PERFORMANCE OF AMOCO A-SOL® AS A MUTUAL SOLVENT SYSTEM

GEORGE E. KING, Amoco Production Research
TIM M. BROWN, Amoco Chemicals Corporation

ABSTRACT

Laboratory tests and field results on Amoco A-Sol, an extremely versatile mutual solvent system, are presented in comparison with a commonly used mutual solvent system. Data contained in the report include corrosion inhibitor performance in A-Sol, special acid mixtures, maximum temperature limits, and special additives to aid in stimulating formations which produce asphaltic or low gravity crude oil. Well treatment volumes and procedures and treatment results are presented on new completions and restimulation attempts.

INTRODUCTION

In acidizing stimulations, emulsions, sludges, and oil-soaked surfaces have proven effective deterrents to successful treatments. To combat these problems, two types of additives have been developed: surfactants and mutual solvents. Both additives will control some of the problems encountered during formation treating; however, for most instances, mutual solvents offer a better opportunity for stimulation. Surfactants, while easily added at proper concentration at the surface, can rapidly adsorb onto the formation, leaving the acid with an improper concentration of surfactant. Since the performance of most surfactants is concentration dependent, the problem which the surfactant was intended to control may remain unaffected or may worsen—demulsifiers, for example, may revert to emulsifiers. Since they are an integral part of the acid stimulation and do not have much of a tendency to adsorb, mutual solvents offer a much better chance of completing their intended functions.[1,2,3,4] Mutual solvent systems operate by imparting to the acid an oil-solubilizing capacity which allows the acid to quickly remove oil layers covering acid soluble material. The mutual solvent also lowers solution surface tension and aids in breaking emulsions and sludges. This lower surface tension aids in penetration of the formation matrix.

Mutual solvent systems, though often more expensive initially, nearly always perform better than the single-phase, soluble solvents such as water-soluble alcohols. Addition of only water-miscible alcohols to the acid mixtures will reduce the surface tension of the acid mixture and sometimes help in reducing the viscosity of an emulsion but will usually leave an oil coating on the solid particles of the formation which prevents contact by the acid. Surfactants are often added to aid dispersion of oily sludges or deposits. These have no significant capability to dissolve oily matter and, being strongly surface active, can stabilize unwanted emulsions. Acid systems which make use of an oil-solvent preflush such as crude xylene or diesel to strip oil coating or emulsions have proved effective in some cases but the two-part treatments often cannot be reliably directed or controlled in the wellbore. The oil preflush also leaves the reactive surface oil wet, a definite hindrance to an acid reaction.

A-Sol, a single phase mutual solvent system was designed for use in general acidizing and cleanout operations and has shown potential in laboratory tests and excellent results in actual treatments. The system, which is composed of water-soluble and oil-soluble alcohols in an optimum mixture for acid solubility, will strip oil coatings and break emulsions, thus exposing acid-soluble material. The treatment also leaves the reactive surface water wet. One of the more important functions of the material appears to be the liquefaction of viscous emulsion sludges which can be formed during any stage in the life of the well. The A-Sol is normally mixed with

HCl in a 65%-HCl and 35% A-Sol split. Other concentrations of acids can be used with A-Sol by changing proportions slightly.

CONCLUSIONS

1. A-Sol/acid has shown excellent results in field stimulations of injection and producing wells.
2. A-Sol can be an excellent initial stimulation aid where mud invasion or sludges exist in new wells.
3. The A-Sol/acid system can be effectively inhibited by use of adequate corrosion inhibitors.
4. No problem with chlorination should be encountered with A-Sol/HCl at circulating temperatures under 200° F.
5. Treatment of formations at temperatures over 200° F can be accomplished with A-Sol and organic acids.

