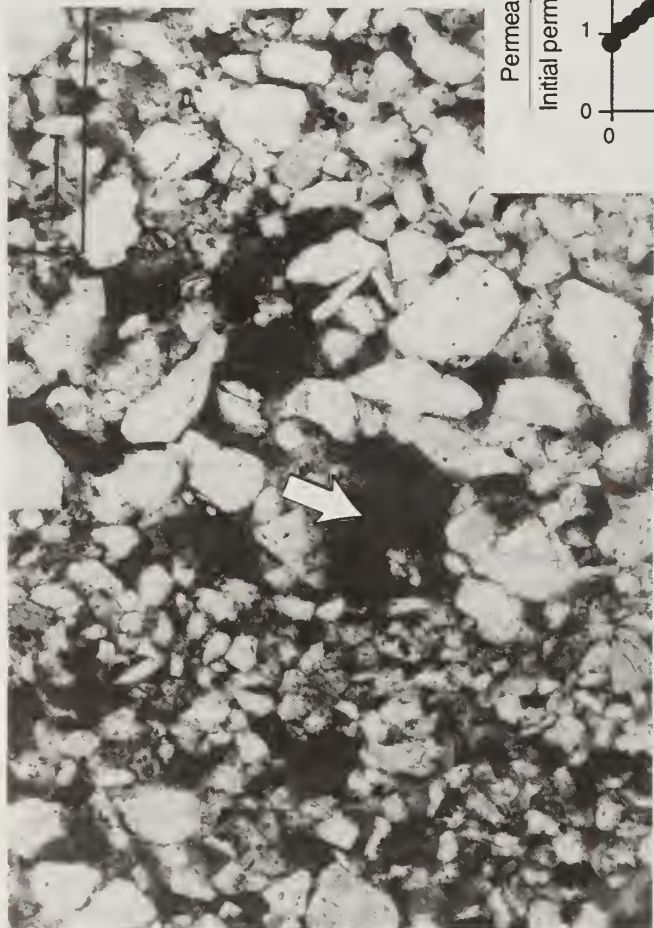
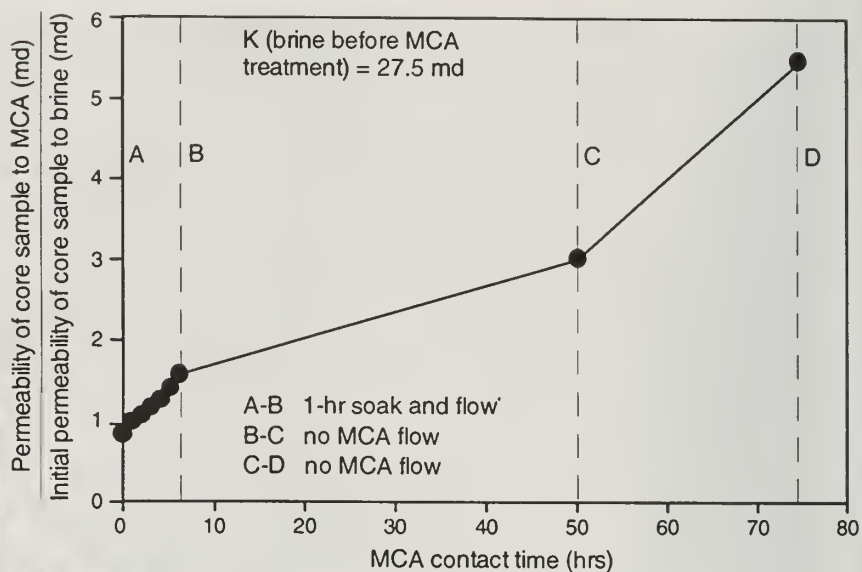
Results from coreflood experiments injecting MCA through Aux Vases sandstone samples from the Dale Consolidated, Energy, and Zeigler Fields showed that permeabilities of the samples increased with increasing contact time (figs. 7a, 8, 9). The permeability increase is caused primarily by the dissolution of calcite by HCl in the MCA according to the reaction:



Carbon dioxide (CO₂) gas was evolved and observed in the effluent.

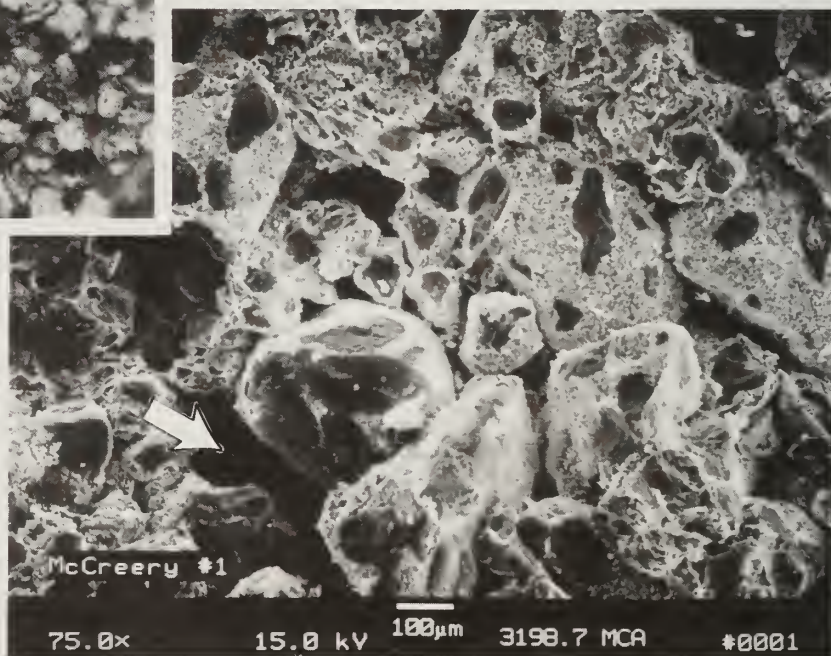
The permeability to MCA increased by almost 100% in a sample from Dale Consolidated Field (fig. 7a; 3,198.7 ft subsurface) after 30 hours of contact time but, by about 50% for an Energy Field sample (fig. 8; 2,392.1 ft subsurface), although the test sample from Energy Field contained slightly more calcite (about 10%, table 4) than did the sample from Dale Consolidated Field (about 6%, table 4). This discrepancy occurred because the core plug from Dale Consolidated Field had

Figure 7 a) An interrupted, constant flow rate, acid coreflood exposed a core plug (3,198.7-ft depth, Farrar 1 McCreery, Dale Cons. Field) to MCA for 74 hours. Permeability increased with MCA-rock contact time as calcite cement dissolved, dislodging some fine grains that were flushed out of the core sample.



b) Photomicrograph of a thin section made from the core plug after 74 hours of exposure to MCA shows that coarse grained laminae, filled with calcite cement prior to the coreflood, developed a channelized pore system due to total dissolution of calcite cement along the laminae. As a result, large over-sized pores formed (arrow).

c) SEM photomicrograph of the same sample after coreflood also shows enlarged pores (arrow) and diagenetic clay minerals coating sili- ciclastic framework grains. The framework grains have a bimodal size distribution and are either very fine grained (100 μm) or medium grained at 250 μm or greater.



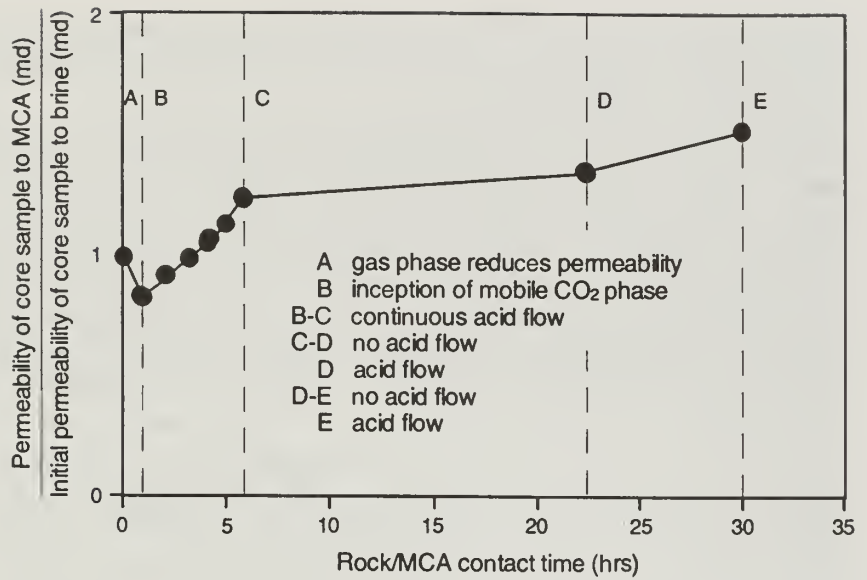


Figure 8 Permeability changes during a 30-hour, interrupted, constant flow rate ($1.5 \text{ cm}^3/\text{min}$) coreflood test using a 1-inch-diameter core plug (2,392.1-ft depth, Budmark 2 Morgan Coal, Energy Field). Permeability increased with MCA-rock sample contact (no flow) and flow times. The increase is more pronounced in the McCreery core plug (fig. 7a) because of the dissolution of large amounts of calcite cement aligned along crossbedding laminae; the Budmark 2 Morgan Coal sample did not have as much calcite cement.

