ACIDIZATION—VI

ON THE EQUILIBRIUM RELATIONSHIPS AND STOICHIOMETRY OF REACTIONS IN MUD ACID

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Abstract—A method is presented for determining the distribution of reaction products and the stoichiometric coefficient for the reaction of mud acid (HF/HCl) with various minerals To illustrate the techniques, the dissolution of two common alumino–silicates, potassium feldspar and kaolinite, in mud acid is investigated for various temperatures and acid concentrations After determining the product distribution from the ionic equilibrium relationships involving the various fluoride ion complexes, the stoichiometric coefficient [moles HF consumed per mole mineral dissolved] is arrived at through a numerical solution of the coupled equilibrium and mole balance equations The HF acid stoichiometric coefficient was found to decrease significantly with increasing temperature and HCl acid concentration This information is of great importance in determining design conditions for the matrix acid stimulation of oil reservoirs

1 INTRODUCTION

Acidization is the process of injecting HF/HCl into petroleum reservoirs In previous papers in this series on acidization, the kinetics of the reaction of HF and HCl acid mixtures with some of the more common minerals found in sandstones have been discussed[1–3] along with the experimental techniques and correlations for the acidization of linear cores[4, 5] A linear model has been developed which predicts the movement of the permeability and acid fronts through sandstone cores as well as predicting the overall permeability as a function of acid injection time[6] A radial model describing injection of acid into well reservoirs has also been presented[7]

In order to obtain a fuller description of the acidization it is necessary to determine the distribution of reaction products along with the stoichiometric coefficient as a function of temperature and acid concentration The stoichiometric coefficient referred to in this work is defined as the number of moles of hydrofluoric acid consumed per mole of mineral dissolved Our previous work concentrates solely on Phacoides sandstone, a feldspathic quartzite, and in order to extend the linear and radial models to other sandstones to predict changes in permeability resulting from acidization, knowledge of the stoichiometric coefficient is required Information about the variation in the stoichiometric coefficient with mud acid concentration and temperature is of vital importance in designing acid stimulations to determine how much and in what proportions mud acid must be injected

The typical sandstones of interest in our studies were composed primarily of quartz, feldspars and clays It has been shown that during acidization the clays and feldspars, which are both alumino–silicates, dissolve at a much faster rate than the quartz as the acid flows through and reacts with the porous media It is primarily the removal of these alumino–silicates that increases the porosity and permeability and hence the productivity of the formation The expenditure of the acid has been observed to be dependent upon the temperature of the formation, the content of the minerals and clays, and the relative ratio of the acid concentrations mixed together Therefore, if one has knowledge about the extent of dissolution of these commonly found alumino–silicate minerals as a function of temperature and initial acid concentrations, one can determine the amount dissolved for a given composition and temperature and what is the most suitable combination of HF and HCl acids to be mixed together

In this paper we shall present a method for determining the product distribution and stoichiometric coefficients for reactions of mud acid To illustrate the technique we shall determine these quantities for the dissolution of each of two pure alumino–silicates, potassium feldspar and kaolinite, in HF/HCl acid mixtures as a function of acid composition and temperature In addition we shall show how one can use the values of these stoichiometric coefficients for the dissolution of these two pure materials to estimate the coefficient of a composite sandstone undergoing acidization at a particular temperature
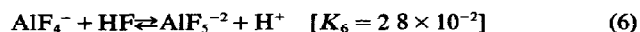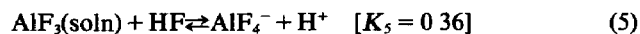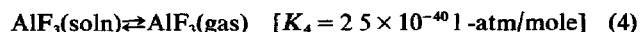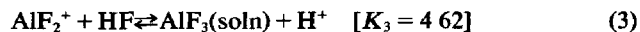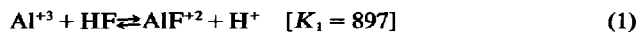
2 DETERMINATION OF THE STOICHIOMETRIC COEFFICIENTS

In order to determine the stoichiometric coefficients, we must first determine the distribution of products resulting from the reaction of hydrofluoric acid with alumino–silicates After achieving this through evaluation of the ionic equilibrium relationships involving the various fluoride complexes, one can perform mole balances on the fluoride and hydrogen ions to arrive at the stoichiometric coefficient for the reaction of HF and the specified mineral

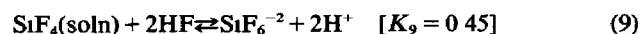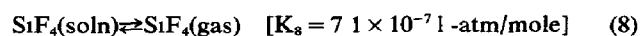### (a) *Ionic equilibrium relationships*

When HF is used to dissolve common clays and minerals containing aluminum and silicon atoms in the
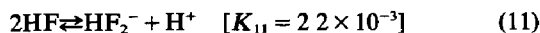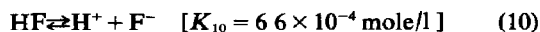
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crystal lattice, fluoride complexes of aluminum and silicon are produced in solution The dissolved aluminum can form six complexes with fluorine The reactions for the formation of these complexes along with the corresponding equilibrium constants at 25°C are given below [8–12]

$$Al^{+3} + HF \rightleftarrows AlF^{+2} + H^+ \quad [K_1 = 897] \quad (1)$$

$$AlF^{+2} + HF \rightleftarrows AlF_2^+ + H^+ \quad [K_2 = 68\ 9] \quad (2)$$

$$AlF_2^+ + HF \rightleftarrows AlF_3(soln) + H^+ \quad [K_3 = 4\ 62] \quad (3)$$

$$AlF_3(soln) \rightleftarrows AlF_3(gas) \quad [K_4 = 2\ 5 \times 10^{-40}\ l\text{-atm/mole}] \quad (4)$$

$$AlF_3(soln) + HF \rightleftarrows AlF_4^- + H^+ \quad [K_5 = 0\ 36] \quad (5)$$

$$AlF_4^- + HF \rightleftarrows AlF_5^{-2} + H^+ \quad [K_6 = 2\ 8 \times 10^{-2}] \quad (6)$$

$$AlF_5^{-2} + HF \rightleftarrows AlF_6^{-3} + H^+ \quad [K_7 = 1\ 9 \times 10^{-3}] \quad (7)$$