LABORATORY TESTS

Permeability Damage in Sandstone Formations

Removal of damage in the formations near the wellbore can often be accomplished with A-Sol/acid mixture more effectively than with comparable volumes of acid without additives. Tables 1 and 2 show results of matrix acidizing and synthetic sludge removal for cores of Berea sandstone and Cardium sandstone. Solutions of A-Sol/acid and Ethylene Glycol Monobutyl Ether/acid gave very similar results (permeability improvement) in cores of Berea sandstone (Table 1) for removal of damage in high permeability cores. On the low permeability Cardium cores shown in Table 2, the A-Sol clearly gives better results than the EGMBE. This difference in performance at low permeabilities may be due to better oil solubilizing characteristics of the A-Sol solvent system. With both sets of cores, the oil stain remained near the surface in cores treated with EGMBE-acid, while the oil stain in the cores treated with A-Sol/acid was spread the full length of the core. This oil stain distribution is a direct measure of the success of the treatment in solubilizing and suspending the oil from the area of damage. The treatment volumes flushed from the core also showed more oil in the A-Sol/acid mixture.

TABLE 1—SLUDGE REMOVAL

Treatment	Berea Core Permeability, Md			% of Original
	Initial	w/Sludge	After Treat.	
EGMBE-HCl/HF	87	∿0	104	119.5
EGMBE-HCl/HF	175	∿0	94	53.7
EGMBE-HCl/HF	214	∿0	115	54.0
A-Sol HCl/HF	102	∿0	108	116.0
A-Sol HCl/HF	73	∿0	93	127.5
A-Sol HCl/HF	152	∿0	79	52.0
A-Sol HCl/HF	221	∿0	107	48.3
HCl/HF	75	∿0	43	59.0

Volume of treatments = 10 PV

TABLE 2—SLUDGE REMOVAL

Treatment	Cardium Core Permeability, Md			% of Original
	Initial	w/Sludge	After Treat.	
EGMBE-HCl/HF	4.20	∿0	2.10	50.0
EGMBE-HCl/HF	2.60	∿0	2.33	89.5
A-Sol HCl/HF	2.11	∿0	3.38	159.5
A-Sol HCl/HF	0.1	∿0	>500*	

Volume of treatments = 10 PV

*Acid channeled through the core.

Matrix Acidizing in Calcareous Formations

For treatment of calcareous formations or sandstone containing large amounts of calcium carbonate, either as a constituent or a cementing agent, A-Sol may be used with hydrochloric to assure rapid cleanup of the formation. Permeable carbonate cores from the Canyon formation (Ector County, Texas) were acidized with A-Sol/HCl and compared with regular HCl and emulsified acids. The results, which are shown in Table 3, indicate that the A-Sol treatment, although not as efficient as an emulsified acid in creating high permeability wormholes or channels, is an effective additive in matrix acidizing of carbonate reservoirs. Also, the chances of permeability impairment due to emulsion blocking is believed to be much less with A-Sol/acid. The A-Sol/acid shows a definite advantage over straight acid in increasing permeability in the test cores. In carbonate reservoirs, A-Sol/acid would be a good candidate for a cleanout additive following fracturing with emulsified acids or other fracturing fluids.

TABLE 3

Initial Permeability to Water (md)	Treatment Used	Final Permeability to Water (md)
7	15% HCl	<2
8	28% HCl	<2
24	15% HCl	<5
16	A-Sol - HCl (15%)	>200.
17	A-Sol - HCl (15%)	>200.
35	Acid Emulsion A (15% HCl)	19.
9	Acid Emulsion A (15% HCl)	Wormhole
15	Acid Emulsion B (15% HCl)	Wormhole
5	Acid Emulsion B (15% HCl)	Wormhole
6	Acid Emulsion B (15% HCl)	>500.

Volume of treatment = 10 PV

High Strength HCl

For economical treatment of sandstone formations damaged by sludge or completion fluids where HF acid cannot be used or in general acidizing of carbonate reservoirs, a solution of 75 vol % of HCl acid at a strength of 28% and 25 vol % A-Sol will give exceptional oil-solubilizing and carbonate-dissolving capacity with lower surface tension than straight 28% HCl.

