CLAY TECHNOLOGY AND WELL STIMULATION

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ABSTRACT

Pores in sedimentary rocks may be lined or filled with a variety of different clay minerals. These clays can greatly reduce permeability, increase acid or fresh-water sensitivity, totally alter the electric log response, and increase irreducible water saturations. The composition of the clays is of great importance in reservoir management. Different clays have different compositions, and thus will react differently to various drilling and completion fluids. As a result, fluids should be designed for the specific variety of clay present in the pores.

Four families of clay minerals exist, and each causes different reservoir problems: (1) kaolinite is primarily responsible for the migration-of-fines problem associated with many reservoirs, (2) smectite can be extremely sensitive to fresh water, (3) illite increases pore tortuosity, and (4) chlorite is very acid sensitive. If well stimulations are designed without a knowledge of the type of clay minerals present in the pores, rapid production declines may occur after treatment. In some instances, the damage is permanent. In other instances, a new, properly designed acid job may result in dramatic increases in flow. Therefore, in designing a mud system, a frac job, or even a waterflood project, it is vital to know what sort of clays occur in the pores of the reservoir rock.

INTRODUCTION

Reduction in primary porosity by cementation and compaction during early burial is inevitable in most sediments. For example, sand when deposited has a very high porosity (30% to 40%) and permeability (several thousand millidarcies). Subsequent post-depositional changes result in a dramatic reduction of original porosity and permeability, and a consequent reduction in reservoir quality. This reduction results from the deposition of secondary minerals in the sediment pores. Clay minerals are of particular importance in this regard.

Clay minerals are fine-grained (less than 4 microns), platy to rod-like silicates. They are of considerable importance because they have resulted in more "bad" wells than probably any other type of precipitate. There are good wells and there are bad wells. Many bad wells are bad because of poorly designed mud systems and poorly designed frac jobs. In designing a mud system, a frac job, or even a waterflood project, it is vital to know what sort of clays occur in the rock pores. The presence of clay minerals in rock pores can totally alter the electric log response. For example, a log may indicate that a sandstone is water saturated, and yet the well may produce water-free oil. This is commonly a result of the presence of authigenic clays which bind water to the framework grains. Clay minerals in pore spaces can also control the acid and fresh-water sensitivity of a sand. Many an acid job has been ruined because the geologist or engineer failed to recognize the important role of certain clay minerals in the pore spaces of a sandstone.

When we talk of clays in sedimentary rocks, we must take into account where and how they occur. Clay minerals can occur as pore-linings (Figure No. 1). These pore-linings are of great significance for two reasons: (1) even a thin pore-lining can effectively block a pore throat. A sandstone may have good porosity and zero permeability because of the presence of such a pore-lining. (2) Pore-linings are 100% in contact with drilling, stimulation, and recovery fluids. These pore-linings may completely coat individual detrital grains in a sandstone. Thus in designing an acid job or a mud system, the detrital grains in the sandstone (quartz, feldspar, micas) may be of little or no consequence. What is important is the material which is in 100%

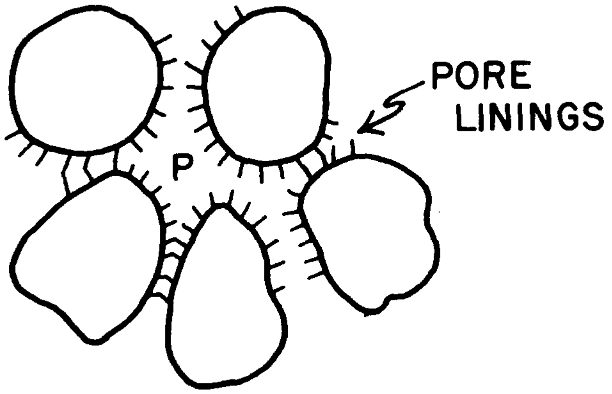

FIGURE 1 PORE-LININGS DEVELOPED AS COATS OVER FRAMEWORK GRAINS, REDUCING THE SIZE OF THE PORE (P) AND OCCLUDING MANY OF THE PORE-THROATS. PORE-LININGS RECEIVE THE GREATEST EXPOSURE TO DRILLING AND COMPLETION FLUIDS.