The formation of the silicon fluoride complexes of primary interest are described by the following relationships

$$SiF_4(soln) \rightleftarrows SiF_4(gas) \quad [K_8 = 7\ 1 \times 10^{-7}\ l\text{-atm/mole}] \quad (8)$$

$$SiF_4(soln) + 2HF \rightleftarrows SiF_6^{-2} + 2H^+ \quad [K_9 = 0\ 45] \quad (9)$$
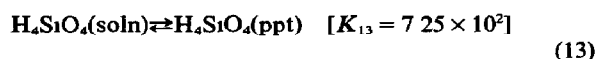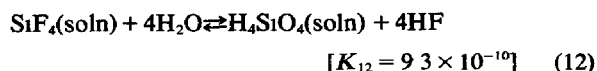
The dissociation of HF in the presence of H^+ as well as the association of HF in concentrated solutions should be considered

$$HF \rightleftarrows H^+ + F^- \quad [K_{10} = 6\ 6 \times 10^{-4}\ mole/l] \quad (10)$$

$$2HF \rightleftarrows HF_2^- + H^+ \quad [K_{11} = 2\ 2 \times 10^{-3}] \quad (11)$$

Under appreciably high pressure, which is the case for stimulation of underground oil reservoirs, the gases produced in eqns (4) and (8) can be considered to be insignificant

The formation of compounds such as $AlCl_3$ and $SiCl_4$ can be ignored, owing to the fact that their free energies of formation are significantly lower than those of the corresponding fluoride complexes However, it is thermodynamically feasible for other compounds such as K_2SiF_6, Na_2SiF_6, Na_3AlF_6, K_3AlF_6 and CaF_2 to precipitate when their solubility products in solution are exceeded These solubility products are listed in Appendix A together with their standard heats of dissolution in aqueous medium at 25°C These precipitates are more likely to form during the initial phases of the dissolution, since high concentrations of HF favor the precipitation of these species which become soluble as the HF is consumed However, the formation of another compound, H_4SiO_4, becomes important when the HF initially present is nearly consumed and the solution has a relatively high concentration of SiF_4 Under these conditions it is possible to precipitate H_4SiO_4 during the dissolution of the alumino–silicates, i e

$$SiF_4(soln) + 4H_2O \rightleftarrows H_4SiO_4(soln) + 4HF$$
$$[K_{12} = 9\ 3 \times 10^{-10}] \quad (12)$$

$$H_4SiO_4(soln) \rightleftarrows H_4SiO_4(ppt) \quad [K_{13} = 7\ 25 \times 10^2] \quad (13)$$

Combining eqns (12) and (13) one obtains the following relationship

$$SiF_4(soln) + 4H_2O \rightleftarrows H_4SiO_4(ppt) + 4HF$$
$$[K_{14} = 6\ 75 \times 10^{-7}] \quad (14)$$
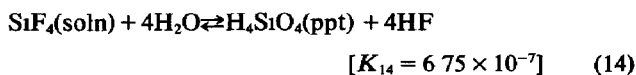
After rearranging in the form, H_4SiO_4 precipitation occurs when the concentrations of HF and SiF_4 are such that

$$\left[\frac{2\ 84 \times 10^{-2}}{HF} \right]^4 [SiF_4] \geq 1 \quad (15)$$

we can easily see that the chance of precipitating H_4SiO_4 increases greatly with the depletion of hydrofluoric acid

(b) *Effect of temperature*

The above equilibrium relationships can be extrapolated to other temperatures with the aid of Van't Hoff's equation as

$$K_i(T) = K_i(T_0) \exp \left[+\frac{\Delta H_{Ri}}{R} \left(\frac{1}{T_0} - \frac{1}{T} \right) \right] \quad (17)$$

In this study the base temperature is 25°C (i e $T_0 = 298\ 0°K$) To evaluate eqn (17) for each of the reactions, eqns (1)–(13), one must know the heat of reaction at 25°C for each of the reactions as well as the corresponding equilibrium constant at 25°C Determination of the heats of reaction for each of the reactions listed above turned out to be quite a formidable task However, the values determined from literature are listed in Table 1 The subscript refers to the corresponding equilibrium reaction given by eqns (1)–(14)

Table 1 Heats of reaction at 25°C (cal/mole HF)[9, 10]

$\Delta H_1 = -2060$	$\Delta H_2 = -2430$	$\Delta H_3 = -3020$
$\Delta H_4\dagger = +75100$	$\Delta H_5 = -2930$	$\Delta H_6 = -3960$
$\Delta H_7 = -4760$	$\Delta H_8^+ = +35350$	$\Delta H_9 = +3260$
$\Delta H_{10} = -3210$	$\Delta H_{11} = -2080$	$\Delta H_{12}^+ = +38430$
$\Delta H_{13} = -3000$	$\Delta H_{14} = +35430$	

$\dagger$cal per mole AlF_3, + cal per mole SiF_4

It was also determined that the effect of pressure upon the active aqueous species is insignificant and can be neglected At this point it should be noted that reaction (14) is endothermic Consequently precipitation is favored at higher temperatures