Asphaltic Crudes

If the formation to be treated with A-Sol produces even small amounts of asphaltic materials, xylene or toluene should be included in the A-Sol/acid formulation or used as a preflush.[8] Figure 1, which contains a tertiary solubility diagram of the xylene, A-Sol, and acid, defines the solubility limits of this type of solution. In lab tests with the heavily asphaltic crude oil from the Elk Basin Embar Tensleep Formation, a solution of 56 vol % A-Sol, 22% HCl, and 22% xylene successfully solubilized the oil and left only minor color and no asphaltic particles on extra fine filter paper. This addition of xylene may also be useful with problem sludges and in low-gravity oil reservoirs to increase oil mobility in near-wellbore treatments.

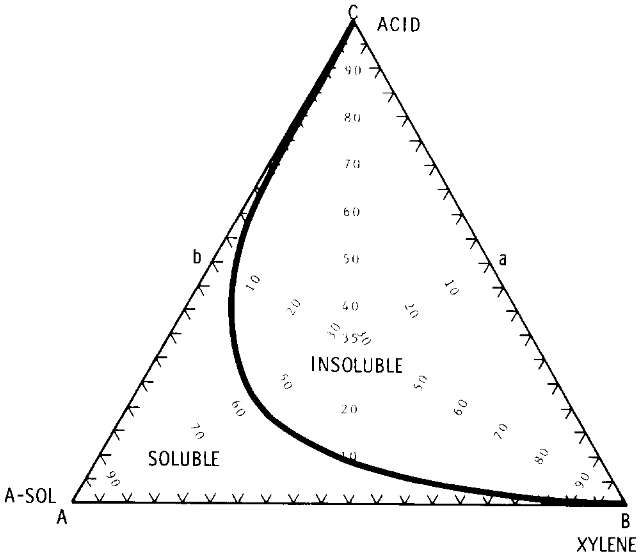

FIGURE 1—SOLUBILITY DIAGRAM FOR A-SOL - HCl (15%)-XYLENE

Corrosion Tests

The A-Sol constituents affect some corrosion inhibitors normally used in acidizing to a small extent. The inhibitor to be used by the service company should be tested with A-Sol to insure compatibility. Table 4 shows various inhibitors recommended by the service companies and their performance in inhibitor tests. It can be seen from the data that inhibitor amounts reommended in some instances are excessive. An acceptable corrosion figure for any inhibitor system for the API Corrosion Test on N-80 steel coupons is 0.05 lb/sq ft. Corrosion inhibitor coatings can be at least partially solubilized and therefore negated by all mutual solvent systems, some hydrocarbons, and other solvents such as the simple alcohols; thus, inhibitor schedules with the solvent addition should be obtained from the laboratory or literature references.[5]

TABLE 4—CORROSION INHIBITOR CONCENTRATION IN A-SOL - HCl (15%)

Inhibitor	Inhibitor Concentration	Temp.	Rate of Corrosion
Wellaid 211	4 gal/1000 gal	200°F	0.0392 lb/ft^2
Wellaid 211	4 gal/1000 gal	200°F	0.0280 lb/ft^2
Wellaid 211	12 gal/1000 gal	200°F	0.0128 lb/ft^2
A + aid (Dowell)	20 gal/1000 gal, 20 lb/1000 gal	200°F	0.0093 lb/ft^2
A + aid (Dowell)	20 gal/1000 gal, 20 lb/1000 gal	200°F	0.0156 lb/ft^2
B (Halliburton)	8 gal/1000 gal	200°F	0.0153 lb/ft^2
B (Halliburton)	8 gal/1000 gal	200°F	0.0231 lb/ft^2
None*	------------------------------	200°F	0.3953 lb/ft^2

All tests run for 2 hours using N-80 coupon in modified API corrosion test cell. An acceptable corrosion rate for these tests is 0.05 lb/ft^2.

*One hour test, pressure rise stopped test.

