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CHEMICAL STIMULATION OF GEOTHERMAL INJECTION WELLS

MASTER

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PREAMBLE

The United States Department of Energy, Division of Geothermal Energy (DOE/DGE) awarded Vetter Research (VR) a contract to perform research work related to the injection and reinjection problems in geothermal operations. This contract (NO. DE-AC03-79ET-27146) is entitled: "Injection, Injectivity and Injectibility in Geothermal Operations". The present work is a combined report of two of the deliverables under this DOE/DGE contract. It deals with various aspects of a chemical stimulation of injection wells in geothermal operations. The present report combined the work of reports:

1. Acidizing and Acidizing Design
2. Chemical Stimulation Methods for Injection Wells.

1.0 ABSTRACT

Injectivity losses in geothermal operations generally arise due to near wellbore damage caused during various stages of any geothermal operation. Such damages have to be repaired through stimulation techniques. It is not believed that a reliable stimulation technology exists at this time.

Various types of chemical stimulation methods have been considered. High pH fluids seem to be a logical choice for some wellbore and/or reservoir stimulations. However, forming of secondary deposits and creating of new reservoir damages due to chemical reactions between the rock material and these stimulation fluids make it adviseable not to consider any of these high pH fluids in high temperature geothermal reservoirs. Fluids having a neutral pH can be successfully used in chemical stimulation methods only in a very few and rare instances. Low pH fluids, i.e. acids, have by far the best chance to be used for these chemical stimulation jobs. The major part of this report is concerned with acidizing techniques for geothermal injection wells.

Acid jobs in a geothermal field can be

1. Experimental or pilot jobs to evaluate a certain acidizing technique.

2. Routine acid jobs to stimulate wellbores and/or reservoirs based on a acidizing technique proven for a given set of field conditions.

The techniques and objectives for acidizing jobs vary between pilot and routine jobs.

Any acidizing job consists basically of three different parts:

1. Design

2. Execution

3. Evaluation

A proper design, execution and evaluation of an acidizing job is a prerequisite for developing a new stimulation technique or for a sucessfully routine repairing of damages. This proper design, execution and evaluation of an acid job depends upon numerous variables:

1. Type, location and amount of damaging materials.

2. Type, composition and chemical reactivity of reservoir rock and fluids.

3. Composition, chemical reactivity, injection rates and amounts of acid, spearhead and overflush stages.
4. Type of well completion, depth and injectivity of open interval, and available hardware.
5. Temperatures of acids, spearheads, overflushes, wellbore intervals and rock materials before, during and after the stimulation job.
6. Time of life of injection well, i.e.:
    - (a) Immediately after drilling, completion and/or work-over or
    - (b) After standing without reinjecting or
    - (c) After prolonged periods of reinjection.

The present report describes the acidizing techniques to be used for an experimental and the routine stimulation of injection wells. A rather pragmatic approach is used to describe our thoughts, some recent field experiences and the results of some laboratory work.

2.0 SUMMARY AND CONCLUSIONS

1. Stimulation of geothermal injection wells may be required because of:
    - a) Naturally low injectivity or
    - b) Loss of injectivity due to any type of field operations.
2. The removal of flow-resistricting materials in a naturally low injectivity well can not be economically achieved by a matrix stimulation job utilizing chemical reactions. The amount of required chemical would be too large to contact all damaging material within the entire damage pore space. Therefore, this method is not considered in this report.
3. The removal of man-made plugging materials and damages in the vicinity of a geothermal injection well seems to be technically and economically feasible. However, no readily useable technology exists.

4. Many of the problems related to those injection well stimulation jobs that use chemicals (including acids) are generally underestimated by the geothermal industry. The precise type amount and location of the damaging materials are generally not known. Without this information, a optimized stimulation job can not be designed and/or executed.

5. Injectivity losses in geothermal operations normally arise because of near wellbore damage. The damage is a result of the various stages of a geothermal operation. These various stages are, (a) the drilling and completion, (b) reinjection operations, (c) injection of imported waters and (d) disposal of various waste materials. The close proximity of the damaging materials to the wellbore make many chemical stimulation jobs technically and economically feasible.

6. The plugging materials causing the damage to the injection wells are generally known. The principal damaging materials consist of the following:

   a) Sepiolite or other clays used in drilling muds,

   b) Silica

   c) Iron compounds

   d) Sulfates of calcium, barium and strontium,

   e) The degradation products of various chemical additives and

   f) Reservoir fines not being removed from the heat-depleted brine prior to reinjection.