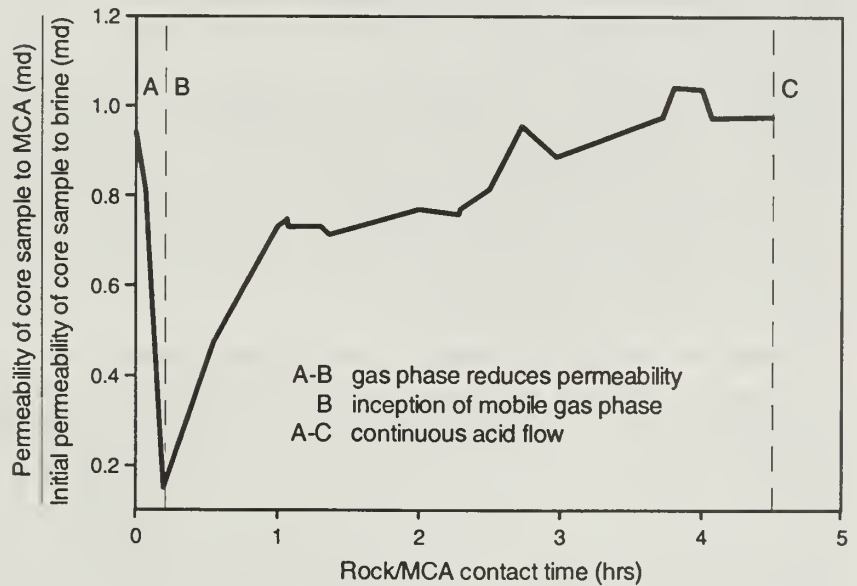


Figure 9 Permeability of a sample (2,627.5-ft depth, Gallagher Drilling Co. 2 Mack, Zeigler Field) varied significantly during a 4.5-hour, continuous, constant rate coreflood test using MCA.

calcite aligned along the coarser grained laminae, whereas the core plug from Energy Field had calcite cement in nodules; channelized permeability would not occur when the nodules dissolved.

The change of permeability with MCA–rock contact time in a core sample from the 2,627-foot depth in the Gallagher Drilling Company no. 2 Mack well in Zeigler Field is shown in figure 9 (Bang and Haggerty 1990). In their experiment, permeability initially decreased sharply to 15% of the untreated value, then began to increase. In the tests for the present study (figs. 7a, 8), permeability values also decreased slightly within the first 15 to 30 minutes and then began to increase. The initial decrease is thought to be the result of a gaseous phase (carbon dioxide [CO₂]) created by the acid dissolution of calcite. With increasing rock–acid contact time, permeability to the MCA and a mobile gas (CO₂) phase also increased. The permeability increase in the Zeigler core sample (fig. 9) was relatively small, however, in comparison with the increase for the sample from Energy Field (fig. 8). After 4.5 hours, the permeability of the core from Energy Field (fig. 8) was only 3% greater than the brine permeability of the untreated sample, and after 30 hours, it was 50% greater.

Differences in the amount by which permeability increased in these samples can be attributed to differences in the amount and type of calcite. Reservoir samples from Zeigler Field contained small amounts of calcite, usually less than 4%, whereas samples from Dale Consolidated and Energy Fields contained significantly more calcite—10% or greater (table 4). Therefore, the effects of the HCl in the MCA were greater because more calcite was dissolved in the samples from Dale and Energy Fields than in the sample from Zeigler Field.

Calcite Dissolution in Thin Section Analysis of MCA Coreflood Sample

Petrographic examination of a thin section from the core plug (3,198.7-ft depth, Farrar no. 2 McCreery, Dale Cons.) used previously in a coreflood experiment (figs. 7b, 7c) confirmed that all calcite cement was dissolved after MCA–core contact for 74 hours. Examination of the untreated rock adjacent to the core plug shows that crossbeds in this sample are alternating finer and coarser grained laminae. The coarser grained laminae are cemented by calcite. Large, oversized pores and channelized high permeability zones were caused by the total dissolution of calcite cement along crossbedded laminae (figs. 7b, 7c).

Dissolution of Calcite in MCA Soak Experiments

Understanding the effect of MCA on pore-lining minerals and evaluating the cause of observed increases in rock permeability required SEM/EDX analysis of pre- and post-test samples from the MCA soak tests (figs. 4a–d). Analysis of an untreated sample from Energy Field (figs. 4a, 3b) showed a loosely cemented, friable sandstone in which every framework grain was coated with diagenetic clay minerals. Small euhedral, late-stage crystals (fig. 4b) and patches of calcite cement (fig. 4d) were among the first carbonates to be partially dissolved after 30 minutes. Examples of euhedral calcite crystals and patchy calcite cement in untreated samples (fig. 4a) may be compared with treated samples (fig. 4c). SEM/EDX examination of samples soaked in MCA showed that after 4 hours of treatment, calcite dissolution was complete.

Effect of MCA on Fines Migration

Treatment of Aux Vases reservoir samples with MCA containing 15% HCl in both coreflood and soak experiments increased porosity and permeability to varying degrees depending on the type, occurrence, and amount of calcite in the sample. In

the reservoir, however, extensive dissolution of calcite cement may lead to pore collapse because of the lithostatic load on the reservoir. Removal of cement can also dislodge sand grains and clay particles, which can then migrate and impair permeability in sandstone reservoirs (Amaefule and Masuo 1986). Fines migration was observed in coreflood experiments using both MCA and 15% HCl in Aux Vases reservoir samples, particularly after 24 hours of exposure to these stimulation fluids. Microscopic examination using reflected and transmitted light showed that fines filtered from the effluent in these experiments consisted of fine-grained sand and silt-sized grains of nonclay minerals as well as particles of diagenetic clay minerals. It was not possible to separate these migrated fines from the residue formed during evaporation of 15% HCl or MCA. XRD and SEM/EDX analyses of these evaporated solids were not successful in identifying the mineralogical composition of the migrated fines.

Effect of MCA on Other Minerals

Other pore-lining minerals that may react with MCA include clay minerals, halite, and K-feldspar; for example, a geochemical model (Demir 1995) simulating the reaction of MCA with a clay mineral suite of iron-rich chlorite, smectite, and illite predicted precipitation of the zeolite mordenite as a byproduct. Trace amounts of pyrite and graphite were also predicted in Demir's model. Because pyrite and graphite (carbon) are naturally occurring minerals in Aux Vases reservoirs samples, and the amounts predicted by the model were below the detection limits of the XRD and SEM/EDX, none of these minerals could be attributed to precipitation from this reaction.

A mineral resembling mordenite, $(\text{Na}_2, \text{K}_2, \text{Ca})[\text{Al}_2\text{Si}_{10}\text{O}_{24}] \cdot 7\text{H}_2\text{O}$, was identified in the SEM/EDX analysis as a precipitate in a postflood core sample from the Budmark no. 2 Morgan Coal well in Energy Field. Mordenite crystals have an elongate, orthorhombic morphology and a characteristic chemical composition, unlike the morphology and composition of any naturally occurring Aux Vases pore-lining minerals (fig. 10). Several SEM/EDX analyses of mordenite show that this mineral precipitated on top of the last natural pore-lining diagenetic clay mineral. The thin, delicate, needle-shaped crystals, which protrude into pores (fig. 10), would have been broken or abraded during coreflooding had they been present prior to the experiment. In addition, no mordenite was found during petrographic examination of more than 150 Aux Vases reservoir samples using SEM/EDX and thin section techniques, including the two samples taken adjacent to the core plug. The amount of mordenite precipitated was minor in terms of pore volume, therefore porosity was not measurably affected.

