HEATED ACIDS FOR IMPROVED STIMULATION RESULTS

S. E. Fredrickson, M. L. Walker, J. Brad Crump
Halliburton Services

ABSTRACT

Heated acids have been used extensively with excellent results as shown by field data and laboratory tests. A primary use of heated acids is to increase dissolution and reactivity in relatively cold formations for improved flow capacities in, for example, cold dolomites. This technique aids treatment effectiveness by (1) increasing the acid reaction rate, (2) removing acid retarding materials such as oil, asphaltenes, and paraffins from formation surfaces for a better acid-formation contact, (3) helping prevent the precipitation of organic materials from oils that have been cooled by acids, and (4) limiting temperature contraction of tubing during a treatment.

On acidizing treatments conducted during the winter, acid temperatures can be less than 32°F. The effectiveness of these treatments can be improved by heating the acid and thus avoiding the problems of slow reaction rate,-precipitation, and tubing contraction.

Three general acid heating techniques are used: (1) an exothermic chemical reaction with a portion of the acid as one of the reactants, (2) adding live steam to the acid, or (3) using hot oilers to heat the water portion prior to dilution.

INTRODUCTION

In the past, much emphasis has been placed on retarded acids or retarding systems so that deeper formation penetration could be obtained with live acid. However, in many areas accelerated acid systems are necessary because of cold formations or short acid pumping times. While surfactants can aid to some degree, the most practical means determined to accelerate acid reaction is to heat the acid. Not only does heated acid give a more rapid reaction, but it can also help remove organic materials such as oil, paraffins, or asphaltenes which can coat formation surfaces and physically prevent or reduce effective acid-formation contact. By heating acid to at least bottomhole temperature (BHT), the chance of precipitating these organic materials from formation fluids with possible damaging effect is also reduced.

DISCUSSION

Ideally, and from a practical standpoint, methods used to heat acids should be relatively inexpensive, safe, and generally easy to perform with normally available chemicals or equipment. Hot oilers and steamers have been effectively used to heat acid for a number of years with good results; however they are not always readily available. Several chemicals which produce an exothermic reaction when mixed with an acid system have been evaluated to determine their effectiveness and safety. It has been determined that addition of anhydrous ammonia, which is readily available as fertilizer, is an effective, easy to handle, and relatively inexpensive means of heating acid (Fig. 1). Ammonia and acid can be batch mixed in the acid tank or added on the fly to a pressurized suction line prior to the high pressure pumps. In the exothermic chemical reaction between ammonia and HCl, the portion of the acid used to generate the heat produces a reaction product (ammonium chloride) which is a highly soluble, and generally compatible material.

One of the main benefits from heated acids is a faster reaction with the formation. This faster reaction can be obtained in two ways: by either increasing the reaction rate of the acid on the actual formation, or by removing material that is physically preventing the acid-formation contact.

Many carbonate formations are fracture acidized by flowing acid through natural or created fractures, and dissolving a portion of this fracture face. This in turn produces the necessary flow channels for adequate fracture conductivity. Factors which can limit acid effectiveness include (1) the type of rocks present such as dolomite, (2) the formation being too cold, (3) the acid being too cold, or (4) the face of the fracture being coated with asphaltene, paraffins, or formation oil. Since nothing can be done about the type of formation, the emphasis must be placed on these other factors. Heated acid can eliminate or reduce the influence of the factors which tend to reduce acid reactivity.