7. The injection well damages can be repaired through chemical stimulation methods, namely, through the use of:

   a) Acidizing

   b) In some instances, use of high pH chemicals and

   c) In some very rare cases, neutral pH fluids.

8. Acidizing of injection wells consists of removing the flow obstructions created by the damaging materials. The majority of the known and/or suspected damaging materials can be removed from injection wells by means of acidizing.

9. Different objectives and techniques apply for

   / a) Pilot or experimental stimulation jobs

   c) Routine stimulation jobs.

   Both types of jobs are designed to increase the injectivity of injection wells.

10. Hydrochloric acid is normally useful for the acidizing of injection wells. Hydrochloric-hydrofluoric and other acid mixtures may be useable in some instances.

11. The precise composition of acids including all additives to be applied in these stimulation jobs is extremely important. The composition of (a) the acids themselves, (b) the various additives and (c) the dilution water is critical for the success of an acid job.

12. Some laboratory experiments to determine the acid reactions between sepiolite and HCl/HF mixtures have been conducted under this contract at 90°C and 150°C (under static conditions).

13. These static experiments gave the following results:

    a. The sepiolite crystal structure is easily destroyed when reacting with acids. These chemical reactions leave amorphous silica and some original quartz as residues.

    b. Adding of HF to 15% HCl increases the dissolution of silica phases and results in decreased amounts of residual solids.

    c. Increasing the temperature increases the amount of magnesium and silica leached into solution.

    d. Increasing the HF concentration and temperature has no advantageous effect over the effect of 15% HCl on leaching aluminum and iron into the solution.

14. Some flow experiments were conducted to determine the effectiveness of acidizing the porous media that are invaded by sepiolite particles. Both HCl and HCl-HF as stimulation fluids can remove the damaged region due to sepiolite. However, the presence of HF makes the cores to disintegrate by removal of cementing material of the formation.

3.0 RECOMMENDATIONS

1. Prior to any acidizing design for the stimulation of injection wells, the nature, location and amount of the damage causing material and the location of the damage itself should be determined as much as possible. This critical information must be considered in the job design. This may sound trivial. However, concrete proof for the nature, location and/or amount of damaging material can hardly ever be gathered in the field. This lack of information may require the need for experimental or pilot jobs prior to performing routine stimulation jobs in a given field under a given set of conditions.

2. Laboratory tests to study the reactions involving the actual rock material in the vicinity of the injection well and the potential acids should be done prior to performing an acid job. This should be done preferably at the bottomhole temperature of the injection well to determine if any secondary and damaging reactions occur between the acid and the formation or flow restricting material.

3. Procedures should be developed for a clean-up of the well after acidizing to remove any unreacted acids, chemical additives and any loose fines. Forcing the reaction products from the vicinity of the well into the reservoir may or may not lead to severe damage collars further away from the wellbore.

4.0 INTRODUCTION

Injectivity losses in geothermal operations generally arise due to a near wellbore damage of injection wells. There are many sources in the routine geothermal operations that can give rise to such damages [1]. The various reports written as part of the injectivity studies under the present contract describe the reasons for injectivity losses and the procedures to be followed to minimize such losses [2,3,4,5]. In principle, the nature of the plugging material causing the damage to the injection wells can be determined:

1. If all the fluids entering the formation are properly characterized.
2. If all the formation components are known.
3. If all the reactions among the various components are known at the various conditions of the reinjection.

Normally, the operator lacks this information in its entirety.

No matter what type of source causes the damage, many injection wells will have to be stimulated. One of the more promising methods of stimulation is through the use of acids. The design of acidizing to stimulate injection wells would require a knowledge of the type, amount and location of the damage. The present report describes the information needed in acidizing design to stimulate injection wells. High and neutral pH fluids have a chance for success only in a few rare cases. This report attempts also to take a look at these fluids.

5.0 OBJECTIVE OF CHEMICAL STIMULATION OF GEOTHERMAL INJECTORS

Geothermal injection wells are prone for (a) having a naturally low injectivity and/or (b) exhibiting serious injectivity losses at various stages of their life. This is especially true in the case of high temperature geothermal operations. The main reasons for sometime rapid injectivity losses are (a) the need to inject very large amounts of brine per well and (b) the plugging of originally good injectors due to the specific conditions of a geothermal operation as outlined later in this report.

Also due to these specifics of a geothermal operation, it may become very difficult, if not impossible, to compare the stimulation of oilfield water injection wells with that of the geothermal reinjection wells as we will also outline later in this report.

Reinjection wells in geothermal operations quite often need various types of stimulation. Oilfield technology does not apply for these stimulation jobs. Normally, the stimulation of geothermal producing wells [13,16] is also quite different from the stimulation technique used for a geothermal injection well.