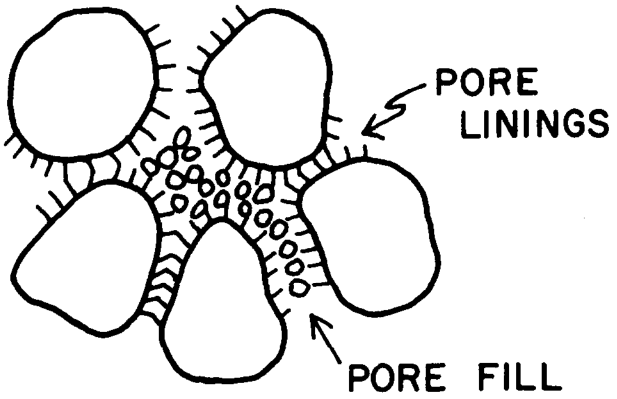

FIGURE 2—PORE-FILL CEMENTS DEVELOPED WITHIN THE PORES OR THE PORE THROATS. PORE-FILLS MAY OR MAY NOT SUCCEED EARLIER GENERATIONS OF PORELININGS.

contact with the fluid—that is the authigenic pore-lining.

Clay minerals (and other non-clay precipitates) can also occur as loose pore-fill aggregates (Figure No. 2). The pores themselves may or may not have a pore-lining.

Clay minerals possess a high surface area to volume ratio (Table 1). This is a reflection of their atomic structure. Clay crystals are generally platy or rod-like, and are also very small. Thus, when compared with quartz, clays have an exceedingly large surface area (Table 1, Figure No. 3). Consequently, clay minerals tend to react readily and rapidly with fluids introduced into a sedimentary rock. They react more rapidly and more vigorously than detrital grains of quartz, feldspar, etc., because of their smaller size and larger surface area.

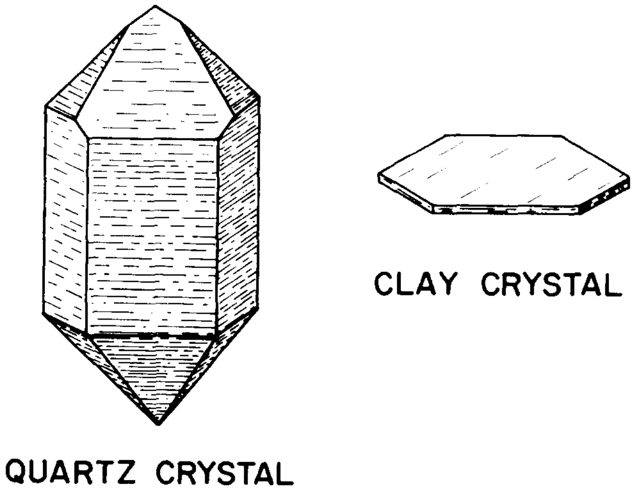

FIGURE 3 A CRYSTAL OF QUARTZ AND A CRYSTAL OF CLAY. THE CLAY CRYSTAL IS MUCH SMALLER THAN THE QUARTZ CRYSTAL, AND HAS A VERY HIGH SURFACE AREA TO VOLUME RATIO. IT IS THUS HIGHLY SUSCEPTIBLE TO ATTACK BY MOVING FLUIDS.

CLAY COMPOSITION AND RESERVOIR MANAGEMENT

The composition of the clay pore-linings and pore fills is of great importance in reservoir management. Different clay minerals have different compositions. Because of this, different clay minerals will react quite differently to different fluid and acid treatments. I would like to look now at the principal

TABLE 1—SURFACE AREA OF 1 GRAM OF QUARTZ COMPARED WITH SURFACE AREAS OF 1 GRAM OF DIFFERENT CLAY MINERAL VARIETIES (MEASURED BY NITROGEN ABSORPTION)

SURFACE AREAS

QUARTZ	**0.15 cm^2/gm**
KAOLINITE	**22 m^2/gm**
SMECTITE	**82 m^2/gm**
ILLITE	**113 m^2/gm**
SEPIOLITE	**392 m^2/gm**

clay minerals found in sandstone and carbonate reservoirs, and to discuss the particular production and completion problems posed by each of these families of clay minerals (Table 2). It is important to remember that these are clay mineral families. Each family contains several different members, which can vary among themselves, particularly in terms of their respective morphologies. Different members of each family may also show differences in chemical composition. Thus the rate of reaction between clays and completion fluids may vary significantly even within a single family.