Dissolution or disintegration of diagenetic clay minerals treated with MCA was not visually apparent during SEM/EDX examination. Chemical analysis of the MCA, which would have verified these visual observations, was not permitted because of proprietary considerations. Some dissolution in samples treated with MCA could have taken place without detection by SEM/EDX; however, the widespread dissolution and disintegration of clay minerals observed in some samples treated with 15% HCl was probably avoided because of clay-stabilizing additives in the MCA.

Effect of 15% HCl Coreflood on Aux Vases Reservoir Sandstones

Injecting a 15% HCl solution into a core plug from a depth of 2,393.5 feet in the Budmark no. 2 Morgan Coal well in Energy Field showed that the permeability of the core increased with increasing volumes of fresh acid (fig. 11). These results, attributed to the dissolution of calcite in the sample, were contrary to expectations. Literature on formation damage (Simon and Anderson 1990, Somerton and Radke

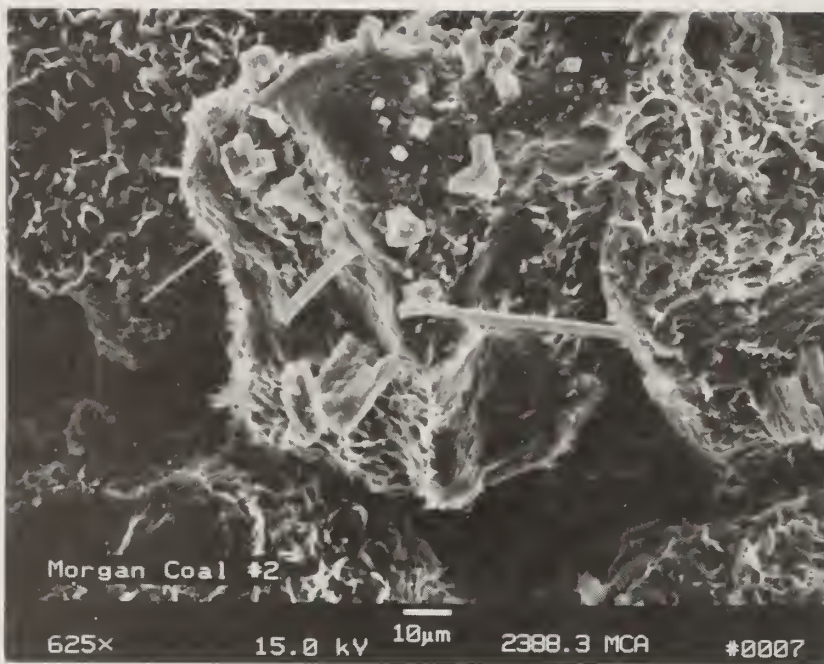


Figure 10 SEM of needle-shaped precipitates in pores of a sample (2,388.3-ft depth, Budmark 2 Morgan Coal, Energy Field). It is believed that this precipitate resulted from MCA reacting with pore minerals, particularly diagenetic clay minerals and calcite. EDX analysis shows Si, Al, Na, Ca, and Mg in this precipitate; the elemental composition and morphology suggest mordenite, a zeolite.

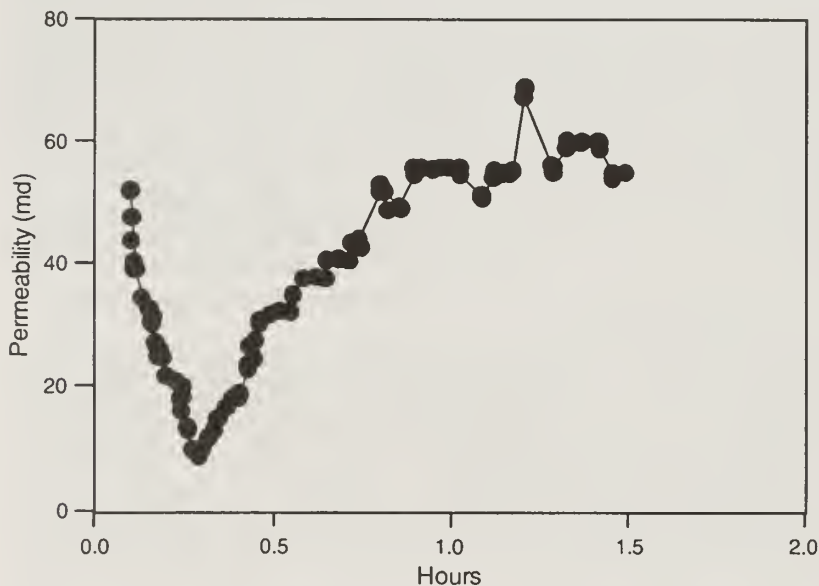


Figure 11 Permeability of a core plug (2,393.5-ft depth, Budmark 2 Morgan Coal, Energy Field) changed as the HCl-rock contact time increased during a continuous, constant rate acid flood test using 15% HCl.

1983, Potter and Dibble 1985) suggests that a decrease in permeability is likely when iron-rich chlorite clay minerals are exposed to 15% HCl without additives. This anticipated loss of permeability has been attributed to the precipitation of iron hydroxide gels derived from the dissolution of iron-rich chlorite clay minerals (Somers-

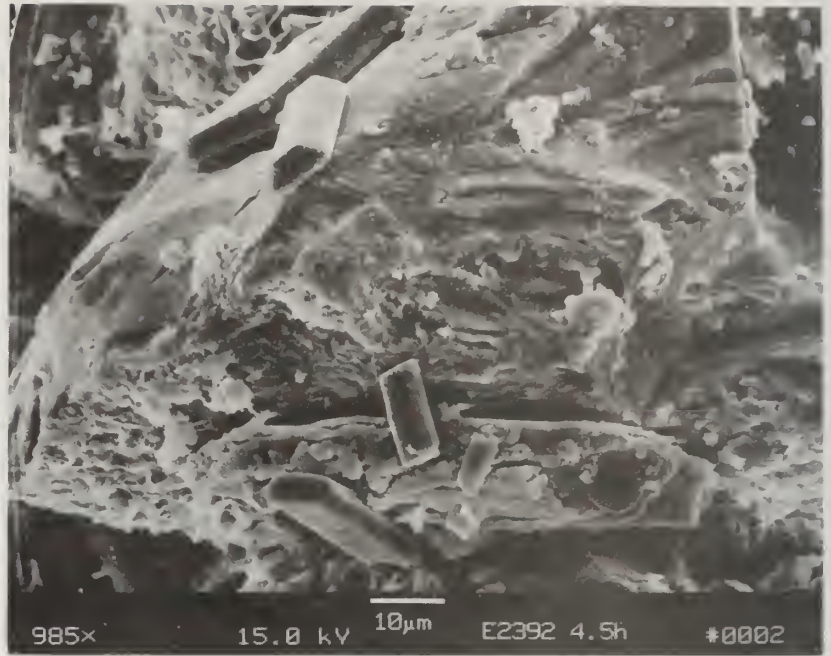
ton and Radke 1983). Chlorite in the Aux Vases is an aluminum- or magnesium-rich variety that apparently does not produce these gels.

Chemical analyses of the effluent from the 15% HCl core flow experiment showed that prolonged acid contact with the reservoir sample (more than 1 day) may have caused leaching and disintegration of pore-lining diagenetic clay minerals, in addition to the total dissolution of calcite and dolomite. Table 5 shows the results of analyses of effluent samples collected at 1 hour, 2 hours, and 2 days. Significant amounts of sodium, magnesium, aluminum, calcium, manganese, and iron were found. With the exception of calcium and manganese, most of the major ions in the effluent were most likely supplied by the reaction of diagenetic clay minerals with 15% HCl. Lesser amounts of potassium, copper, barium, and chromium were also present in the effluent. Although widespread leaching, disaggregation, or dissolution of pore-lining diagenetic clay minerals were not visually obvious in many SEM images, some samples from soaking experiments (discussed below) do show disintegration or dissolution of clay minerals. Figure 12d, for example, shows that no clay mineral coatings remain on many of the framework grains, an indication of disintegration and dissolution of diagenetic clay minerals. Therefore, it is likely that leaching of clay minerals does occur but may not always be detectable using SEM/EDX techniques.