In treatments where a relatively short acid pump time is used, the actual acid contact time may not be long enough to sufficiently dissolve the formation face to create adequate fracture conductivity. Since the equation for fracture flow capacity (as given in the SPE Fracturing Monograph) is $FFC\ (md\ ft) = 4.47 \times 10^9\ [width(in)]^3$, it can be seen that doubling the fracture width will produce eight times the theoretical flow capacities. Generally, this can be accomplished by either pumping twice as much acid, or by increasing the reaction temperature by approximately 20°F (Fig. 2). If this is still not sufficient, larger volumes with corresponding longer pump times can be used, or the acid can be heated to a higher temperature. Since cold acids have a cooling effect on the formation, the larger volumes necessary are many times self defeating because they provide additional cooling effect, whereas heated acid increases the actual surface reaction rate. In addition, laboratory tests have shown that the decreased viscosity of heated acid enables it to be pumped in turbulent flow, which in turn gives an additional reaction acceleration effect, and also tends to produce an even higher flow capacity because it can create a channelling or grooving effect on the fracture face.

Heated acid can be extremely beneficial in treating wells when either the naturally fractured system or the created fractures contain sufficient organic material such as paraffins, asphaltene, or formation oil to create a physical barrier between the acid and the formation. While surfactants can aid in removal of these compounds, the results are generally not adequate. By heating the acid to a temperature above the normal BHT, which is relatively close to the melting point of these materials, the softened or flowable organic materials can be washed away. Higher temperature also improves the effectiveness of surfactants, which work as detergents to help remove organic materials and allow acid to contact the formation.

In many instances production may be reduced primarily because of organic deposits mixed with acid soluble scales. Low viscosity emulsions of acid and aromatic solvents have been used to remove both of these in a generally simultaneous manner; however the reaction of cold solvents or acids is still very slow. Heating these systems can greatly increase their effectiveness. To illustrate the improvement in solvent effectiveness when heated, the solubility of an oil field paraffin sample in xylene increased fourfold from 200 lb/1,000 gal to 800 lb/1,000 gal, when the fluid was heated from 60°F to 80°F. A temperature increase of 18°F allows the concentration of a typical surfactant to be reduced by 50 to 60% without reducing solvent effectivenss.

Another benefit of heated fluids is to allow certain wells to be treated that could not be practically treated with cold fluids. Tubing contraction caused by any cold fluid can be a significant problem since this contraction can unseat a packer, pull a seal out of a permanent packer, or place excessive tension on the tubing or casing string if this movement is confined. Heating both the acid and non-acid fluids with hot oilers or steamers can be used to limit contraction. Consider the following situation: a 10,000 ft, 2 7/8 in. OD, 6.4 lb/ft tubing string with a 70°F surface temperature and 240°F BHT is treated with a large volume of 60°F fluid. Thermal contraction could be 6.3 ft, or an additional 33,600 lb of force could be placed on the tubing if the bottomhole tubing temperature is cooled to 70°F. By heating the fluid to 120°F, contraction would be held to 2.45 ft, assuming an average tubing temperature of 120°F top and bottom, or a confined force of 13,060 lb. If the fluid could be heated to approximately 155°F, theoretically there would be no thermal movement or force.

Caution must be taken to use proper corrosion inhibitors to protect pumps, blenders and other surface equipment if they are used to pump hot acids. It is also possible to soften, dislodge, or even dissolve organic material from the injection string; this material could create problems if pumped into the formation. If the injection fluid temperature is significantly higher than the BHT, it may be advantageous to clean the tubing with solvents or hot oil prior to stimulation to prevent or reduce this possible problem.

METHODS OF HEATING FLUIDS

Chemically Heated Acids

Acids can be heated by adding either gaseous or liquid ammonia to HCl with the following reaction: $HCl + NH_3 \longrightarrow NH_4Cl$ + Heat. Gaseous ammonia is added to the bottom of the acid tank using a wand or air injection system at a moderate rate to allow the reaction to take place before the ammonia gas breaks out at the surface . The operation is quite noisy when the ammonia gas bubbles collapse. Volume of ammonia is controlled and the acid temperature and concentration are monitored until desired results are obtained (Fig. 3).

Liquid ammonia can be added into a pressurized pump suction hose at 45 psi, which will keep it from gasifying and reduce noise or possible rough-running pumps caused by bubble collapse. Tests have shown that a 50°F temperature rise was noted when pumping 3 bbl/min through a 4 in. ID pressurized suction hose only 4 ft from the ammonia inlet. This system is generally applicable for long low rate jobs, however rates up to 12 bbl/min on a continuous basis with the acid temperature increased from 50°F to 140°F have been run (Fig. 4).