TABLE 2 MAJOR CLAY MINERAL FAMILIES AND THEIR IMPORTANT CHEMICAL ELEMENTS

CLAY MINERAL	IMPORTANT ELEMENTS
KAOLINITE	**Al Si O H**
SMECTITE (Montmorillonite)	**Na Mg Ca Al Si O H (±Fe)**
ILLITE	**K Al Si O H**
CHLORITE	**Mg Fe Al Si O H**

Kaolinite Family

Kaolinite is a hydrated alumino silicate (Table 2). It is thus very stable from a chemical point of view. It will react to acid in nearly the same way that quartz reacts (or should I say fails to react). Thus acid and acid jobs have no real effect on kaolinite. Yet kaolinite poses production problems in sandstones for two main reasons: (1) its loose attachment to the host grains, and (2) the large size of individual particles. Kaolinite is attached only very loosely to the surface of the host grain. Fluid turbulence within a pore can rip the delicately attached kaolinite from its substrate. This is particularly true in areas of high fluid turbulence, e.g., close to the wellbore. The loosened kaolinite will migrate to the pore throat, where it will lodge and act as a check valve because of the large size of the individual crystals of which it is made.

The principal engineering problem in kaolinite-rich sands is one of the migration of fines. This problem is easily resolved through use of any of the clay stabilization systems (such as polyhydroxy aluminum), as long as the treatment is carried out early in the history of a well.

Smectite Family

The term smectite refers to a whole group of water-sensitive clays. The clay mineral montmorillonite is one of the members, and the term montmorillonite is in common usage in the oil industry. However, it is wise to remember that all water-sensitive clays are not montmorillonite. Several other clays are water-sensitive and are included in the smectite family. Smectite is a hydrated alumino silicate which may also contain Ca, Mg, Na, and Fe (Table 2). It is water-sensitive; the degree of sensitivity to a large extent depends on the amount of sodium in the structure. Production problems in smectite-lined sandstones are two-fold: (1) the clay can be extremely water-sensitive, and (2) the structure of the clay results in high microporosity. This results in high irreducible water saturations which can cause a log to read water wet, although the well can still produce water-free oil. Swelling of the clays, due to the addition of fresh water into the pores, will result in a sealing-off of the pore-throats and a resulting loss of permeability. Smectites rich in sodium can swell by 600% to 1,000% of their volume.

Swelling problems can be overcome through use of oil-based or KCl drilling systems. If water-swelling has occurred in a sandstone, due to poor engineering, the addition of weak hydrofluoric acid together with appropriate chelating agents may improve production through dissolving the smectite.

Illite

Illite also is a hydrated silicate, which contains K and Al (Table 2). It can form in several shapes (or morphologies) and may be intimately associated with smectite. The main engineering problem posed by illite is that its development in a sandstone creates large volumes of microporosity. This microporosity can bind water to the host grains and result in high irreducible water saturations. Illite sometimes grows in pores as masses of long, hair-like crystals, which can considerably reduce the permeability of a sediment. If these "hairy" illites are not dissolved prior to production, they may break during production and migrate to the pore-throats and act as a check valve.

Illite may be dissolved using an acid mixture consisting of hydrochloric and hydrofluoric acid.

Chlorite

Chlorite, also a hydrated alumino silicate, often contains high amounts of Fe and Mg. It is extremely sensitive to acid and to oxygenated waters. Indeed it dissolves readily in dilute HCl. When exposed to acid treatment, it will dissolve and the iron liberated during dissolution will reprecipitate as a gelatinous ferric hydroxide, $Fe(OH)_3$, when the acid is spent. This ferric hydroxide has a large crystal size. It is generally bigger than the pore throats and cannot pass through them. This possible iron-precipitation problem can be avoided if the appropriate chemicals are added to the acid (an oxygen scavenger and an iron chelating agent) and if care is taken to recover all the acid introduced into the well. If ferric hydroxide has been precipitated in the sands due to a poorly designed acid job, it can be removed by treatment with weak HCl (5%) together with appropriate iron chelating agents and an oxygen scavenger. It is important to recover all the acid before it is spent.