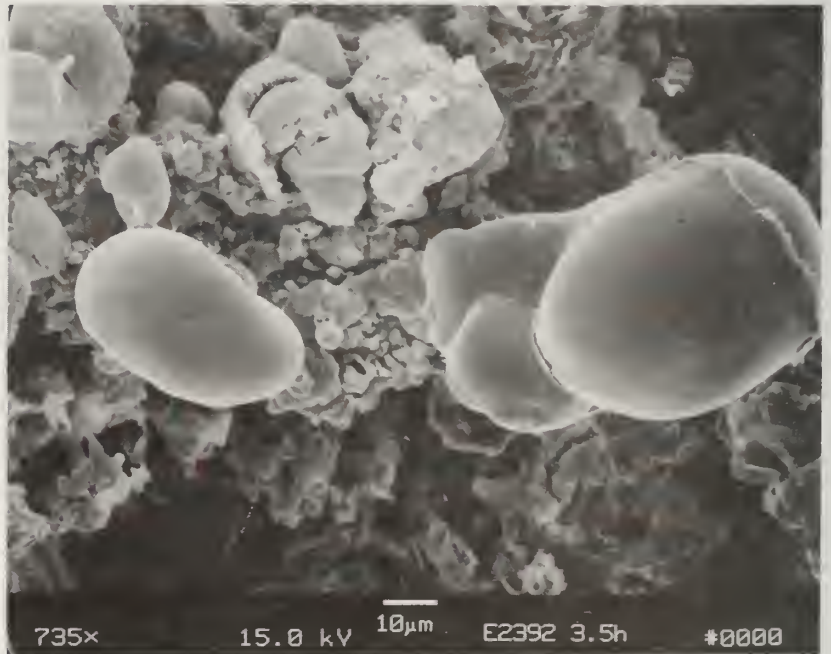
Magnesium chloride ($MgCl_2$; fig. 13), the most common precipitate observed in the core plug after completion of the 15% HCl coreflood experiment, is very soluble in water; it would remain in solution under most reservoir conditions. It likely precipitated during sample drying after completion of the coreflood experiment prior to SEM/EDX analysis. Although not a factor under reservoir conditions, the presence

Table 5 Composition of effluent from HCl coreflow: Energy Field sample, 2,392.6-foot depth, Budmark 2 Morgan Coal well

Effluent sampled at	<i>mg/l</i>					
	Al	As	B	Ba	Be	Ca
1 hour	26.5	0.2	0.26	2.18	0.004	8250
2 hours	250	.1	0.11	0.68	.001	1550
2 days	56.4	.1	0.1	0.83	0.002	3130
	Cd	Co	Cr	Cu	Fe	
1 hour	0.04	0.40	8.1	19.4	109	
2 hours	0.46	0.46	11.1	10.6	409	
2 days	.01	0.34	15.1	9.21	158	
	K	La	Li	Mg	Mn	Mo
1 hour	9	0.52	0.19	92.6	15.4	40.8
2 hours	7	0.19	0.47	177	4.09	21.2
2 days	6	0.28	0.12	48.5	7.49	15.4
	Na	Ni	Li	Mg	Mn	Mo
1 hour	895	131	08	0.010	.1	17.8
2 hours	168	57.4	0.14	0.009	.1	15.7
2 days	154	49.4	0.04	0.022	.1	19.2
	Sr	Ti	Tl	V	Zn	Zr
1 hour	17.1	0.10	.1	0.02	1.64	0.07
2 hours	1.63	0.13	.1	0.70	1.74	0.07
2 days	2.35	0.11	.1	0.20	0.80	0.10



a

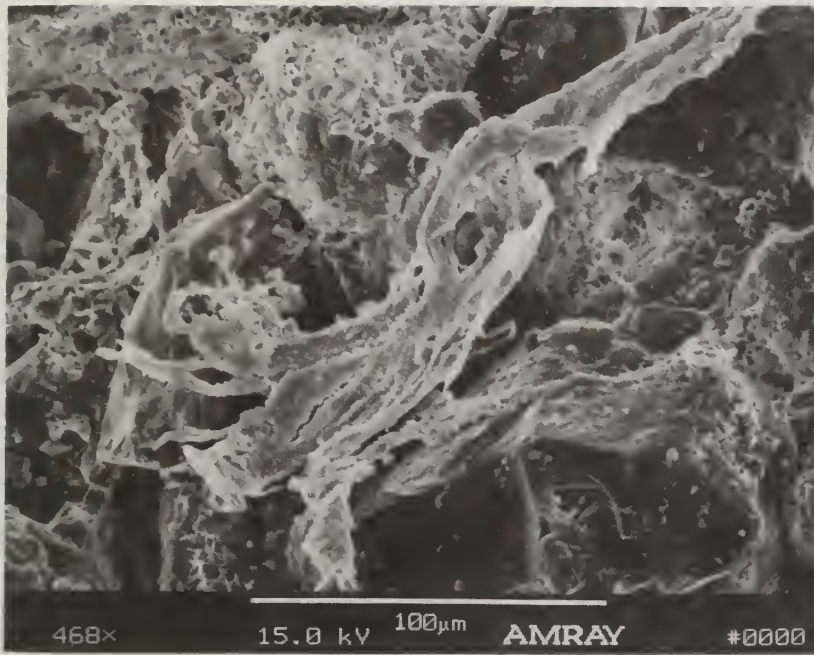


b

Figure 12 SEMs illustrate the effects of soaking Aux Vases core plug wafers (2,392.4-ft depth, Budmark 2 Morgan Coal, Energy Field) in a 15% HCl solution without any of the additives found in MCA. The most common precipitates in these samples are shown in figures 12a–c.

a) Gypsum crystals precipitated because of the reaction of pore minerals and formation brine with 15% HCl. EDX analysis shows that S and Ca are the predominant detectable elements in these crystals.

b) Blebs that do not display any crystalline structure and appear to be an amorphous or gel-like substance containing Fe and Cl, as identified by EDX analysis. (The EDX unit used in this study detects elements with atomic numbers of 6 or greater.)



c



d

c) In another amorphous material, EDX analysis has identified Ca, Cl, Al, Si, and Fe. All these precipitates are attributed to the reaction of pore minerals and formation brine with 15% HCl because they have not been observed in any untreated samples.

d) The smooth quartz grains without their original clay mineral coatings (fig. 3b) indicates widespread removal, disintegration, or dissolution of diagenetic clay minerals—the effects of long-term soaking in 15% HCl.

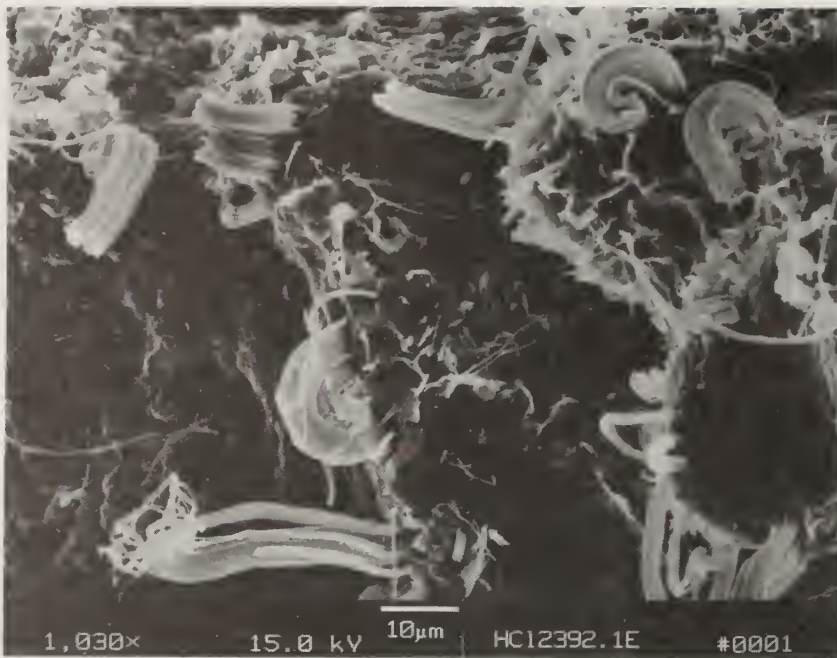


Figure 13 SEM of magnesium chloride ($MgCl_2$), a precipitate evolving from the reaction of 15% HCl and pore minerals during the core flow experiment. Both $MgCl_2$ and halite have a ramshorn morphology; $MgCl_2$ was identified by EDX analysis. Because of its high solubility in water, the magnesium chloride probably formed after the coreflood experiment when the sample (2,393.5-ft depth, Budmark 2 Morgan Coal, Energy Field) was drying.

of $MgCl_2$ shows that large amounts of magnesium were leached from the samples during the experiments (fig. 13). The source of the magnesium could be chlorite, dolomite, or both.