For example, 1,000 gal 15% HCl at 120°F can be obtained from 20% HCl at 55°F by adding approximately 40 lb commercial agrigrade anhydrous ammonia fertilizer. This does not take into account the heat loss in the system, so a higher initial concentration of acid and more ammonia will have to be used.

Advantages of chemically heated acids over hot oilers or steamers are as follow:

1. Acid can be heated directly while still in the transport or holding tank. This method saves time, and the transports or holding tanks are the only large volume equipment needed.

2. Large volumes can be heated by continuous methods with almost no heat loss. Heating by hot oilers or steamers must be done by the batch method.

3. A by-product of the chemical reaction is a clay stabilizer, ammonium chloride. Clay swelling and fines migration may be inhibited by the presence of this chemical in the formation.

4. Space and logistics requirements on location are reduced. No hot oilers or steamers are required on location and availability of such equipment is not a concern to the job planner.

Disadvantages of chemically heated acids are as follow:

1. A portion of the acid is used in the reaction with anhydrous ammonia to furnish heat which adds to the actual cost.

2. If too much ammonium chloride is formed, solid crystals may form and act as plugging agents or nuclei for emulsions. Proper planning and job design can help prevent this occurrence. The planner should provide that the solubility of the ammonium chloride at BHT is not exceeded, or add preflushes or spacers that will dissolve ammonium chloride.

3. Special ammonia compatible lines, valves, and gauges are necessary.

4. Acid concentrations above approximately 25% generally cannot be pumped at high temperature because a portion of the acid is used to generate the heat.

5. The chemically heated system can only be used with acids; other heating systems are needed if preflushes or overflushes are to be heated.

Hot Oilers

Acids can be heated using hot oilers, but not directly. The most commonly used method is to heat the water that is normally used to dilute the raw or concentrated acid to the desired strength. Most of the necessary corrosion inhibitors, surfactants, or other additives can be added to the water phase as it is being circulated and brought up to the desired temperature. After this temperature is reached, the raw acid can be pumped into the hot water and mixed. This hot, diluted acid is then pumped into the well (Fig. 5). Some treatments have been run where the hot water is pumped with one pump while at the same time 28 to 30% HCl is pumped with another, with the acid and water mixing before going into the well. Temperature can be controlled by varying the pump rate of either pump. A main advantage of this latter system is that only cold acid goes through the pump thus helping reduce surface corrosion problems, especially in very hot acid systems (Fig. 6).

For example, to obtain 15% HCl at 120°F using 20 Be (31.45%) HCl at 60°F, the mixing water would have to be approximately 155°F. Since this is without any heat loss in the system, the water temperature would have to be higher depending on volumes, etc.

The advantages of hot oilers are:

1. Their general availability in most parts of the country.

2. No other special equipment is involved and the temperature of the water phase can be closely controlled.

3. The entire system can be monitored for acid concentration, temperatures, viscosities, etc., prior to pumping if an entire tank is premixed.

4. If a hot oil treatment or circulation is needed prior to pumping the acid, the hot oiler is already available.

5. Non-acid fluids can also be heated. This permits use of non-acid preflushes to heat tubing, wellbore, and formation before acid is pumped. It also allows diverting systems, gelled preflushes, etc., to be used when necessary.

The disadvantage of hot oilers is that a dilution of the acid has to occur. The greater the acid temperature rise must be, the more the dilution. This makes it almost impossible to pump 25 to 30% HCl at a reasonably high temperature; however it is generally not a major problem since in many cases a larger volume of weaker acid will compare satisfactorily with a smaller volume of high strength acid. Temperature of hot mixing water may be limited in some instances due to potential damage to tank's lining.