OCCURRENCE IN SANDSTONE PORES

It is possible to have several different varieties of clay mineral in a single sandstone pore, and one may coat a preceding variety. Such an occurrence can cause problems in designing mud systems and frac jobs for individual wells. In a like manner, different sands within a single formation may have different diagenetic pore-linings and pore-fills. Thus each sand may require its own uniquely designed drilling fluid and completion treatment. Let us look at an actual example—a Gulf Coast Paleocene formation which has three different sands within a few hundred feet of each other (vertically). In the uppermost sand, the pores are lined with kaolinite with an illite/smectite pore-coating on top. Locally the pores are also filled with dolomite. This uppermost sand has two main engineering problems: (1) migration of fines and (2) fresh-water sensitivity. A KCl or oil-based drilling system is necessary, together with a polyhydroxy aluminum additive (CLASTA or an equivalent) to prevent migration of fines. An acid job would not damage this sand. The middle sand contains no smectite, just kaolinite. Thus this sand is not water sensitive, but does have a migration-of-fines problem. The lowest sand in the formation contains abundant pore-fill chlorite. It also contains pore-fill calcium carbonates. This sand is extremely acid sensitive. Addition of mud clean-up acid (MCA), such as 15% HCl + 5% HF, or even small amounts of HCl as an acid spearhead on a frac job will severely damage this reservoir sand, unless a chelating agent and oxygen scavenger are added and care is taken to ensure that all the acid is rapidly removed from the hole.

Let us look at another example, in which reservoir damage was suffered because of poor engineering practice. The wells were frac'd using crude oil as a carrying agent. Prior to fracing, 250 gal of 15% HCl was used. From these data it is easy to conclude that the field engineers were worried about (1) swelling clays and (2) carbonate cement. Following the frac job, productivity declined from an average per well output of 250 BOPD to 10 BOPD. SEM analysis of the sand revealed the presence of clay pore-linings of high iron chlorite, pore fills of iron oxide, pyrite, and calcite. Further analysis of the calcite revealed it to be of the high-iron variety. Indeed the acid did its job. It dissolved the pore-lining and pore-fill minerals liberating large amounts of iron. The iron reprecipitated as a gelatinous ferric hydroxide in the pore throats, causing the dramatic reduction in productivity. What should be done? This damage is reversible, and was reversed in this instance through the use of 5% HCl and 5% HF plus an iron chelating agent and an oxygen scavenger.

It is important to note here that the presence of several different clay minerals in a sandstone pore may require several different additives. For example, consider a rock with pores containing chlorite and kaolinite. Stimulation of this well requires a weak acid (HCl) and an iron chelating agent (probably citric acid) to dissolve the chlorite. It also requires a clay stabilizing compound to prevent the migration of the kaolinite. The HCl, citric acid, and clay stabilizing compound should not be mixed together and introduced into the well as a single mixture. Rather, the treatment procedure should be as follows:

1. Run HCl plus iron chelating agent
2. Flush with water

3. Run a trailer with clay stabilizing compound

ROLE OF BULK ANALYSIS

From the preceding discussion, it should be fairly obvious that it is important not only to know what the composition of the clay mineral is but how and where it is distributed. To do this it is necessary to undertake both scanning electron microscope (SEM) analysis and X-ray diffraction analysis. SEM analysis allows us to determine *where* the clays are located—are they in the pores, or are they interlaminated with the sand grains? X-ray diffraction analysis allows us to determine exactly *what* clay minerals are present.

It is currently fashionable for clay analysis to be carried out using bulk X-ray diffraction analysis. Bulk X-ray diffraction analysis involves X-raying the whole sediment sample—hence the term bulk analysis. *Bulk* X-ray analysis is largely useless for accurate determination of clay minerals in rock pores for the following reasons:

1. Clay minerals are very poor reflectors of the X-ray beam. X-ray analysis of a bulk sandstone sample will yield good results for the major mineral components (quartz, etc.), but the clays will be ignored. Clay minerals require special treatment prior to analysis—treatment which is not given in bulk analysis.
2. X-ray diffraction is accurate to only 5% to 10%. When clays occur in sandstones or carbonates, they generally comprise less than 10% of the total rock. Thus X-ray analysis of the bulk sample will not yield an accurate determination of the volumetrically minor components—such as clay minerals.
3. Bulk X-ray analysis does not tell you whether the clays are in the pores or in interlaminae. Figure No. 4 is a schematic representation of a sandstone consisting of alternating laminae of sand and shale. The shale is composed largely of detrital kaolinite. The sand consists of detrital quartz with a thin coating of diagenetic smectite. Bulk X-ray analysis of this rock would yield high kaolinite and insignificant smectite. However, note that although the smectite is quantitatively minor, it will be in 100% communication with any fluids introduced into this rock. The critical question is not "How much smectite is there in this rock?" Rather we should ask "Where is the smectite, and how much effect will it have on artifically introduced fluids?" Many a waterflood project has failed to live up to expectations because bulk X-ray results were used in designing the waterflood.