High Temperature Chlorination

Under certain conditions some hydrocarbon compounds can become chlorinated from prolonged contact with hydrochloric acid. These chlorinated hydrocarbons are refinery catalyst poisons and their occurrence should be minimized. As reported by Keeney and Frost, high temperatures may induce chlorination of simple alcohols at reaction temperatures above 200° F.[6] The effect of temperature and pressure on possible internal reactions in the A-Sol/acid mixture was studied in non-reactive pressure vessels with the reaction of interest being chlorination of alcohols which are used in A-Sol. Table 5 shows the results of these pressure and temperature tests. The maximum possible amount of chlorination reported in Table 5

TABLE 5—TENDENCY OF A-SOL TO CHLORINATE

Acid Strength (% HCl)	A-Sol in Total (vol. % A-Sol)	Temp. (°F)	Time (Hrs)	Pressure (psi)	Maximum Possible Chlorination* (% High Boiling Volume)
15	35	150	15	50	0.00
15	35	150	15	500	0.00
15	35	200	5	50	0.3
15	35	200	2	1000	0.4
15	35	200	15	50	0.8
15	35	200	15	500	2.0
15	35	200	15	1000	1.6
7.5	38	200	1	50	0.0
10	36	200	5	50	0.4
28	21	200	5	50	3.8
15	35	350	2	500	6.0

There were no acid soluble materials in the reaction cell.

*Volume includes chlorinated and non-chlorinated materials.

is the sum of the volume percents of chlorinated and nonchlorinated compounds boiling in the general range of possible chlorinated materials. Due to the use of unsophisticated distilling equipment, this high temperature boiling fraction could not be separated.

It should be noted that these figures are on the very high end of possible values and will not be likely due to the acid rock reactions which will leave very little of the acid available for chlorination-type reactions. Ethylene Glycol Monobutyl Ether and other mutual solvent systems, as well as some hydrocarbons which are used for cleanout operations, can also undergo chlorination from hydrochloric acid under similar high temperature conditions. Probably an upper limit for the use of most mutual solvents with HCl would be where the circulating temperature reaches 200°F. Below 200°F, no problem would be expected with the chlorination.

Acid Concentration

Changing the concentration of hydrochloric acid requires a small adjustment in the amount of A-Sol added to the mixture. Table 6 shows the miscibility of A-Sol and various concentrations of hydrochloric acid. It should be noted from this data that, as the initial strength of raw acid is reduced, a larger percentage of A-Sol is required to maintain a miscible solution. A-Sol is not favorably soluble in nonacidic solutions such as fresh or brine waters.

TABLE 6—ACID - A-SOL REQUIRED CONCENTRATION FOR TOTAL MISCIBILITY

Hydrochloric Acid Strength	A-Sol in Total Volume
7.5%	38% (By Volume)
10.0%	36%
15.0%	31%
28.0%	21%

The above volumes of A-Sol are minimum volumes required for solubility.

Phase Separation

Phase separation of the A-Sol/HCl solution during HCl spending does occur under quiescent conditions; however, this separation is not considered to be a serious problem since the surface and interfacial tensions of the acid phase remain low. Surface and interfacial tensions of acids and mutual solvents reflect a measure of the ease of penetration through the matrix. Solutions with lower values of surface and interfacial tensions require less driving energy to move through an oil- and/or gas-containing pore. The best acid-treating solutions should not only have low surface and interfacial tensions in the unreacted state but should maintain similar low values when the acid is spent. As seen in the data of Tables 7 and 8, both A-Sol and EGMBE solutions have low initial and maintained values of surface and interfacial tension.

TABLE 7—SURFACE AND INTERFACIAL TENSIONS

Sample	Surface Tension Dynes/CM	Interfacial Tension* Dynes/CM
15% HCl	72.0	32.0
28% HCl	77.2	33.7
15% HCl w/10% EGMBE	33.0	11.6
15% HCl w/30% EGMBE	32.8	5.5
15% HCl w/35% ASol	27.5	1.7
28% HCl w/10% EGMBE	43.6	13.9
28% HCl w/25% ASol	31.0	0.8

*Against a C_{10}-C_{12} hydrocarbon.