(c) *Mole balances during dissolution*

In illustrating the technique we shall first consider the dissolution of one of the common feldspars found in sandstones, K-feldspar in hydrofluoric and hydrochloric acid mixtures The overall reaction is written in terms of HF and H^+ (i e HCl) as

$$KAlSi_3O_8 + xHF + yH^+ \rightarrow K^+ + AlF_n^{+(3\ n)}$$
$$+ 3SiF_m^{+(4-m)} + 8H_2O \quad (18)$$
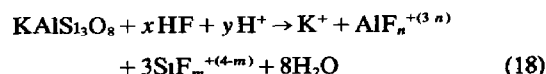
The stoichiometric coefficients x and y are the ratio of

the respective acid consumed per mole of mineral dissolved Mole balances on fluorine (F^-) and hydrogen (H^+) require the following relations to be satisfied

$$F^- \quad x = n + 3m \tag{19}$$

$$H^+ \quad x + y = 16 \tag{20}$$

Combining (19) and (20)

$$y = 16 - n - 3m \tag{21}$$

The subscripts n and m on the Al–fluoride and Si–fluoride complexes are evaluated as a mole average of the individual complex concentrations present in the solution The distribution of these complexes is affected by the HF, HCl acid concentrations actually present through the ionic equilibria given in the previous section The values of n and m are calculated from the equations

$$n = \frac{\sum_{i=0}^{6} i \mathrm{AlF}_i}{\sum_{j=0}^{6} \mathrm{AlF}_j} \tag{22}$$

and

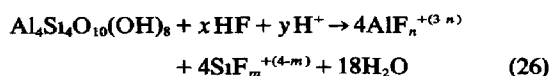$$m = \frac{\sum_{i=4}^{6} i \mathrm{SiF}_i}{\sum_{j=4}^{6} \mathrm{SiF}_j} \tag{23}$$

where (AlF_i) represents the concentration of the complex in moles/l

The total amounts of aluminum and silicon dissolved for the specified mineral are

$$\text{total Al dissolved} = \sum_{i=0}^{6} \mathrm{AlF}_i \tag{24}$$

$$\text{total Si dissolved} = \mathrm{H_4SiO_4} + \sum_{j=4}^{6} \mathrm{SiF}_j \tag{25}$$

It is possible to obtain the distribution of the individual AlF_i and SiF_i concentrations which satisfy the above relationships when the HF and H^+ concentrations are known at a given time during the dissolution Consequently, a numerical trial and error solution is necessary to determine the stoichiometric coefficients at a given extent of dissolution (e g at the start of dissolution or after a certain amount of dissolution has occurred) It is evident that while the ionic equilibria is not affected by the origin of supply of the Al and Si, the atom balances (i e eqns 19 and 20) change from mineral to mineral For example, the dissolution reaction of kaolinite can be written with the accompanying mole balances as follows

$$\mathrm{Al_4Si_4O_{10}(OH)_8} + x\mathrm{HF} + y\mathrm{H^+} \rightarrow 4\mathrm{AlF}_n^{+(3\,n)}$$

$$+ 4\mathrm{SiF}_m^{+(4-m)} + 18\mathrm{H_2O} \tag{26}$$

Fluoride balance $\quad x = 4n + 4m \tag{27}$

Hydrogen ion balance $\quad x + y = 28 \tag{28}$

Combining eqns (27) and (28) the stoichiometric coefficient for hydrogen can be determined from the equation

$$y = 28 - 4n - 4m \tag{29}$$

The quantities m and n are calculated as before from eqns (22) and (23)

3 METHOD OF SOLUTION

Considering the complexity of the dependency of the HF acid consumption on the HF and HCl acid concentrations and the complex fluoride concentrations, a finite difference solution was chosen to evaluate the stoichiometric coefficients, x and y, as a function of the amount of mineral dissolved A brief outline of the method used in this respect is given as follows

First, the initial hydrofluoric and hydrochloric acid concentrations, the type of mineral, and the temperature of dissolution are specified A finite amount of mineral is dissolved and the total Al and Si concentrations liberated are determined The resulting acid concentrations following dissolution are assumed and the individual complex concentrations are estimated using the equilibrium relationships given in eqns (1)–(3), (5)–(7), and (9)–(12) Using these concentrations, the hydrochloric and hydrofluoric acid concentrations are readjusted as follows

$$[\mathrm{HF}] = [\mathrm{HF}]_0 - \sum_{j=1}^{6} j[\mathrm{AlF}_j] - \sum_{j=1}^{2} j[\mathrm{H}_{j-1}\mathrm{F}_j]^- - \sum_{j=2}^{3} 2j[\mathrm{SiF}_{2j}] \tag{30}$$

$$[\mathrm{H^+}] = [\mathrm{HCl}]_0 + \sum_{j=1}^{2} [\mathrm{H}_{j-1}\mathrm{F}_j]^- + \sum_{j=1}^{6} j[\mathrm{AlF}_j] + 2\mathrm{SiF_6^{-2}} \tag{31}$$

Using these new acid concentrations, the individual fluoride-complexes and other soluble species concentrations are recalculated Readjustment of the HF and H^+ concentrations is continued until the acid concentrations between two consecutive iterations converge within a certain value The convergence routine has been found to reduce the computation time significantly compared to the direct-substitution method Using these converged HF and H^+ concentrations, eqns (22) and (23) are employed together with the appropriate fluoride and hydrogen balances for the specified mineral (for the eqns (19) and (20) for K-feldspar, and (26) and (27) for kaolinite), to evaluate the stoichiometric coefficients x and y for HF and HCl with the mineral The amount of dissolved mineral is incremented and new values for the stoichiometric coefficients are determined This iterative type of calculation is carried out until either the available mineral is dissolved, or the individual acid concentration drops below a specified limit A suitable limit might be $0\,01M$ below which no significant dissolution is expected during acidization owing to the low reaction rates at this concentration The hydrated silica ($\mathrm{H_4SiO_4}$) deposition which primarily takes place at reduced HF concentrations in the solution is also computed