Steamers

Steamers have not been as widely used as chemically heated acids or hot oilers primarily because they are not as readily available; however steamers can be the most effective heating system used.

Steamers add very little actual water to the fluid system to be heated because of the high heat of condensation of steam. Calculations show that 28% HCl can be raised from 60°F to 120°F with an acid dilution of less than 1%, neglecting heat loss. Steam is safe, easy to control, and since no circulation occurs as in a hot oiler, live steam can be injected directly into acid or other aqueous systems (Fig. 7). For example, calculations show that 1,000 gal of 28% HCl at 60°F can be raised to 120°F by adding approximately 40 gal of live steam at 212°F, diluting the acid to approximately 27.4%, without considering heat loss in the system.

LABORATORY ACID ETCHED FRACTURE FLOW CAPACITY TESTS

These tests are run to measure the flow capacity under closure pressure of a created and acid etched fracture.

Procedure: Core sample is cut into circular disks 2.25 to 4 in. OD by 0.75 to 1.0 in. thick, such that the surface exposed to acid is in the same plane as a vertical fracture. The face of the sample is turned flat with a lathe and a hole is drilled through the axis of the sample. It is then placed in the etching test cell which is then brought up to test temperature; a micrometer is attached and set at zero. The core faces are then adjusted so they are separated 0.05 inches from each other. Acid is flowed through the hole and radially across the sample face at 1000 psia. After a specific time interval, the acid is removed and replaced with kerosene. The sample then has closure pressure applied and a fracture flow capacity reading is obtained. The amount of sample removed or crushed can then be measured by the micrometer. This process can be repeated several times but the common practice is to perform two flow periods. Any specified closure pressure can be used. If none is given, a closure pressure of 1/3 psi per ft of depth is used with a minimum of 1,000 psi. At times acid is flowed through the closed fracture for an additional time period.

LABORATORY TEST RESULTS

Area	Formation	Depth BHT	Acid Type	Acid Temp. (°F)	Etching Time (min.)	Fracture Flow Capacity (md-ft)
Ohio	Trenton	1,300 ft 60-70°F	15% HCl	78	18	256
					36	1,746
				Closed	54	50,228
				140	18	704
					36	10,358
Michigan	Trenton	4,000 ft 100°F	15% HCl	85	18	252
					36	304
				140	18	33,312
					36	48,912
Michigan	Scipio Core No. 1	4,000 ft 100°F	28% HCl	85	18	108
					36	2,040
				130	18	12,812
					36	78,748
	Scipio Core No. 2	4,020 ft 100°F	28% HCl	85	18	124
					36	1,532
				130	18	8,684
					36	65,484
Montana	Madison	1,500 ft 80°F	28% HCl	80	18	2,668
					36	3,636
				Closed	54	72,408
				150	18	9,000
					36	67,860
West Texas	Clearfork	6,000 ft 115°F	15% HCl	115	18	8,940
					36	22,812
				150	18	37,408
					36	45,788
Michigan	Richfield	3,860 ft 95°F	15% HCl	95	18	<10
					36	384
				150	18	1,728
					36	27,960
			28% HCl	95	18	344
					36	808
				150	18	3,916
					36	43,076

FIELD RESULTS & CASE HISTORIES

Case History No. 1
Mississippi Dolomite in Ness Co., KS, at 4,450 ft with 120 to 130°F BHT:

Previous treatment with 2,500 gal unheated 15% HCl produced 2 BOPD and 15 BWPD. Cold xylene (250 gal) was run followed by 2,500 gal of 15% HCl heated from 42°F to 115°F with steam. Production stabilized at 12 BOPD and 68 BWPD.

Case History No. 2
Chert Formation, Hodgeman Co., KS, at 4,600 ft with 130°F BHT:

A well drilled in 1973 was making 30 to 35 BOPD and water with rapidly declining production. The well was treated with 500 gal unheated 15% HCl, resulting in production of 8 BOPD and 20 BWPD. Production fell off sharply and was not pumped for one year.