TABLE 8—SURFACE AND INTERFACIAL TENSIONS

Spent Acid Solutions

Sample	Surface Tension	Interfacial Tension*
Water	76.9	33.4
Spent 15% HCl	59.0	26.9
Spent 28% HCl	77.2	33.7
Spent 15% HCl w/10% EGMBE	35.5	5.4
Spent 15% HCl w/35% ASol	29.2	7.2
Spent 28% HCl w/25% ASol	36.0	13.7
Spent 28% HCl w/10% EGMBE	35.1	6.8

*Against C_{10}-C_{12} hydrocarbon

In the laboratory tests where A-Sol/HCl was used on limestone cores, separation was noted in the effluent only after several minutes of standing quiescent. This observation is significant since the strength of the acid after passing the core was below 5%.

Additives

The use of lactic or citric acids in low concentrations as iron stabilizers requires no special blend of A-Sol. Ten or 15% formic or acetic acids may also be used with A-Sol in the same proportions as used for 15% HCl and should be considered when the temperature of the formation is above 200° F and a matrix-acidizing treatment is required. These organics and A-Sol may also be used in water sensitive formations, or where byproducts of HCl-HF acid or hydrochloric acid reactions could cause plugging in the formation.

Foamed A-Sol

Where special conditions exist such as deep-formation damage or oil-soaked scale in perforations before a foam frac, A-Sol can be used as a foamed spearhead. The use of nitrogen or carbon dioxide gas with a foaming surfactant can create foam from an A-Sol/acid solution. Although this foam is not nearly as stable as an acid or water foam, it does have good dynamic stability; hence, it should possess some of the qualities of foam such as better solids-lifting capacity and good backflow after the treatment. Fluid leakoff from the A-Sol/HCl foam in a dynamic test apparatus described by King is compared in Figure 2 to a straight acid foam on inert test cores 2 in. in diameter and 4-1/2 in. long.[7] The higher leakoff and lower stability of the A-Sol/HCl foam is probably due to the low surface tension of the A-Sol. In instances of formation cleanout, where deep acid penetration is desired, the increased leakoff of the low surface tension acidic solution coupled with the tremendous kickoff capacity of nitrogen gas should be capable of removing deep formation damage.

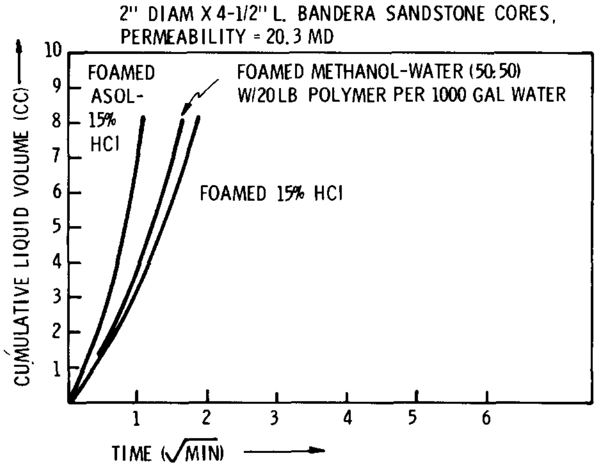

FIGURE 2—LIQUID LEAKOFF VS SQUARE ROOT OF TIME

FIELD RESULTS

In a direct field comparison with A-Sol and Ethylene Glycol Monobutyl Ether, 18 wells in the Frio sand were stimulated using HCl/HF acid and the mutual solvent systems. The 9 wells stimulated with a 10% EGMBE/90% acid mixture showed an average increase of 89 BOPD, while the 9 wells treated with 35% A-Sol/65% acid averaged 119 BOPD production increase. The data and conclusions for this example comparison are shown in Tables 9 and 10. Super Mud Acid in these data refers