4 DISCUSSION OF THE RESULTS

The numerical technique outlined briefly above was used to evaluate the stoichiometric coefficients for the

reaction of mud acid with K-feldspar and with kaolinite for temperatures ranging from 10 to 55°C and for initial HCl acid concentration ranging from 10^{-3} to 10 M

Figures 1 and 2 show the stoichiometric coefficients as a function of the amount of mineral dissolved (expressed as moles of mineral in solution per liter) during the course of the reaction for kaolinite and K-feldspar respectively These figures which correspond to an initial HF concentration of 1 M, show the stoichiometric coefficients for various initial concentrations of HCl at 25°C One observes that the stoichiometric coefficient for HF

Fig 1 Stoichiometric coefficient of kaolinite as a function of initial hydrochloric acid concentration

Fig 2 Stoichiometric coefficient of K-feldspar as a function of initial hydrochloric acid concentration

decreases with increasing HCl concentration That is for a one molar HF solution at 25°C, it initially takes 40 moles of HF to dissolve one mole of kaolinite at a 0 3 M HCl concentration, while it initially takes only 25 5 moles of HF to dissolve one mole of kaolinite for a 10 M HCl concentration One also observes that the stoichiometric coefficient for HF decreases during the course of the reaction and this change is more dramatic for the lower HCl concentrations The stoichiometric coefficient for the consumption of H^+ (HCl) changes from a negative to a positive value during the course of the reaction for initial concentrations below approximately 3 M In other words, hydrogen ions are generated[1] during the first part of the reaction and consumed during the last phase of the reaction for an initial HF concentration of 1 M At high HCl concentration LéChatlier's principle shows that the equilibrium shifts to the left in the reactions (1)–(3), (5)–(7), and (9)–(12) Consequently, the fluoride ion will be bound in the lower number fluoride aluminum complexes (e g AlF^{+2}, AlF_2^+) so that less HF will be consumed At low HCl (i e H^+) concentrations, HF is observed to dissociate to a significant extent (see eqns 10 and 11) in addition to entering into the complex ion equilibrium involving dissolved Al and Si

Figures 3 and 4 show the initial value of the stoichiometric coefficient for HF as a function of the initial concentration of HCl for various temperatures for kaolinite and K-feldspar The values of the stoichiometric coefficients at the start of the dissolution in these figures correspond to a one molar initial concentration of HF It is shown here that the stoichiometric coefficient is a strong function of the HCl concentration in the range of 0 03–3 M HCl for the range of temperatures investigated For example, at an initial HCl concentration of 0 3 M one observes from Fig 3 that 38 moles of HF acid are initially required to dissolve 1 gram mole of kaolinite at 10°C, while only 29 5 moles of HF acid are required to dissolve the same amount of kaolinite at a temperature of 55°C This is a consequence of the fact that most all heats of reaction for the formation of the aluminum–fluoride and silicon–fluoride complexes, reactions (1)–(3), (5)–(7) and (9)–(11), are exothermic Consequently, the equilibrium is shifted to the left producing complexes having a fewer number of fluoride ions as the temperature is increased