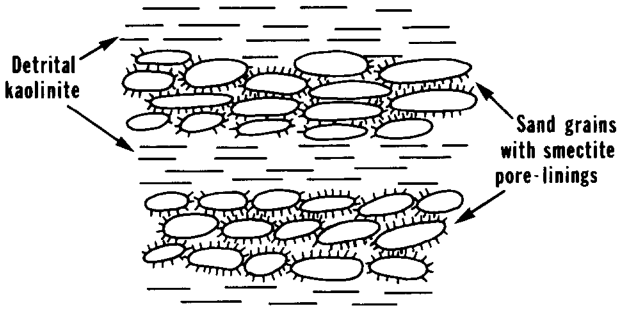

FIGURE 4 SCHEMATIC DIAGRAM OF A BULK SANDSTONE SAMPLE CONSISTING OF SAND GRAINS WITH INTERLAMINATED CLAYS. NOTE CLAYS (DASHED AREAS) ARE COMPOSED DOMINANTLY OF KAOLINITE, WHILE THE SANDS CONTAIN PORE-LININGS OF SMECTITE. BULK X-RAY ANALYSIS OF THIS SAMPLE WOULD INDICATE SMECTITE AS A QUANTITATIVELY NON-SIGNIFICANT COMPONENT. HOWEVER, ANY FLUIDS INTRODUCED INTO THIS SAMPLE WOULD BE 100% IN CONTACT WITH THE SMECTITE, NOT THE KAOLINITE. SERIOUS WATER-SENSITIVITY PROBLEMS WOULD ARISE IF FRESH WATER WERE PASSED THROUGH THE PORES OF THIS SANDSTONE.

This discussion does not mean that X-ray diffraction analysis should not be used for clay mineral determination. What it means is that *bulk* X-ray diffraction analysis should not be used. The clays must be separated from the sands prior to analysis, and only the clay-size material should be analyzed by X-ray diffraction. Meaningful X-ray analyses are obtained through analyzing only the fine-grained-size fraction of the sands (generally either the less-than-5-micron or less-than-2-micron size). The differences between bulk X-ray analysis and analysis of the fine-grained fraction are startling.

For example, bulk X-ray analysis of 75 sandstone samples of a West Texas formation revealed no smectite and low amounts of illite, chlorite, and kaolinite (Table 3). Based on these results, the company concerned commenced a waterflood project. Problems were encountered soon after the project was underway. Subsequent analysis of the less-than-5-micron-size fraction of the same samples revealed the presence of water-sensitive smectite (Table 4). (Note the considerable differences between Tables 3 and 4.)

TABLE 3—AVERAGE VALUES FOR X-RAY DIFFRACTION ANALYSIS OF BULK SAMPLES FOR 75 SANDSTONE SAMPLES FROM ONE FORMATION

ILLITE	SMECTITE	CHLORITE	KAOLINITE	OTHER MINERALS
2%	0	1%	trace	97%

TABLE 4—AVERAGE VALUES FOR X-RAY DIFFRACTION ANALYSIS OF LESS-THAN-5-MICRON SIZE FRACTION OF THE SAME 75 SANDSTONE SAMPLES LISTED IN TABLE 3

ILLITE	SMECTITE	CHLORITE	KAOLINITE	OTHER MINERALS
16%	6%	5%	trace	73%

In another actual example, 80 ft of oil saturated Tertiary sand was penetrated in a Gulf Coast well. Samples were analyzed at 20 ft intervals in the sand. Bulk X-ray analysis revealed that the only clay present was chlorite and that it was present at two horizons only. The analysis also revealed the presence of carbonates (Table 5). On the basis of this analysis the well was acidized with 15% HCl. Before treatment the well was tested at 400 BOPD. After treatment the well tested at 100 BOPD. X-ray diffraction analysis of the less-than-5-micron-size fraction reveals that chlorite is an extremely important constituent of the sand, some horizons containing up to 75% high-iron chlorite (Table 5).