TABLE 9—A-SOL-ACID TREATMENTS

FRIO FORMATION

Test Before Oil	Test Before Water	Test After Oil	Test After Water	Treatment	Perforations
0	0	15	133	250 gals. 15% HCl + 1000 gals. Super Mud Acid w/ 35% A-SOL + 250 gals. 15% HCl	5956-5963'
74	19	848	127	200 gals. 15% HCl + 500 gals. Super Mud Acid w/ 35% A-SOL + 200 gals. 15% HCl	5966-5972' & 5973-5980'
113	0	27	1	200 gals. 15% HCl + 600 gals. Super Mud Acid w/ 35% A-SOL + 200 gals. 15% HCl	5894-5899'
0	0	45	247	200 gals. 15% HCl + 500 gals. Super Mud Acid w/ 35% A-SOL + 200 gals. 15% HCl	6011-6016'
0	0	10	275	250 gals. 15% HCl + 600 gals. Super Mud Acid w/ 35% A-SOL + 250 gals. 15% HCl	6056-6070'
0	0	165	1003	200 gals. 15% HCl + 300 gals. Super Mud Acid w/ 35% A-SOL + 200 gals. 15% HCl	5875-5882'
0	0	66	1090	250 gals. 15% HCl + 550 gals. Super Mud Acid w/ 35% A-SOL + 250 gals. 5% HCl	5862-5866'
0	0	5	238	250 gals. 15% HCl + 550 gals. Super Mud Acid w/ 35% A-SOL + 250 gals. 5% HCl	6031-35' & 6039-45'
0 20.7	0 2.1	81 140	194 367	250 gals. 15% HCl + 500 gals. Super Mud Acid w/ 35% A-SOL + 250 gals. 15% HCl	5977-5986'

TABLE 10—EGMBE-ACID TREATMENTS

FRIO FORMATION

Test Before Oil	Test Before Water	Test After Oil	Test After Water	Treatment	Perforations
0	0	359	1083	100 gals. 15% HCl + 300 gals. Super Mud Acid + 10% EGMBE + 100 gals. 5% HCl	5868-5872'
0	0	6	113	100 gals. 15% HCl + 200 gals. Super Mud Acid + 10% EGMBE + 100 gals. 5% HCl	6099-6102'
0	0	21	405	300 gals. 15% HCl + 500 gals. Super Mud Acid w/ 10% EGMBE + 500 gals. 5% HCl	5933-5936'
18	129	28	170	250 gals. 15% HCl + 500 gals. Super Mud Acid + 10% EGMBE + 250 gals. 5% HCl	5989-6000'
34	276	42	312	200 gals. 15% HCl + 600 gals. Super Mud Acid + 10% EGMBE + 200 gals. 5% HCl	5990-6000'
6	37	26	468	300 gals. 15% HCl + 750 gals. regular Mud Acid + 10% EGMBE + 500 gals. 5% HCl	5945-5958'
28	0	426	10	150 gals. 15% HCl + 250 gals. Super Mud Acid + 10% EGMBE + 150 gals. 15% HCl	5971-5975'
0	0	Sanded Up		200 gals. 15% HCl + 400 gals. Super Mud Acid + 10% EGMBE + 200 gals. 5% HCl	5954-5964'
70 17.3	53 55	45 105	50 290	200 gals. 15% HCl + 500 gals. Super Mud Acid + 10% EGMBE + 200 gals. 5% HCl	5973-5980'

to a hydrochloric-hydrofluoric mixture of 12% HCl and 6% HF.

Tables 11 and 12 show individual well-treatment procedures and response data for two wells in the Frio sand which were treated with A-Sol/acid to remove suspected formation damage. These wells had not been previously stimulated; thus, the treatment probably removed drilling mud debris and other damage-causing mechanisms from the near-wellbore region.