At this point, it is of interest to see the effects of non-ideality in estimating the stoichiometric coefficients of minerals An extensive search of the literature was carried out to obtain correlations relating activities of HF and electrolytes to temperature and the ionic strength of the solution The relationships used in the computer program for evaluating the activity coefficients are presented briefly in Appendix B The effects of including the activity coefficient in the calculations to estimates of stoichiometric coefficients of kaolinite and K-feldspar are observed from the dashed lines on Figs 3 and 4 A similar trend is observed for the other minerals and conditions studied However, the absolute values of these estimates of the stoichiometric coefficients show a difference of 20–30% with and without the use of activity coefficients It is of interest to note that the simplified treatment of the dissolution stoichiometry gives a more conservative
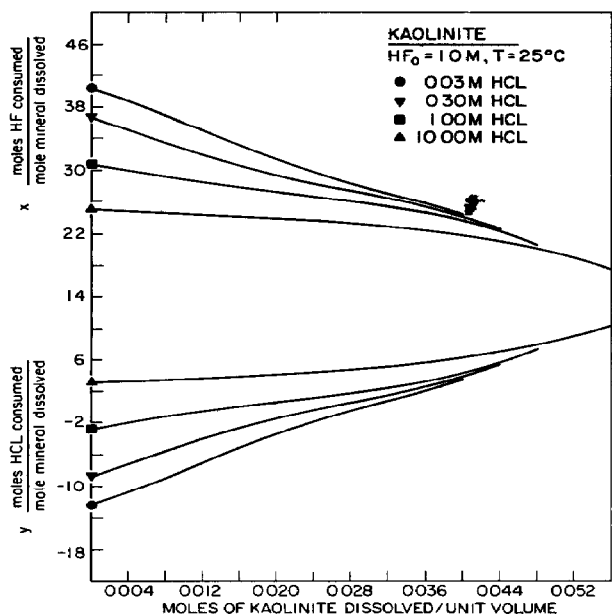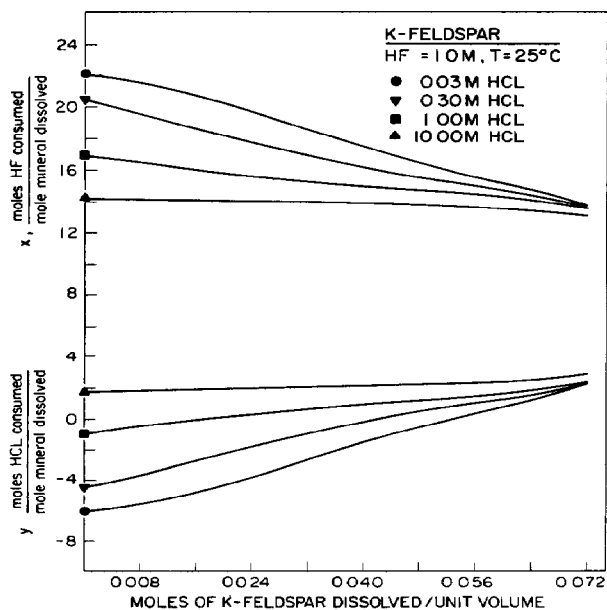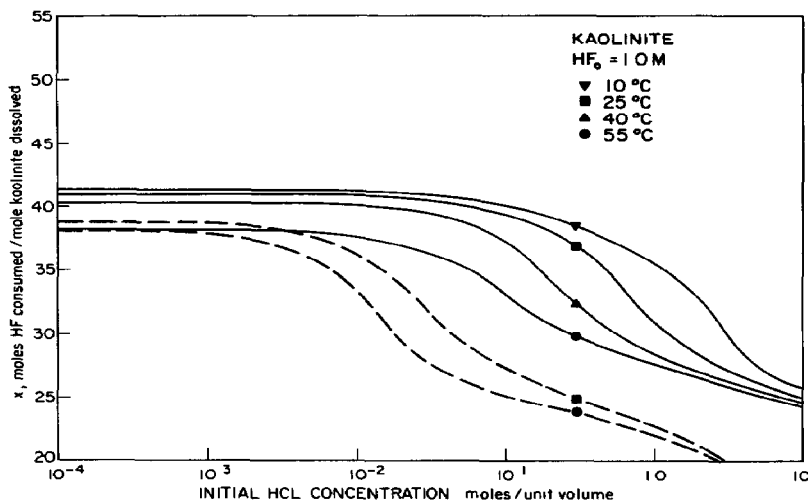
Fig 3 Initial stoichiometric coefficient of kaolinite as a function of temperature and hydrochloric acid concentration initially present
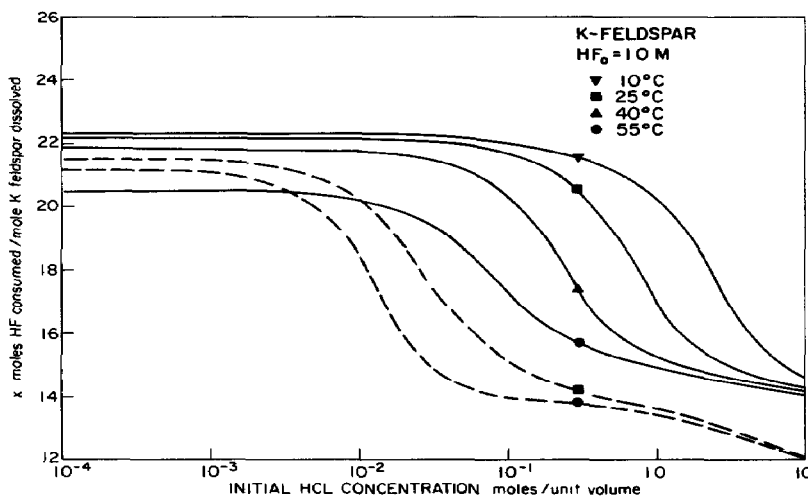

Fig 4 Initial stoichiometric coefficient of K-feldspar as a function of temperature and hydrochloric acid present initially

estimate of the stoichiometric coefficient for the design of acidization jobs than the detailed one using activity coefficients

Figures 5 and 6 show the HF stoichiometric coefficient as a function of initial HCl concentration for various temperatures and initial concentrations of HF for kaolinite and K-feldspar respectively Overall, the effect of the initial HF concentration on the stoichiometric coefficient is that the HF consumed per mole of mineral dissolved increases with increasing HF concentration initially present This is a direct result of the increased dissociation of HF at higher HF concentrations (see reactions 10 and 11)

The effect of precipitate formation on the dissolution stoichiometry was found to be insignificant Only two of the salts are relatively important because of their low solubility products, namely K_2SiF_6 and CaF_2 If the K_2SiF_6 precipitates during dissolution of K-feldspar at 25°C, the following change in stoichiometry is typical of