Soaking Experiments Using 15% HCl

Soaking experiments were conducted with 15% HCl and a core plug from the same well (Budmark no. 2 Morgan Coal) and depth (2,392.5 ft) as the core plug used in the 15% HCl core flow experiment for Energy Field. The soaking experiments are saturation tests that more closely resemble the conditions of incompletely swabbed zones of the reservoir, in contrast to the constant injection coreflood tests. In coreflood experiments, the opportunity for precipitation of minerals due to the reaction of stimulation fluids with minerals in the reservoir samples was more limited; fluids were constantly flushed through the pore system, thus diluting and transporting any reaction products out of the sample in the effluent. In the soak experiments, there was no flushing of fluids through the pores of reservoir samples; therefore, the opportunity for mineral precipitation was greater than it was in the coreflood experiments. If the rock remains unflushed, it is likely that any precipitates would remain as pore occlusions.

The soaking experiments resulted in precipitates that evolved from the reaction of pore-lining minerals with 15% HCl. Greater abundance and variety of potential pore-occluding precipitates were found in wafers soaked in 15% HCl than in samples soaked in MCA, or in core plugs flooded with ten or more pore volumes of 15% HCl or MCA.

As the SEM/EDX analyses indicated, the precipitates that formed during the core soak experiments included gypsum, microcrystalline iron chloride, microcrystalline aluminosilicates, and other microcrystalline phases containing significant amounts of chlorine but no other detectable elements (figs. 12a–d). None of these minerals or compounds have been observed in untreated reservoir samples. With the exception of the gypsum, a common low temperature evaporite mineral, none of these precipitates has an obvious crystal morphology. Instead, they have a botryoidal or gel-like appearance, as shown in figure 12b. The lack of identifiable crystal morphology may be attributed in part to the short time available for crystallization, and the low temperature and pressure conditions of the experiments. Such conditions sometimes result in the formation of mineraloids or gels, which are amorphous natural solids that show no signs of crystallinity (Hurlbut 1971).

The lack of carbonates in samples soaked for more than 4 hours suggests that porosity and permeability may increase under reservoir conditions. The experiments also show that disintegration or dissolution of pore-lining clay minerals can occur when they are exposed to 15% HCl for 6.5 hours (fig. 12d) or longer. Migration of disintegrated clay minerals and fine-grained material dislodged by calcite dissolution can occlude permeability. Thus, the net effect of acid-treatments in reservoir rocks with little or no calcite may be to reduce the permeability.

The potential for adverse reactions when 15% HCl or poorly formulated MCA is used in well completion treatments is confirmed by the data in table 6 (adapted from Economides and Nolte 1989). The table lists minerals found in Aux Vases reservoir samples and shows their relative reactivities with and likelihood for exposure to introduced fluids under reservoir conditions; for example, although 65–90% of the typical reservoir sample was composed of quartz, it has a low likelihood of exposure to introduced fluids because most Aux Vases quartz grains are coated with diagenetic clay minerals. Quartz also has a very low reactivity to HCl; therefore, the diagenetic clay minerals, not the quartz grains, have more exposure to reservoir fluids. Of the common minerals in Aux Vases reservoir sandstones, calcite is the

Table 6 Reactions of Aux Vases Sandstone minerals with well fluids*

Mineral	Exposure to fluids	Solubility in 15% HCl	Chemical composition	Released
Quartz	Low	Insoluble	SiO ₂	None
K-feldspar	Low to med	Low	K(AlSi ₃ O ₈)	K ⁺¹ , Al ⁺³ , Si ⁺⁴
Na-feldspar	Low to med	Insoluble	Na(AlSi ₃ O ₈)	None
Illite	High	Low	(Fe,Mg)K _x Al ₂ (Si _{4-x} ,Al _x)O ₁₀ (OH) ₂	K ⁺¹ , Al ⁺³ , Si ⁺⁴
Mixed-layered	High	Low	(Fe,Mg)K _x Al ₂ (Si _{4-x} ,Al _x)O ₁₀ (OH) ₂	K ⁺¹ , Al ⁺³ , Si ⁺⁴
Illite/smectite		Low	(½Ca,Na)·7(Al,Mg,Fe) ₄ - (Si,Al) ₈ O ₂₀ (OH) ₄ ·nH ₂ O	Ca ⁺² , Na ⁺¹ , Fe ⁺² , Mg ⁺² , Al ⁺³ , Si ⁺⁴
Chlorite	High	Low to med	(Mg,Fe) ₅ (Al,Fe)(Al,Si ₃ O ₁₀)(OH) ₈	Mg ⁺² , Fe ⁺² , Al ⁺³ , Si ⁺⁴
Calcite	Low to high	High	CaCO ₃	Ca ⁺² , CO ₃ ⁻
Magnesian dolomite	Low	High	(Ca,Mg,Fe)CO ₃	Mg ⁺² , Fe ⁺² , Ca ⁺² , CO ₃ ⁻
Rutile	Low	Insoluble	TiO ₂	None
Barite-celestite	Low	Insoluble	(Ba,Sr)SO ₄	None
Solid H-carbon	Low to med	Med	C,OH,H,S,N	C ⁺⁴ , S ⁺⁴
Pyrite	Low	Insoluble	Fe ₂ S	None

*Adapted from Piot and Pertuis (1989).

most reactive to 15% HCl. Ferroan calcite, dolomite, and ferroan dolomite, when present, are also highly reactive carbonates, but are less common than calcite. As a comparison of table 6 with table 4 shows, Aux Vases reservoir rocks contain several minerals that release a variety of ions and precipitate as permeability-occluding secondary byproducts. Secondary byproducts observed in samples treated with 15% HCl include gypsum (fig. 12a), gel-like substances rich in chlorides (fig. 12b), amorphous or gel-like material rich in aluminosilicates (fig. 12c), and magnesium chloride (fig. 13).

The gel-like chlorides apparently precipitated or solidified when iron, magnesium, sodium and/or calcium cations combined with chlorine anions and were abundant in soaked samples. These ions would be available from the dissolution of clay minerals and carbonates; the chloride anion was in abundant supply from the 15% HCl (Economides and Nolte 1989). The gel-like aluminosilicates were less common than the gel-like or botryoidal chloride-rich precipitates, a condition that likely reflected the lesser availability of aluminum and silica (table 5) than that of chlorine during the experiments. Most of the amorphous aluminosilicates were composed of aluminum, silica, and minor amounts of sodium, magnesium, potassium, calcium, and/or iron. These elements would have been released by dissolution of diagenetic clay minerals (table 6). Gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) was found in samples soaked for 1.5 hours or more in 15% HCl, but it was never detected in any untreated samples. The likely source of sulfate (SO_4) is the formation brine. Analyses of brines from several Aux Vases reservoirs have detected SO_4 concentrations of 500 mg/L or greater, providing ample SO_4 for gypsum precipitation. Formation brine chemistries and their potential for reaction with injection fluids is discussed in greater detail by Demir (1995).

Oil–Acid Compatibility Tests

Aux Vases crude oil emulsified immediately when 15% HCl was added. After 24 hours at atmospheric pressure and 77°F (25°C), a viscous sludge formed in crude oil samples from Dale Consolidated, Energy, and Zeigler Fields. (An example from Energy Field is shown in fig. 14a.) In contrast, no sludge formed when MCA was added to the same oil (fig. 14b). These results demonstrated that the Aux Vases crude oil from Dale, Energy, and Zeigler Fields is HCl-acid-sensitive. MCA solutions usually contain demulsifying and/or antisludging agents. Without the demulsifying agents, acids react with crude oil to form sludges that can reduce permeability and alter reservoir properties of relative permeability and rock wettability, resulting in reduced oil flow and higher water production (Allen and Roberts 1989). These results indicate that MCA containing appropriate proportions of antisludging chemicals should be used for Aux Vases cleanout operations.

Avoiding Acid-Induced Formation Damage in Aux Vases Reservoir Sandstones

The use of lower concentrations of HCl in MCA to maintain a weaker acidic environment in the reservoir has been suggested as one way of combating formation damage associated with MCA treatments (Simon and Anderson 1990). One operator at Energy Field reduced the acid concentration to 7.5% HCl, but has not observed adverse effects on production from the treatments (Hiram Hughes, Budmark Oil Co., pers. comm. 1992). Despite this, it is recommended that only an MCA properly formulated with appropriate additives be used to avoid potentially deleterious reactions with crude oil and clay minerals. The use of iron-sequestering agents in the MCA is also suggested to prevent iron ions leaching from wellbore tubing or acid reaction with soluble iron-rich minerals.