TABLE 5—COMPARISON OF BULK X-RAY DIFFRACTION ANALYSIS AND LESS-THAN-5-MICRON SIZE FRACTION X-RAY DIFFRACTION ANALYSIS OF A SINGLE TERTIARY SAND PENETRATED IN A GULF COAST WELL

Depth	Size Fraction Analyzed	Chlorite	Illite	Anhydrite	Carbonate
10510 ft	BULK	0%	0%	20%	15%
	<5μ	20%	0%	10%	30%
10530 ft	BULK	10%	0%	-	30%
	<5μ	75%	10%	-	Trace
10550 ft	BULK	0%	0%	-	15%
	<5μ	45%	10%	-	15%
10570 ft	BULK	10%	0%	-	15%
	<5μ	60%	15%	-	5%
10590 ft	BULK	0%	0%	-	5%
	<5μ	60%	15%	-	5%

The reduction in production was due to the precipitation of iron hydroxide in the pore system of the reservoir. SEM analysis revealed that the chlorite in the reservoir was present as pore coatings which were perfectly placed to react with the acid introduced to remove the calcium carbonate cement.

The formation damage caused by the precipitation of iron hydroxide from the spent, unrecovered acid more than canceled any benefit derived from the removal of calcium carbonate cement.

RECOMMENDED ANALYTICAL PROGRAM

Any analysis of the fluid sensitivity of any formation should consist of three steps:

1. *Bulk Sediment Analysis*—This is essential in order to know the overall composition of the rock. X-ray diffraction analysis should be avoided. Instead it is recommended that bulk analysis be carried out by petrographic analysis of thin sections. This enables an accurate determination to be made of the volumetric abundance of the minerals in the carbonate or sandstone.
2. *X-Ray Diffraction Analysis of Less-Than-5-Micron Fraction*—This analysis will reveal the exact mineralogy of the clays in the reservoir.
3. *Scanning Electron Microscope Analysis*—This analysis reveals where the clays are located—in the pores or as interlaminae. It is strongly recommended that the SEM used be fitted with its own X-ray unit (generally referred to as an EDAX or Energy Dispersive X-ray System). The built-in EDAX unit enables the analyst to determine the qualitative chemical composition of the pore-lining and pore-fill minerals. Without the attached EDAX unit, the analyst is forced to rely on the morphology of the clay minerals to distinguish one from the other. It is true that different clays can have different crystal shapes; however, *sometimes* kaolinite, smectite, and illite have the same shape and cannot be distinguished by visual observation using the SEM. More often than not, clays in sediment pores have such a poor morphology that they cannot be visually identified. The EDAX unit attached to an

SEM enables the analyst to get an instant qualitative analysis of the clay in the pore.

CONCLUSIONS

Clay minerals may be grouped into several different families—kaolinite, smectite, illite, and chlorite being the most important. Each clay variety causes a different problem in reservoir rocks (Table 6). No one treatment will solve all clay problems. Each clay family has its own chemical composition, which is different from the composition of the other families. Thus each clay mineral has its own degree of sensitivity to different fluids, and each has to be treated differently.

TABLE 6—MAJOR CLAY MINERAL FAMILIES AND THE SPECIFIC RESERVOIR ENGINEERING PROBLEMS CAUSED BY EACH FAMILY

CLAY MINERAL	MAJOR RESERVOIR PROBLEM
KAOLINITE	MIGRATION OF FINES
SMECTITE	WATER SENSITIVITY MICROPOROSITY
ILLITE	MICROPOROSITY
CHLORITE	ACID SENSITIVITY

Any analysis of the fluid sensitivity of a formation should involve three steps:

1. Bulk sample analysis using a thin section, not X-ray diffraction.
2. X-ray diffraction analysis of the fine-grained fraction (less-than-5-micron or 2-micron size).
3. Scanning electron microscope (SEM) analysis using an SEM fitted with an energy dispersive X-ray system.

Three points should be made in conclusion.

1. It is important to tailor drilling and stimulation techniques to suit the needs of a particular sandstone. Designing and using proper mud systems and frac jobs can be expensive. But do not be cent wise and dollar foolish. The long-term benefit far outweighs the short-term cost.
2. There are bad wells and bad wells. Some are bad because the reservoir is poor. Others are bad because we have ignored the composition of the clay minerals in the pores. Our inattentiveness to detail has made them bad.
3. Effective and efficient reservoir exploration and exploitation demands an understanding of the clays in the reservoir rock.