what is observed For $1\,0\,M$ HF/$1\,0\,M$ HCl mixture, the stoichiometric coefficient changes only from 16 2 to 16 6 moles HF/mole of feldspar No precipitate formation should result for acid mixtures with higher HCl concentrations, such as a $1\,0\,M$ HF/$3\,0\,M$ HCl acid mixture Figure 7 shows the moles K_2SiF_6 precipitated during the course of dissolution of K-feldspar at 25°C for a number of acid mixtures At the very start of the dissolution, very little K^+ is in solution so that the solubility product of K_2SiF_6 is not exceeded However, after some dissolution occurs, precipitation is initiated and the amount precipitated increases linearly with the moles of mineral dissolved up to a maximum After this point, the precipitate dissolves, owing to the decrease in the SiF_6^{-2} concentration in solution as the HF is consumed by the reaction Comparison of the maximum amounts of precipitate formation shows that the amount of salt precipitated increases as the ratio of HF to HCl is increased in the acid mixture used
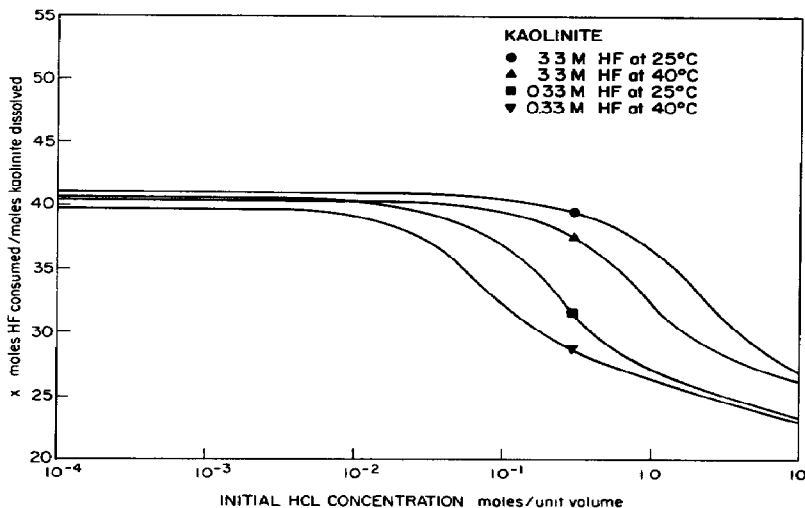
Fig 5 Initial stoichiometric coefficient of kaolinite as a function of temperature and hydrochloric acid concentration initially present
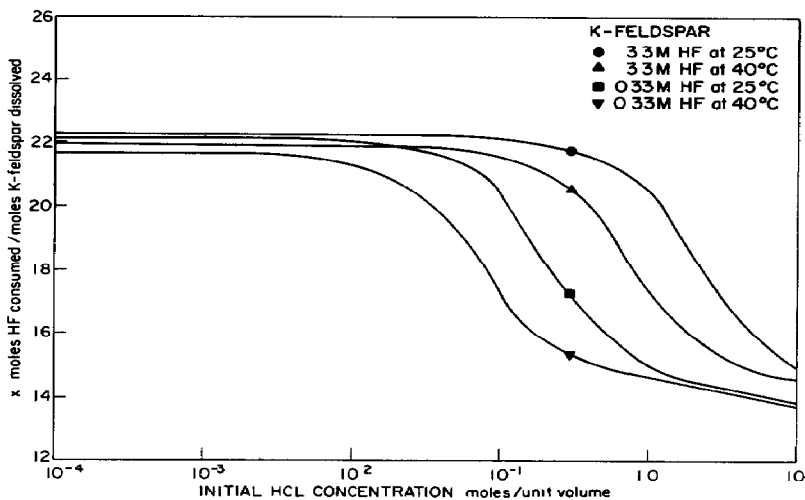

Fig 6 Initial stoichiometric coefficient of K-feldspar as a function of temperature and hydrochloric acid present initially
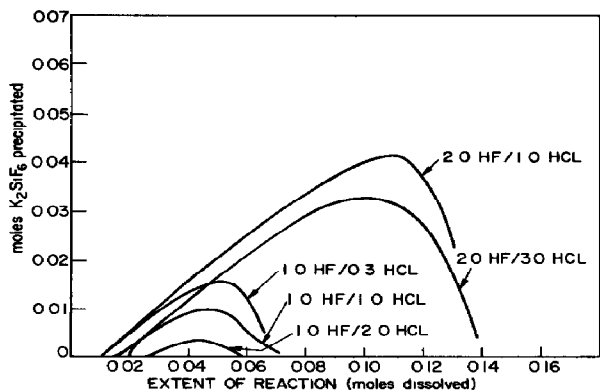

Fig 7 The amount of K_2SiF_6 precipitated during the dissolution of K-feldspar at 25°C for a number of acid mixtures

A permeability drop was observed by Lund[12] during the initial phases of the acidization of Phacoides cores at low acid injection rates and high HF to HCl ratios This reduction in permeability could be a consequence of K_2SiF_6 precipitating and clogging the pores Fluorosilicate salts such as K_2SiF_6 could easily precipitate during acidization since at high HF to HCl ratios, SiF_6^{-2} is favored in comparison to SiF_4 and the dissolution of the feldspar produces cations such as K^+ and Na^+ in solution A way to remove these deposited salts from the pore passages is to post-flush acidized wells with an HCl solution One notes that a striking difference between these fluorosilicate and fluoroaluminate salts and the other well known precipitate, hydrated silica (H_4SiO_4), is that the former class is soluble in HCl, and the latter is not

Experimental values of the stoichiometric coefficients

for the dissolution of potassium feldspar and of kaolinite in mud acid have recently been reported by Labrid[13] Although these results were reported in terms of cubic centimeter of solid mineral dissolved per gram of HF acid consumed, α/ρ, one can easily convert these values to our basis since both the sandgrain densities and molecular weights are known An exact comparison between the experimental and theoretical values is not possible, since the corresponding acid concentration was not reported This may have been a consequence of the fact that the stoichiometric coefficient was believed to be independent of acid concentration However, in Table 2, we have compared the experimental values with the calculated values of the stoichiometric coefficient in the concentration range of 0 01M HCl/1M HF–10 0M HCl/1M HF at 25°C

Table 2 Comparison of experimental and calculated values

| Mineral | Experimental (Ref [13]) | | Calculated (Range) |
	α/ρ $\left[\dfrac{cm^3 \text{ of solid}}{gram\ HF}\right]$	ν $\left[\dfrac{mole\ HF}{mole\ mineral}\right]$	$\left[\dfrac{mole\ HF}{mole\ mineral}\right]$
Kaolinite	0 34	29 2	$17 \leq \nu \leq 38$
K-Feldspar	0 24	22 6	$12 \leq \nu \leq 21$
Na-Feldspar	0 32	15 6	$12 \leq \nu \leq 21$