Results of water-injection well treatment with A-Sol are shown in Table 13 for two locations in West Texas. The success of these stimulations, which show good injectivity improvement with A-Sol-acid, probably results from the removal of fine particles and sludges. These silt-stabilized sludges often mask over injection zones and reduce injectivity severely. The sludge used in the core tests of

TABLE 11—INDIVIDUAL WELL DATA

FORMATION: Frio

PERFORATIONS: 10,524-10,538'
10,593-10,609'
10,666-10,682'

	A-Sol Stimulation	Previous Stimulation
STIMULATION:		None (new well)
DESCRIPTION OF STIMULATION:	750 gal 15% HCL 1000 gal 6% HF mixed with 525 gal A-Sol 1500 gal 5% HCL w/35 ball sealers 750 gal 15% HCL 1000 gal 6% HF mixed with 525 gal A-Sol 1500 gal 5% HCL w/35 ball sealers 750 gal 15% HCL 1000 gal 6% HF mixed with 525 gal A-Sol 1500 gal 5% HCL Displaced with 15-1/2 bbls FSW (44-1/2 bbls capacity to top of perts.) Well came back in flowing.	

WELL TEST	Before Treatment	After Treatment	After Two Months
METHOD	Flowing	Flowing	Flowing
OIL (BOPD)	19	21	28
WATER (BWPD)	28	9	13
GAS (MCFD)	2086	2661	2390
FTP	800	800	800

TABLE 12—INDIVIDUAL WELL DATA

FORMATION: Frio

PERFORATIONS: 10,118-10,135'
10,138-10,147'

	A-Sol Stimulation	Previous Stimulation
STIMULATION:		None
DESCRIPTION OF STIMULATION:	1000 gal 15% HCL 2000 gal 6% HF mixed with 1100 gal A-Sol Displaced with 33 bbls diesel (31-1/4 bbls capacity to top of perfs.) Swabbed well in.	

WELL TEST	Before Treatment	After Treatment	After 24 Hours
METHOD	Flowing	Flowing	Flowing
OIL (BOPD)	12	47	53
WATER (BWPD)	1	29	20
GAS (MCFD)	509	5887	6323
FTP	550	950	950

Tables 1 and 2 is a laboratory-made mixture of components found in injection backflow samples from several injection units. The success of A-Sol/acid in removing these test deposits confirms the usefulness of the treatment in injection facilities.

TABLE 13—A-SOL STIMULATIONS IN INJECTION WELLS

	No. Wells	Before BWPD	After BWPD
Levelland Area	6	1030	2345
Brownfield Area	19	13319	15009

Numerous other successful producing and injection well treatments have been carried out using A-Sol-acid during the last five years.

REFERENCES

1. Gidley, J. L.: "Stimulation of Sandstone Formations with the Acid-Mutual Solvent Method," *J. Pet. Tech.* (May, 1971) 551-558.
2. Hall, B. E.: "The Role of Mutual Solvents in Sandstone Acidizing," Paper SPE 5377 presented at SPE 45th Annual California Regional Meeting, April 2-4, 1975.
3. Penberthy, W. L., Jr., Shaughnessy, C. M., Gruesbeck, C. and Salathiel, W. M.: "Sand Consolidation Preflush Dynamics," Paper 6804 presented at the 52nd Annual Fall Technical Conference and Exhibition, Dallas, October 9-12, 1977.
4. Gidley, J. L., Ryan, J. C. and Mayhill, T. D.: "A Field Study of Sandstone Acidizing," Paper SPE 5693 presented Houston, Texas, January 29-30, 1976.
5. Woodroof, R. A., Baker, J. R. and Jenkins, R. D.: "Corrosion Inhibition of Hydrochloric-Hydrochloric Acid/Mutual Solvent Mixtures at Elevated Temperatures," Paper SPE 5645 presented at SPE 50th Annual Fall Meeting, Dallas, September 28-October 1, 1975.
6. Keeney, B. R. and Frost, J. G.: "Guidelines Regarding the Use of Alcohols in Acidic Stimulations Fluids," *J. Pet. Tech.* (May, 1975) 552-554.
7. King, G. E.: "Factors Affecting Dynamic Fluid Leakoff from Foam Fracturing Fluids," Paper SPE 6817 presented at the 52nd Annual Fall Technical Conference and Exhibition, Denver, Colorado, October 9-12, 1977.
8. Jones, Loyd W. and Holman, George B.: "Method of Stimulating Wells Completed in Oil Bearing Earth Formations," U.S. Patent 3,970,148 (July 20, 1976).