The well was treated with 200 gal cold xylene, followed by 750 gal 7½% iron control acid containing paraffin dispersing additives. The acid was heated from 45°F to 110°F with steam. The well is now making 20 BOPD and 90 BWPD.

Case History No. 3
Mississippi Dolomite and Fort Scott Limestone in Ness Co., KS, at 4,500 ft with 120°F BHT:

In 1983 a treatment consisting of 1,500 gal unheated 15% HCl using ball sealers was performed, resulting in production of 11 BOPD and 18 BWPD on one well. In 1985 the rods were pulled and the well was circulated with hot water; then 2,000 gal 15% heated acid containing paraffin dispersing and fines suspending additives were run, heating the acid from 55°F to 120°F. The well is now making 75 BOPD and 100 BWPD. Four wells have been treated in this lease using this technique increasing production from 40 BOPD to 210 BOPD. Three wells were heated by steam and one by a hot oiler.

Case History No. 4
Niagaran Limestone/Dolomite Formation in Manistee Co., MI, at 4,750 ft with a BHT of 98°F:

A well making 90 BOPD and 450 MCFD gas was treated with 1,000 gal 7.5% HCl, including a paraffin dispersant followed by 1,000 gal 28% HCl. Acid temperature was heated from 30°F to 120°F using ammonia as a heating agent. The well was making 180 BOPD and 450 MCFD gas one month after treatment. This well had been stimulated the preceding year in cold weather with 10,000 gal unheated HCl-xylene emulsion with no production improvement.

Case History No. 5
Richfield Dolomite in Ogeman Co., MI at 4,315 ft with 93°F BHST:

Well had been treated with 500 gal unheated 28% HCl with no production after treatment. Well was then treated with 500 gal 28% HCl, heated from 32°F to 150°F, by using ammonia which spent the acid to 21%. The well responded by making 14 to 17 BOPD with produced gas, which was not measured.

Case History No. 6
Onondaga Limestone in New York State at 3,400 ft with 75°F BHT:

A previous treatment with unheated HCl showed a surface treating pressure of 1,800 psi with a stabilized ISIP of 1,700 psi. Results indicated no production other than a trace of oil, with only a small amount of the acid spent. The well was retreated with 1,000 gal 28% HCl followed by 1,000 gal 20% HCl, both heated to 100°F with ammonia. The ISIP fell off to 1,350 psi and was still dropping after 5 minutes, with considerable acid spending. Production stabilized at 140 BOPD.

Case History No. 7
Copper Ridge Formation, Johnson Co., KY, at 5,800 to 6,000 ft with 120 to 130°F BHT:

Previous acidizing or proppant fracturing treatments on wells were generally successful; however high injection pressures required P-110 tubing. Using heated acid a typical well was treated with 6,000 gal 28% HCl heated with ammonia on the fly to 140°F, with production increasing from a show of gas to 1.0 MM ft^3/day. This basic treatment has been run on eight other Copper Ridge and Black River formation wells at rates of 8 to 10 bbl/min at surface treating pressures below 4,500 psi with excellent results.

An additional advantage is that since these wells can be treated at lower Pw with the same production increase compared to fracturing with proppants, the well owners can use a much less expensive grade of tubular goods.

Case History No. 8
Offshore California at 7,000 ft at 240°F BHT:

The last three acidizing treatments had pulled the stinger out of the packer. Thirty thousand gal 15% HCl-3% HF acid mixture was heated with ammonia to a final 12% HCl-3% HF concentration, raising the temperature from 55°F to 120°F at 4 bbl/min pump rate. The well was treated without problems. Additional wells are planned to be treated with hot acid since cold acids have precipitated asphaltenes resulting in reduced permeability.