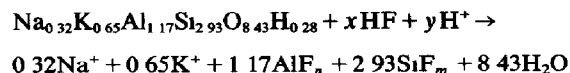As one observes the experimental values fall directly in the range of the calculated values

The technique we have developed for the dissolution of pure alumino-silicates in mud acid can also be applied to the dissolution of sandstone to predict the overall stoichiometric coefficient Once we know the overall stoichiometric coefficient, porosity, and aluminum petrolog for a given sandstone, we can then predict the amount of acid that needs to be injected to achieve a specified increase in permeability[14] Extension of the computational procedure to determine the product distribution and overall stoichiometric coefficient of a sandstone consisting of different minerals will be illustrated for Phacoides sandstone This feldspathic quartzite, which has undergone extensive acidization studies, has the following mineralogical composition

Table 3 Phacoides sandstone Refs [4–6]

	Wt%		
Quartz	80 3%	Inerts	80 3%
Plagioclase	17 5 { 5 9%		
K-feldspar	11 6%	Dissolvables	19 7%
Kaolinite	2 2 { 0 8%		
Illite	1 4%		
	100%		100%

It has been shown that owing to the low reactivity of quartz relative to the other minerals, it can be considered to be essentially inert We shall lump the dissolvable minerals in Table 3 into two groups, feldspars (17 5 wt%) (taken as K-feldspar) and clays (2 2%) (taken as kaolinite) The reaction describing the dissolution of the dissolvable

minerals in Table 3 in 2 00/3 65 wt% HF/HCl mixture is

$$Na_{0\ 32}K_{0\ 65}Al_{1\ 17}Si_{2\ 93}O_{8\ 43}H_{0\ 28} + xHF + yH^+ \rightarrow$$

$$0\ 32Na^+ + 0\ 65K^+ + 1\ 17AlF_n + 2\ 93SiF_m + 8\ 43H_2O$$

Fluoride ion balance $x = 1\ 17n + 2\ 93m$
Hydrogen ion balance $x + y = 16\ 58$

Using the same procedure as for the pure minerals, the overall HF stoichiometric coefficient in ideal solution is estimated to be 17 15 mole HF consumed per mole of rock dissolved at 25°C Assuming a non-ideal solution, the coefficient is changed to 13 66 mole HF consumed per mole of rock dissolved using activity coefficients

However, the number of different mineralogical compositions of sandstones is nearly infinite and it would not be practical to carry out the computer calculations to determine the stoichiometric coefficient of every sandstone considered as a potential candidate for matrix acid stimulation Consequently, it is desirable to obtain estimates of the overall stoichiometric coefficient for a given sandstone of known composition from the stoichiometric coefficients of the pure minerals in the sandstone To estimate the overall stoichiometric coefficient we assume that it is to be given by the sum of the products of the stoichiometric coefficients of the individual minerals and the corresponding mole fraction of that mineral in the sandstone, i e

$$\nu = \sum \nu_i y_i \tag{33}$$

where y_i is the mole fraction of mineral "i" determined from an aluminum petrolog of the sandstone

To illustrate this approximate technique we shall again lump all the feldspars as K-feldspar and all the clays as kaolinite The corresponding weight fractions, W_i, for feldspar and kaolinite, determined from the mineralogical analysis in Table 3 are 0 175 and 0 022 respectively The mole fraction of mineral "i" is

$$y_i = \frac{W_i/M_i}{\sum \dfrac{W_i}{M_i}} \tag{34}$$

For kaolinite

$$y_K = \frac{W_K/M_K}{\dfrac{W_K}{M_K} + \dfrac{W_F}{M_F}} \tag{35}$$

Where M_i is the molecular weight of species "i" and the subscripts F and K refer to Potassium feldspar ($M_F = 278$) and kaolinite ($M_K = 516$), then

$$y_K = \frac{0\ 022/516}{\dfrac{0\ 022}{516} + \dfrac{0\ 175}{278}} = 0\ 0634$$

and

$$y_F = 0\ 9366$$

For a mud acid mixture of 1 0 M in both HF and HCl at

25°C, the corresponding stoichiometric coefficient for kaolinite (Fig 3) is 30 85 and for K-feldspar (Fig 4) is 16 95 The overall stoichiometric coefficient is estimated as

$$\nu = \nu_k y_k + \nu_f y_f = (30\ 85)(0\ 0634) + (16\ 95)(0\ 9366)$$

$$= 17\ 83\ \text{moles HF consumed/mole rock dissolved}$$

If the activity coefficients are used to represent the non-ideality of the acid mixture, the coefficient is estimated to be

$$\nu = (0\ 0634)(22\ 65) + (0\ 9366)(13\ 66)$$

$$= 14\ 23\ \text{mole HF consumed/mole rock dissolved}$$

Comparing the value of the overall stoichiometric coefficient for the sandstone estimated from the coefficients of the individual minerals with the value obtained by considering each of the equilibrium relationships along with eqn (32), we see these values agree quite well The approximate technique for predicting the stoichiometric coefficient of a composite sandstone has also been recently extended to other sandstones with excellent results[14]