This means, a new technology has to be developed for the stimulation of these geothermal injectors. To define the need and critical parameters of this new technology is the main objective for this report.

This objective is not self-understood in today's geothermal industry and needs some elaborations as outlined in the following paragraphs.

5.1 REPAIR OF MAN-MADE DAMAGE AFTER WELL DRILLING AND COMPLETION

The newly drilled or completeed geothermal reinjection well differs drastically from the same well after large amounts of heat-depleted brine are injected. The damage is caused by drilling and completion operations [4] which is quite different from the damage caused by a prolonged and faulty injection of the heat-depleted brine (Section 5.2). In addition, the temperature in the well and in the reservoir within the vicinity of the well may be high, at this time thus requiring special precautions. Dispersion of the damaging materials (caused by drilling and completion operation) into the reservoir and the need for back-flowing the chemical reaction products from a stimulation job may also require special considerations. To evaluate these problems is another objective of this report.

5.2 REPAIR OF MAN-MADE DAMAGE AFTER PROLONGED REINJECTION PERIODS

After a prolonged reinjection of heat-depleted geothermal brine or the injection of imported water, the reservoir is considerably cooled down and has little chance to heat up again during any chemical stimulation job. This is a situation quite different from that described in the previous paragraph. Also, the damage caused during these prolonged reinjection or injection periods is quite different from that caused during drilling and completion [4].

This new situation may require a stimulation technology quite different from that required for a stimulation of the well and/or reservoir after drilling and completion. To evaluate the possibilities for a stimulation of reinjection and injection wells after prolonged reinjection and/or injection periods is also a major objective of this report.

5.3 LABORATORY EXPERIMENTS

The chemical reactivity of many damaging materials with acids under the conditions of a geothermal injection well is not described in the literature. It is mandatory for a successful stimulation technique to know the critical parameters of the chemical reactions between damaging materials and stimulation fluids. A few laboratory experiments were to be performed under this contract to shed some light on this problem. To describe these lab experiments is another objective of this report.

5.4 SUMMARY OF OBJECTIVES

Summarizing, we can say that the objectives of the present report include the following:

1. To summarize the various sources of damages to injection

wells at various stages of the well life.

2. To characterize the nature of the various damages expected in injection wells and to postulate various ways of repairing the damages.

3. To describe acidizing as a way of cleaning the injection wells.

4. To describe some laboratory studies on acidizing damage caused by sepiolite with HCl and HCl/HF mixtures.

5. To describe some laboratory studies on damage to porous cores due to drilling mud particle invasion followed by acidizing.

6. To describe the acidizing design principles in acidizing of injection wells (specifically the do`s and don`ts of acidizing operations).

6.0 MAJOR SOURCES OF DAMAGE TO INJECTION WELLS

The damage to injection wells can occur at every stage of a geothermal operation, starting with (a) the drilling and completion operations, going to (b) the final production, and utilization and, finally, ending with (c) injection operations. The various aspects of the damage are briefly described in this section to serve as a basis for an injection well stimulation design.

The damage to a geothermal injection well may be defined as the reduction in injectivity caused by the plugging of the pore channels or fractures of the formation near the injection wellbore. Most of the plugging of the pore channels will be caused by particulate matter entering the porous formation.

The particulate matter can originate at every stage of a geothermal operation. Three of the major stages of a geothermal operation to be considered in analyzing the damage of injection wells may be listed as follows:

1. Drilling and completion of injection wells.
2. Reinjection operations.
3. Injection operations using imported waters.

6.1 DRILLING AND COMPLETION OPERATIONS

The damage to injection wells during drilling operations arise due to the invasion of drilling mud components into the porous formation [4]. The components of the drilling mud consist of the liquid phase of the mud (including dissolved species) and a suspended solid phase such as clay particles and chemical additives (including fluid loss agents, corrosion inhibitors, etc.). In addition, other external particulate matter (such as corrosion products, drill cuttings, etc.,) can enter the wellbore and block the pore passages to the rest of the reservoir . The details on the nature of damage to the reservoir caused during well drilling and completion operations are given in a separate report [4].

Basically, there are two types of damages expected during or after drilling operations. They are (a) physical damage and (b) chemical damage. Under the physical damage comes the plugging of the pores of the formation by clays (or particles) of the drilling mud entering the reservoir. In this category are included the damages, with no chemical changes occuring to the invading and invaded materials . The details on the nature of damage caused by suspended particles are given in a separate report [3]. For geothermal drilling application, sepiolite or attapulgite clays are normally added to the drilling mud. Therefore, one of the most probable damaging material to be considered are these clay particles clogging the pores and, thereby, causing a near wellbore damage. Thus, acidizing to remove sepiolite particles from the damaged zone should be considered.