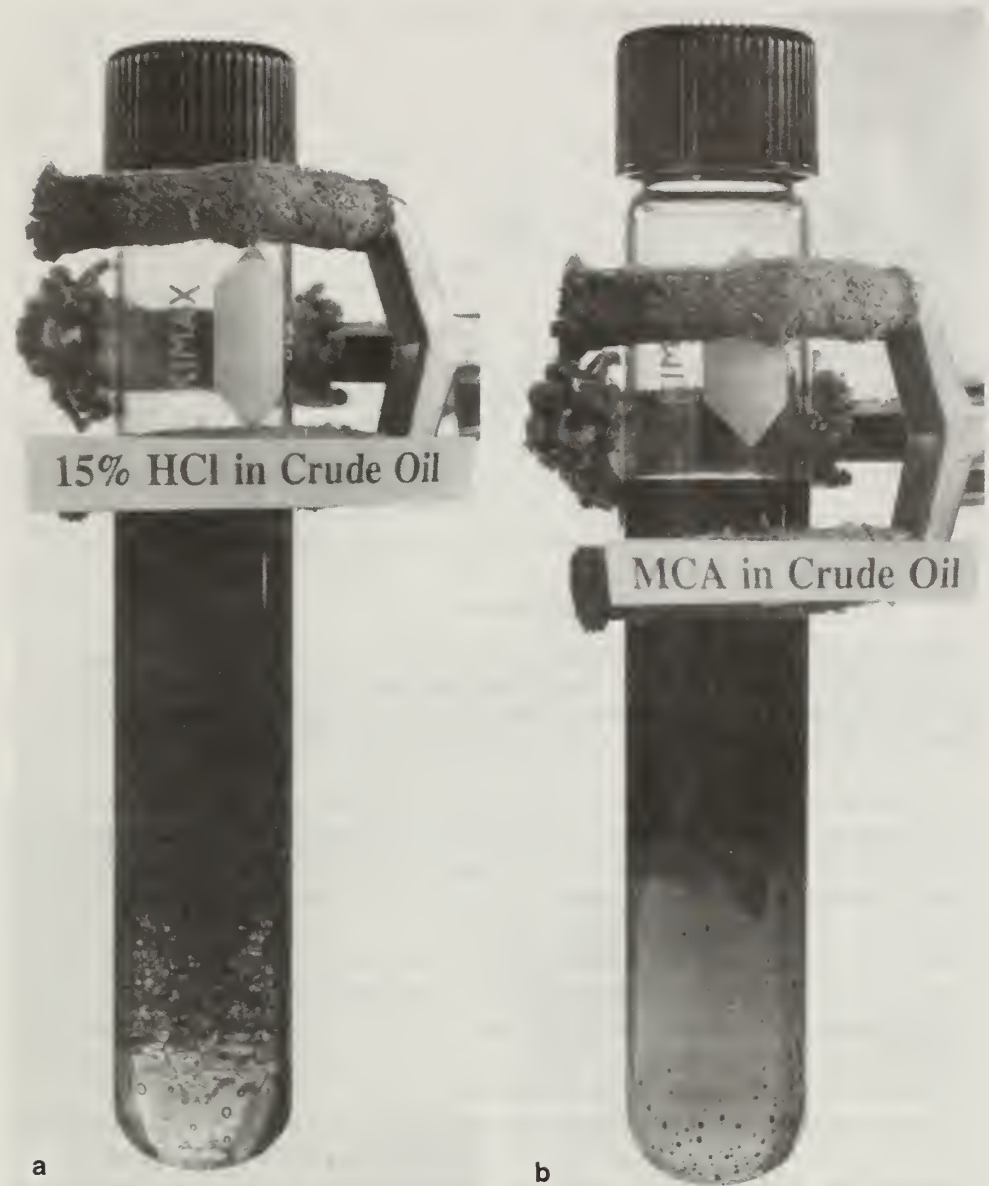


Figure 14 a) Emulsified sludge formed immediately upon contact of Aux Vases oil with 15% HCl. b) When MCA was added to Aux Vases oil, sludge did not form, presumably because of the surfactant in the MCA.

Water Sensitivity of Aux Vases Reservoir Sandstones

Water sensitivity data for Aux Vases reservoir sandstones are sparse. An early study on waterflooding operations in the oil-producing sandstones of Illinois (Whitherspoon 1952) reported the potential for reactions of clay minerals with injected water. Witherspoon cited the work of Grim (1947), a pioneering clay mineralogist, who identified montmorillinite (smectite) as “the worst offender in this respect because of its ability under certain conditions to absorb indefinite amounts of fresh water into its crystalline structure.” However, XRD analyses of Aux Vases sandstone reservoir samples showed illite, chlorite and mixed-layered illite/smectite in appreciable quantities but no pure smectite or kaolinite. Of the clay minerals present in the Aux Vases, only the mixed-layered illite/smectite varieties have been reported to show water sensitivity (Monaghan et al. 1958, Allen and Roberts 1989, Thomas 1985).

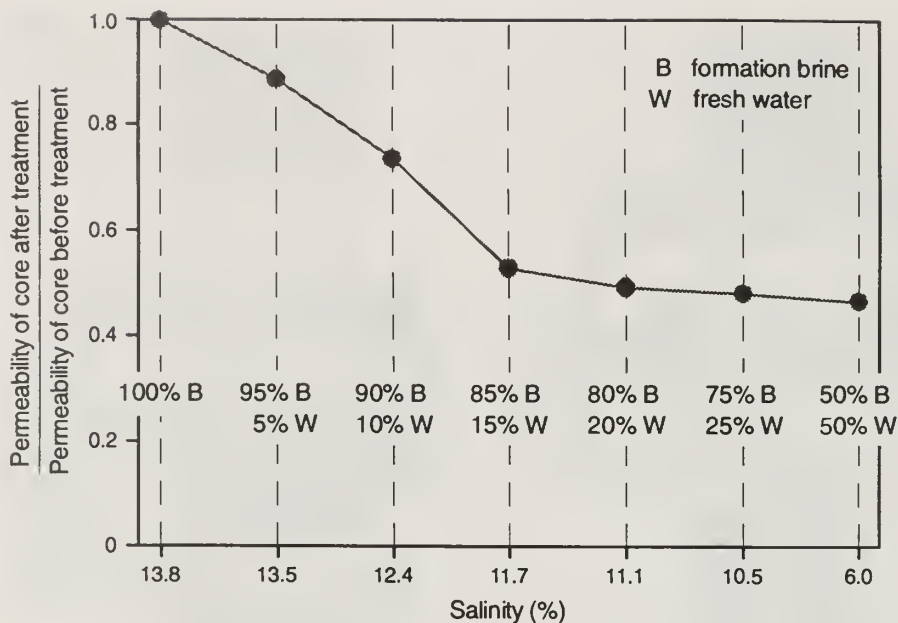


Figure 15 Various mixtures of produced brine and deionized water were injected into a core plug (2,388-ft depth, Budmark 2 Morgan Coal, Energy Field). Decreasing salinity corresponded with decreasing permeability, which suggests that injection of fluids less saline than formation brine can cause formation damage.

Various mixtures of produced brine and deionized water were injected into a sample from the 2,388-foot depth in the Budmark no. 2 Morgan Coal well in Energy Field (fig. 15) in a sequential manner to ascertain the minimum salinity that did not impair permeability. It was found that the addition of 5% deionized water to the brine reduced the permeability to water by 15%, and subsequent mixtures of 50% formation brine and 50% fresh water reduced permeability to water by 52% (fig. 15, table 7). This result showed that (1) all injected waters with salinities below that of the formation brine impaired the permeability of the Energy Field sample, and (2) that the Aux Vases sandstone at Energy Field is very sensitive to brine solutions that are less saline than the formation water.