SUMMARY

In the above analysis we have found how the HF stoichiometric coefficient in the reaction between mud acid and two alumino-silicates varies with acid concentration and temperature The HF stoichiometric coefficient is defined as the moles of HF acid consumed per mole of mineral dissolved The information obtained in this study is of great importance in the design of the acid stimulation of well reservoirs It was found that the same stoichiometric coefficient can result for two different sets of mud acid concentrations Consequently, one could evaluate which set of mud acid concentrations would be most economically feasible In addition to the economical considerations, the prediction of the overall stoichiometric coefficient for the dissolution of a sandstone is of vital importance in determining the acid capacity number From this number, one can calculate the penetration radius of the permeability front resulting from matrix acid stimulation of the reservoir

In calculating the stoichiometric coefficient we first determined the distribution of the aluminum-fluoride and silicon-fluoride complexes resulting from the dissolution of the mineral using the ionic equilibrium relationships A numerical solution of the coupled mole balance and equilibrium equations was then carried out to determine the stoichiometric coefficient with respect to HF and HCl for the specified mineral dissolution These results were found to agree satisfactorily with previously reported experimental values

The results of this analysis showed that the HF stoichiometric coefficient decreases with increasing temperature In addition it was found to decrease during the course of the mud acid-mineral reaction The most important results of this study are related to the variation of the HF stoichiometric coefficient with HCl concentra-

tion This coefficient was found to be virtually independent of HCl concentration below concentrations of ca 5×10^{-2} M HCl Above this concentration it was found to decrease significantly with increasing HCl concentration

A technique for estimating the overall stoichiometric coefficient for a sandstone from the coefficients of the individual minerals has been found to be in satisfactory agreement with the numerical technique involving the ionic equilibria for the sum of all minerals present which had to be carried out on the computer, for each sandstone composition

NOTATION

I ionic strength of electrolyte solution
K equilibrium constant
m number of fluoride ions complexed with Si (defined by eqn 23)
M molecular weight, m/mole
n number of fluoride ions complexed with Al (defined by eqn 22)
R gas constant (1 99 cal/mole)
T absolute temperature, °K
W weight percent of mineral in the sandstone
x moles of HF consumed/unit mole of mineral dissolved
y moles of HCl consumed/unit mole of mineral dissolved (mole fraction of dissolvable mineral, if subscripted)
z charge of electrolytic species

Greek symbols

α grams mineral dissolved/gram of HF consumed
ν moles HF consumed/mole of mineral dissolved
ρ density, grams/cm^3
ΔH_R standard heat of reaction, cal/mole
γ activity coefficient of species

Subscripts

K kaolinite mineral
F feldspar mineral

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APPENDIX A

Solubility products and standard heats of formation of selected fluoride compounds at 25°C [1, 10]

Species	K_{sp} (at 25°C)	ΔH_R° (kcal/mole)
Na_2SiF_6	$2\ 36 \times 10^{-4}$	10 49
K_2SiF_6	$2\ 08 \times 10^{-6}$	13 53
Na_3AlF_6	$4\ 22 \times 10^{-10}$	10 67
K_3AlF_6	$1\ 25 \times 10^{-7}$	23 45
CaF_2	$1\ 44 \times 10^{-10}$	2 76
MgF_2	$7\ 34 \times 10^{-11}$	−2 08

APPENDIX B

Activity coefficients in HF/HCl acid mixtures

The equilibrium constants used in the evaluation of stoichiometric coefficients were evaluated from the free energies of formation of the species in aqueous solution These constants can be used directly in evaluating the dissolution product distribution in dilute solutions by replacing the activity by the concentration However, for acid concentrations normally used in acidization, this approximation can be misleading, since the activity is then equal to the product of concentration and the activity coefficient The following set of equations were utilized in the evaluation of activity coefficients as a function of temperature in electrolytic solutions

The activity coefficient of HF was correlated [15] as a function of the molality of HF present and the absolute temperature in °K as follows

$$-\log \gamma_{HF} = \frac{A\sqrt{(m_{HF})}}{1\ 0 + B\sqrt{(m_{HF})}} \tag{A1}$$

where

$$A = 7\ 8215 \times 10^{-6} - 3\ 03476 \times 10^{-2}T + 2\ 13476 \times 10^{-4}T^2 \tag{A2}$$

$$B = -3\ 12284 \times 10^{-6} - 2\ 37431 \times 10^{-2}T + 1\ 39795 \times 10^{-4}T^2 \tag{A3}$$

The activity coefficients of electrolytes were evaluated as a function of the ionic strength of the solution proposed in the Debye–Huckel theory of electrolytes [16]

$$-\log \gamma_{\pm} = \frac{C\sqrt{(I)}[z_i]}{1\ 0 + Da\sqrt{(I)}} \tag{A4}$$

where

$$C = 0\ 59414 - 1\ 5074 \times 10^{-3}T + 4\ 1019 \times 10^{-6}T^2 \tag{A5}$$

$$D = 0\ 33659 - 2\ 5417 \times 10^{-4}T + 7\ 6324 \times 10^{-7}T^2 \tag{A6}$$

The value of "a" is taken as an average value of 5 Å for all electrolytic species, and $[z_i]$ is the absolute charge of the specific electrolyte

For concentrated HCl solutions, two additional terms are used for the evaluation of the H^+ ion activity in electrolytic solution [7]

$$-\log \gamma_{H^+} = \frac{C\sqrt{(I)}}{1\ 0 + Da\sqrt{(I)}} + EI + F \tag{A7}$$

where

$$E = -0\ 29529 + 5\ 5123 \times 10^{-4}T \tag{A8}$$

$$F = 1\ 3696 - 1\ 3223 \times 10^{-2}T + 4\ 2895 \times 10^{-5}T^2 - 4\ 6465 \times 10^{-8}T^3 \tag{A9}$$

The value of 4 47 Å is used for "a" in the above equation as evaluated by Robinson [16]