Case History No. 9
Clearfork Formation, Yoakum and Gaines Co., TX, at 7,500 ft with BHT of 120 to 130°F:

Previous unheated acid treatments had given production of 50 to 60 BOPD average. Present treatment fluids are all heated to 110°F with a hot oiler and weighted to 9.0 lb/gal for density placement control. Over 70 wells have been treated following this same general procedure:

Step 1 - Pump 140 bbl water containing scale inhibitor, then shut down for 1 hour.

Step 2 - Pump 15,000 gal crosslinked gel preflush.

Step 3 - Pump 12,000 gal 20% HCl alternating at 4,000 gal intervals with similar volumes of gelled fluid loss control phases.

Step 4 - Overflush with 4,000 gal

These wells are averaging 85 BOPD after 3 months.

Case History No. 10
San Andres Formation, Yoakum and Gaines Co., TX, at 5,000 ft with 105 to 115°F BHT:

All fluids are heated to 110°F with a hot oiler and weighted to 9.0 lb/gal for density placement control.

Step 1 - Pump 140 bbl water containing scale inhibitor, then shut down for 1 hour.

Step 2 - Pump 6,000 gal crosslinked gelled preflush.

Step 3 - Pump 10,000 gal 20% HCl containing 2.0% gelling agent alternating at 3,000 gal intervals with gelled fluid loss control phases.

Step 4 - Overflush with 4,000 gal.

Step 5 - Shut down for 1.5 hours for the fracture to close.

Step 6 - Pump 2,000 gal 20% ungelled HCl at 1 BPM. Displace only to formation.

No wells in this field were treated with unheated fluids. Thirty wells have been treated making 100 BOPD.

Case History No. 11
San Andres Formation, Cochran Co., TX, at 5,000 ft with 105°F BHT

All acids heated to 110°F with a hot oiler:

Producers:

1. Heated and foamed acid. Before treatment production was 12 BOPD and 3 BWPD. After treatment this well is producing 35 BOPD nd 55 BWPD.
2. Heated acid. Before treatment: 20 BOPD and 4 BWPD. After: 33 BOPD and 29 BWPD
3. Unheated acid. Before: 7 BOPD and 4 BWPD. After: 2 BOPD and 18 BWPD.

Injectors:

1. Heated and foamed. Before: 240 BWPD at 2,300 psi. After: 250 BWPD at 1,450 psi.
2. Heated and foamed. Before: 100 BWPD at 2,300 psi. After: 250 BWPD at 1,750 psi.
3. Heated only. Before: 100 BWPD at 2,300 psi. After: 250 BWPD at 2,150 psi.
4. Heated only. Before: 100 BWPD at 2,300 psi. After: 250 BWPD at 2,150 psi.

5. Unheated and unfoamed. Before: 50 BWPD at 2,300 psi. After: the same.

6. Unheated and unfoamed. Before: 30 BWPD at 2,300 psi. After: 125 BWPD at 2,300 psi.

CONCLUSIONS

1. Heated acids can be very beneficial in stimulation treatments by increasing the effective acid reaction, removing and/or preventing formation damage, or reducing tubular goods or packer problems.

2. Heating with chemicals, hot oilers, or steamers can all be used with the choice being governed primarily by the type of application, the availability of material or equipment, and the economics involved.

3. Problems associated with heating can be reduced or eliminated by using the proper equipment and with careful planning.