Permeability values of samples from the 2,163-foot depth of the Superior Oil no. 9 Sanders well in Boyd Field and the 2,611-foot depth of the Gallagher Drilling Company no. 2 Mack well in Zeigler Field decreased by 61.6% and 7.4%, respectively, when the 100% formation brine was displaced with fresh water (fig. 16, table 8). Initial results for low permeability samples from the 2,390-foot depth of the

Table 7 Water sensitivity of core plug to injection of increasing amounts of fresh water (fig. 15)

% fresh-water	% formation brine	% decrease in permeability
5	95	-14
10	90	-29.2
15	85	-48.7
20	80	-52.9
25	75	-54.7
50	50	-56.0

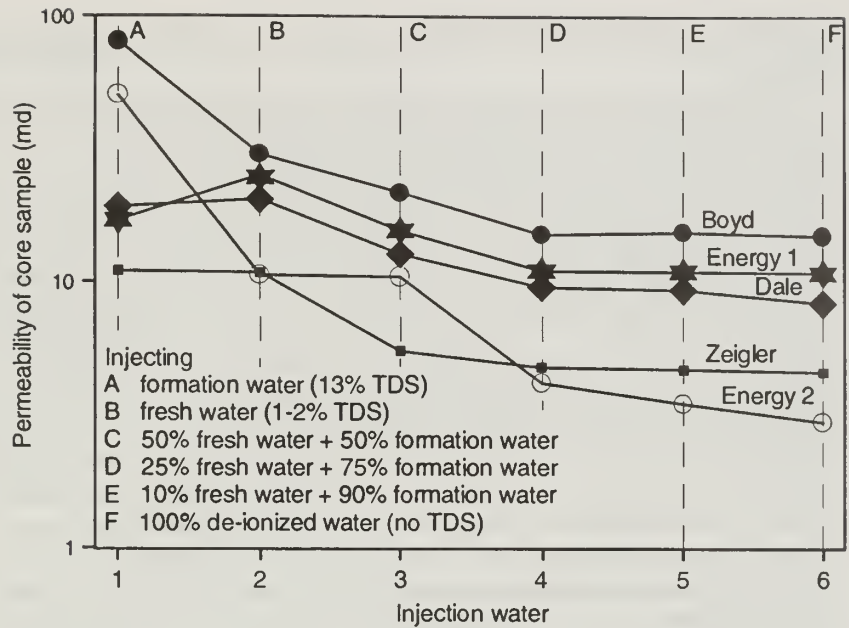


Figure 16 Changes in permeability of core plugs tested with water of varying salinities. The most pronounced decrease occurred in high permeability samples from Energy and Boyd Fields. An early but brief increase in permeability in a low permeability sample from Energy Field was probably due to dissolution of halite precipitated when brine evaporated during air drying.

Budmark no. 2 Morgan Coal well in Energy Field and the 3,200-foot depth of the Farrar no. 1 McCreery well in Dale Consolidated Field varied from this general trend. Permeability values increased from 20 to 30 md when fresh water displaced formation brine from these samples. The experiment was repeated on a core plug higher in permeability—a plug from the 2,388-foot depth of the Budmark no. 2 Morgan Coal well in Energy Field: permeability values initially decreased from 60 to 12 md when formation brine was displaced by fresh water (fig. 16) and did not increase when injected with increasingly saline solutions. The increase in permeability with injection of fresh water in the first Energy and Dale core plugs could have been the result of precipitation of halite crystals from formation brine in the pores of the core sample and their subsequent dissolution in fresh water. Halite has been observed as a

Table 8 Changes (%) in permeability of samples used in water sensitivity corefloods (fig. 16)

Injection fluid	Boyd 2,163-ft depth	Energy 2,388-ft depth	Energy 2,390-ft depth	Dale 3,200.6-ft depth	Zeigler 2,611-ft depth
A Formation water	75 md initial k	47 md initial k	17 md initial k	19 md initial k	12.5 md initial k
B Fresh water	-60.0%	-74.5%	+34.6%	+5.3%	No change
C 50% fresh water 50% formation water	-66.7%	-75.5%	+5.88%	-26.3%	-48.0%
D 25% freshwater 75% formation water	-74.7%	-89.6%	-17.6%	-36.8%	-54.4%
E 10% fresh water 90% formation water	-74.7%	-91.7%	-20.6%	-42.1%	-56.0%
F 100% deionized	-76.0%	-93.6%	-23.5%	-53.7%	-58.4%

k = permeability

pore-filling mineral in some Aux Vases reservoir samples from Zeigler Field (Seyler in prep).

Another purpose of these experiments was to determine whether exposure to fresh water could be followed by injection of water higher in salinity (50% brine plus 50% fresh water), and thus restore permeability to original levels.

Experimental results (fig. 16, table 8) show that permeability was not restored in any of the samples tested. The same result was reported by Monaghan et al. (1958) using sandstone cores from sub-Clarkville Field of east Texas, Frio Field of southwest Texas, and the Cockfield of the Texas Gulf Coast. According to our experimental results, core permeabilities in all the core samples continued to decrease with injection of various mixtures of formation and fresh waters once initially exposed to fresh water. The most likely explanations are that clay minerals permanently swelled with the addition of fresh water or that deflocculated clay mineral crystallites migrated to the pore throats in the samples and constricted fluid flow. Because reverse flow in the plug (at the same rate) resulted in an initial 5% increase in permeability and then a continuous permeability decrease with more flow in the reverse direction, fines migration is most likely (Hewitt 1963).

The fresh-water sensitivity shown by the samples from the four fields (figs. 15, 16, table 8) indicates that injecting an Aux Vases reservoir with brines less saline than the formation brine is likely to impair the permeability of the reservoir. The salinity of the injection water and the formation brine must be equivalent, as shown in the sample from Energy Field (fig. 15), to avoid impairing the permeability of the reservoir. Re-injection of increasingly higher saline solutions did not restore initial permeability; the damage could not be reversed (fig. 16).

CONCLUSIONS AND RECOMMENDATIONS

Experiments on the interactions between well stimulation acids, brines of various salinities, and reservoir rock samples identified the key factors involved in formation damage in the Aux Vases Sandstone. Permeability changes observed during the experiments are summarized in table 9.

Although clay minerals constitute only 1–6% of the bulk mineral content of Aux Vases reservoir samples, they line or bridge every pore of the reservoir. Consequently, determining the composition of these diagenetic clay minerals and their

Table 9 Summary of experimental results

Experiment	Figures	Change in permeability
Crude oil/15% HCl	14	(Decrease)*
Crude oil/MCA	14	(No change)*
Continuous corefloods with MCA	8 and 9	Increase 0–60%
Continuous coreflood with HCl	11	Increase up to 30%
Discontinuous coreflood with MCA	7	Increase up to 600%
HCl soak	12a–d	Could not measure
MCA soak	4b and 4d	Could not measure
Water sensitivity		
Gradual increase in freshwater	15	Decrease 15–56%
Boyd (2,163-ft depth)	16	-60.0% to -76.0%
Energy (2,388-ft depth)	16	-74.5% to -93.6%
Energy (2,190-ft depth)	16	+34.6% to -23.5%
Dale (3,200.6-ft depth)	16	+5.3% to -53.7%
Zeigler (2,611-ft depth)	16	0 to -58.4%

* Inferred from experiment results, not directly measured.

reactions to drilling, completion, and injection fluids is vital for enhancing oil recovery in the Illinois Basin.

1. In contact with acid, calcite is the most reactive pore mineral in Aux Vases sandstone reservoirs; the second most reactive mineral is ferroan dolomite. No calcite remained in Aux Vases core samples after 4 hours of exposure to MCA consisting of 15% HCl, with or without additives. The dissolution of calcite suggests that use of MCA or a 15% HCl solution may increase the permeability of Aux Vases sandstone reservoirs; however, the negative effects of acid treatment on the intimately intergrown mixture of mixed-layered illite/smectite, chlorite, and illite may reduce reservoir permeability.

Our experiments showed that the precipitates derived from the reaction of pore minerals with 15% HCl were greater in variety and quantity than those formed by a commercially formulated MCA; 15% HCl alone should not be used in treating Aux Vases reservoirs.

2. Fines were detected in the effluent from the coreflood experiments. Removal of calcite cement by MCA allowed sand, silt, and clay particles to be dislodged and migrate. These fines are likely to be deposited in pore throats, thus reducing permeability. Dissolution of localized calcite cement in a sandstone may also cause collapse and washout of sandstone around the wellbore.

3. The static soak experiments suggest that prolonged contact of acid with the reservoir rock could result in leaching and disintegration of pore-lining diagenetic clay minerals and the precipitation of pore-plugging material. Rock-acid contact times of less than 1 day created less precipitate material than those exceeding 2 days. In addition, the greater abundance and variety of pore-occluding precipitates in samples soaked in 15% HCl, rather than in MCA, demonstrated another advantage of using MCA.