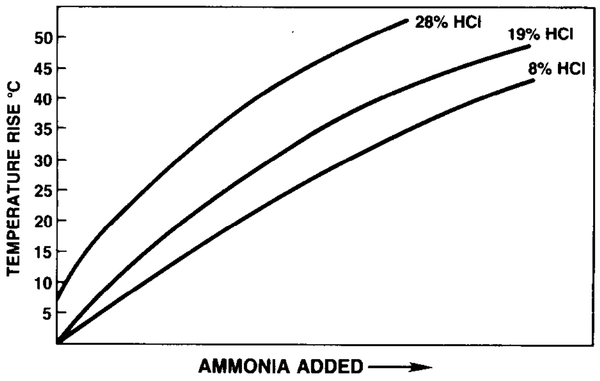


Figure 1

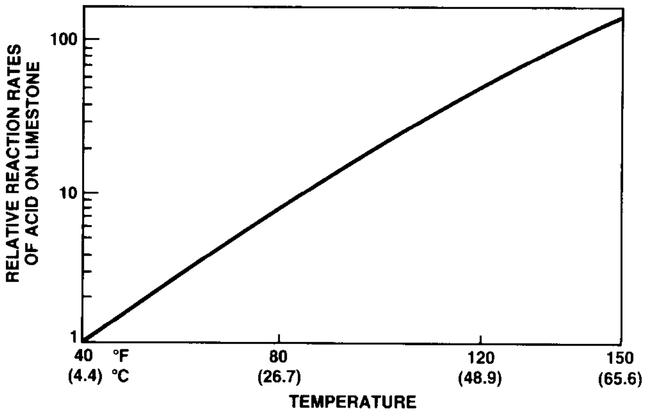


Figure 2

BATCH MIXING IN TANKS

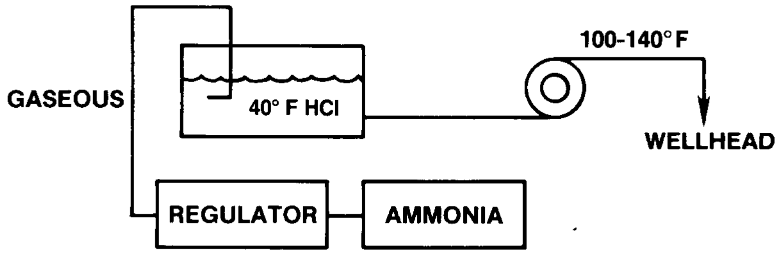


Figure 3

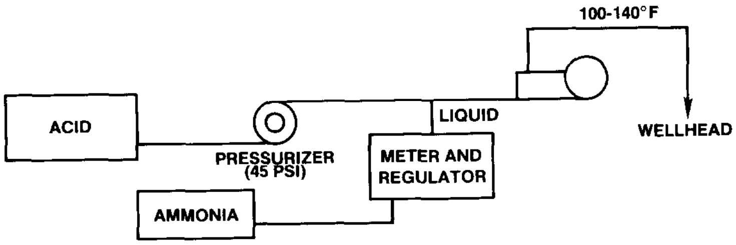
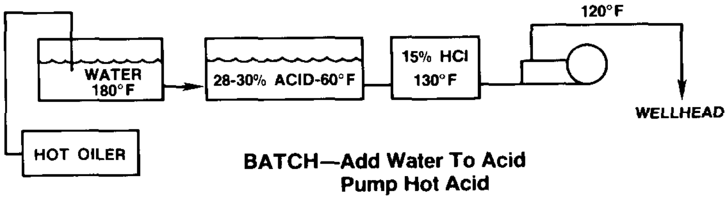
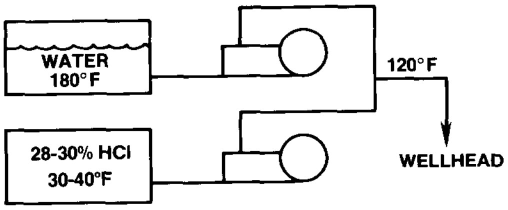


Figure 4



BATCH—Add Water To Acid
Pump Hot Acid

Figure 5



HOT OILER: Pump Hot Water With One Pump
Pump Cold Acid With Other Pump

Figure 6

STEAMER TO HEAT ACID OR WATER

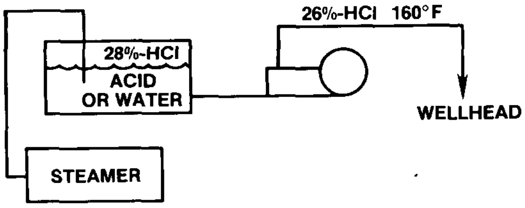


Figure 7