4. Results of oil-acid compatibility tests demonstrated that oil samples from Aux Vases reservoirs in Boyd, Energy, and Zeigler Fields are acid-sensitive. However, no sludges were formed when crude oil was mixed with MCA. This suggests that the MCA used in these experiments was compatible with the crude oil, whereas a 15% HCl solution without additives was not.

5. In Aux Vases reservoir rocks, the intergrown diagenetic clay minerals, especially the mixed-layered illite/smectite, reacted adversely to the salinity of injected waters. Injection of water less saline than the formation brine impaired permeability, slightly to severely. Injection of increasingly saline water did not restore permeability. To avoid permeability impairment in Aux Vases reservoirs, oil field operators should only inject wells with waters as saline as the formation brines.

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APPENDIX I Petrographic Analyses

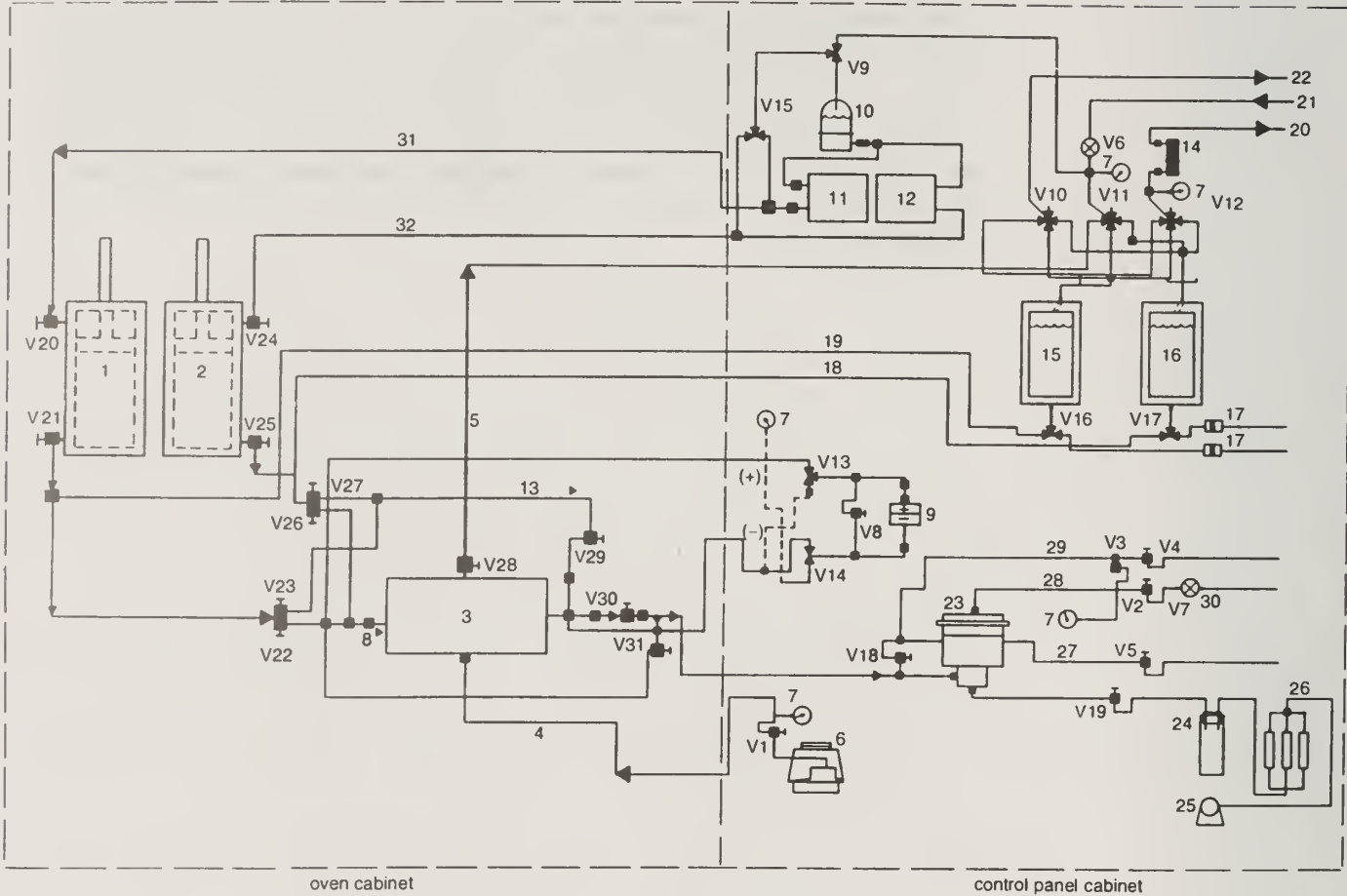
Thin section billets were impregnated with epoxy under vacuum at low temperatures. After preparation, the thin sections were stained with potassium ferricyanide and alizarine red to highlight distribution of carbonate phases.

All SEM/EDX analyses were performed on an Amray 1830 equipped with a Noran (Tracor Northern) Z-MAX 30 Series EDX. SEM analyses were used to identify pore-lining minerals; the EDX was used for analysis of elemental composition. Samples were sputter-coated with gold and palladium.

XRD analyses provide semiquantitative data on mineralogical composition of select samples and were prepared according to ISGS standard operating procedures. The XRD analyses were carried out on a Scintag^R diffraction system using copper radiation and a liquid-nitrogen-cooled germanium detector. Clay mineral determinations were made from smear slides of clay separates (μ), which were analyzed after air-drying, then solvated with ethylene glycol, and analyzed again after heating at 572–662°F (300–350°C) (Hughes and Warren 1989). Further details are available in the manual of standard operating procedures (Oil and Gas Section, ISGS 1993).

APPENDIX II Core Analyses

The TEMCO integrated coreflood apparatus consists of a coreholder placed in an oven cabinet and connected to a confining pressure pump and gauge, water and oil supplies, a pair of oil and water recycling cylinders, an inlet pressure transducer and gauge, a backpressure regulator and gauge, a nitrogen gas supply cylinder, a wet test meter, several rotameters, and pressure valves (fig. A-1) (Oil and Gas Section, ISGS 1993).



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|---|---|---|
| 1 oil rodde cylinder | 22 vent line | V12 vacuum valve |
| 2 water rodde cylinder | 23 back pressure regulator | V13 positive transducer valve |
| 3 core holder | 24 effluent collection burette | V14 negative transducer valve |
| 4 confining pressure fluid-in line | 25 wet test meter | V15 rodde cylinder drain valve |
| 5 confining pressure release line | 26 rotameters | V16 clear cylinder fill valve, oil-base |
| 6 confining pressure pump | 27 back pressure regulator bleed | V17 clear cylinder fill valve, water-base |
| 7 pressure gauge | 28 back pressure regulator in line | V18 BPR outlet valve |
| 8 injection fluid to core line | 29 back pressure regulator equilibrium line | V19 effluent outlet valve |
| 9 differential pressure transducer | 30 external BPR port | V20 rodde cylinder inlet valve, oil-base |
| 10 micro pump fluid reservoir | | V21 rodde cylinder outlet valve, oil-base |
| 11 injection fluid micro pump, oil-base | V1 confining pressure valve | V22 forward flow core inlet valve, oil-base |
| 12 injection fluid micro pump, water-base | V2 BPR in valve | V23 reverse flow core inlet valve, oil-base |
| 13 reverse flow line | V3 BPR equilibrium valve | V24 rodde cylinder inlet valve, water-base |
| 14 vacuum vapor trap | V4 BPR release valve | V25 rodde cylinder outlet valve, water-base |
| 15 external oil clear cylinder | V5 BPR monitoring valve | V26 forward flow core inlet valve, water-base |
| 16 external water clear cylinder | V6 air pressure regulator valve | V27 reverse flow core inlet valve, water-base |
| 17 input fluid filters | V7 BPR release regulator valve | V28 confining fluid purge valve |
| 18 input transfer line, oil-base | V8 zero transducer valve | V29 reverse flow control valve |
| 19 input transfer line, water-base | V9 rodde cylinder utility valve | V30 forward flow outlet valve |
| 20 vacuum line | V10 vent valve | V31 reverse flow outlet valve |
| 21 air pressure line | V11 air valve | |

Figure A-1 Temco integrated coreflood apparatus