Under the chemical damage comes the damage resulting from various reactions involving the drilling mud filtrate (including the various chemicals added to the mud), the formation fluids and the formation solid materials. In this category are included the damages caused by:

1. The salt precipitates (mainly sulfates of Ca, Ba and Sr) as a result of the thermodynamic instability of the mixtures of the mud filtrate and the formation brine.

2. The disaggregation and/or swelling of clay minerals that are native to the formation as a result of certain ionic species of the filtrate.

3. The decomposition of the various chemical additives of the mud leaving residues in the pores of the formation at the high temperature of the formation.

Other chemically related damages can occur as part of any drilling operation. The various possible chemical damages are also discussed in the previously mentioned report [4].

6.2 REINJECTION OPERATIONS

The reinjection of the heat-depleted brines from geothermal production wells can also cause various types of damage to the injection wells. This damage has its origin from both physical and chemical effects similar to the ones mentioned in section 6.1. However, it should be mentioned here that this classification is somewhat arbitrary as most of the damage from reinjection occurs through a combination of physical and chemical effects.

The majority of the damages to the injection well during reinjection operation arises from the plugging of the pore spaces by suspended particles. There are inumerable sources of suspended particles in the brines as described in an earlier report [1]. Some field studies involving suspended particle measurement and monitoring in a geothermal operation at the Mercer 2 geothermal well showed that the majority of the suspended particles entering the injection well consist of silica and iron compounds [6]. These suspended particles can eventually result in the plugging of the pore spaces of the reservoir, and thereby, decreasing the well injectivity [3]. In addition to the above mentioned source of damage, there are other chemically oriented sources of damage in these brines. They are as follows:

1. Various chemical inhibitors are added during the production of the brine to combat scale (and or corrosion) problems in the producing brine. Excess amounts of these chemicals can remain in the brine and enter the injection wells. The high temperature of the wells can disintegrate these chemicals and leave a residue in the pores. This can damage the well by blocking the pores.

2. As part of the brine treatment, the operator may routinely use chemical flocculants. Excess amounts of these flocculants can enter the injection well along with the injected fluids and can cause damage by decomposition reactions [7].

3. The heat-depleted brine has a composition somewhat different from the formation brine and can create incompatiblity problems [8].

6.3 INJECTION OPERATIONS USING IMPORTED WATERS

The injection of imported waters into geothermal injection wells can create damage by the formation of sulfate scale. This topic has been discussed previously [2].

7.0 VARIOUS CHEMICAL METHODS OF REPAIRING INJECTION WELL DAMAGE

The stimulation of injection wells generally consist of repairing the near wellbore damage described in the previous section. Chemical methods are commonly used for such stimulation. There are two common methods of chemical stimulation. They are:

1. Acidizing
2. Use of chemicals other than acids

The next paragraphs describe the chemical reactivity of various stimulation fluids as it applies to the stimulation of the injection wells.

7.1 CHEMICAL REACTIVITY OF VARIOUS STIMULATION FLUIDS

In principle, a properly selected stimulation fluid will chemically or physically remove a damaging material without harming the remaining rock matrix. Unfortunately, very few stimulation fluids, if any, can be used without harming this remaining rock matrix. These secondary damages can be caused by the following reactions:

1. The reaction products from the chemical reactions between stimulation fluids and damaging materials are rather insoluble and form new plugging materials.

2. The stimulation fluids may also react with the native rock materials. This may lead to unwanted reactions by:

    a) The cementing rock materials may be partially dissolved and dislodged, thus causing the migration of moveable fines and, in the worst case, matrix collapse.

    b) The reaction products may be insoluble thus causing an additional plugging by secondary deposits within the pore space.

3. The stimulation fluids and/or the reaction products from the (a) fluid/damaging material and (b) fluid/rock material interactions may chemically react with the reservoir fluids, thus leading to a new type of damage.

4. The stimulation fluids themselves may be chemically incompatible with the reservoir fluids, thus again leading to a new type of damage.

All these types of secondary damages have been observed in field and laboratory experiments. Unfortunately, very little attention is paid by the operators to these secondary damages which, quite often, can be more detrimental to the injectivity than the original damage. Any stimulation job design must consider the potential for forming a secondary damage.

7.1.1 UTILIZATION OF HIGH pH STIMULATION FLUIDS

To utilize a high pH stimulation fluid for geothermal injection wells presents a luring temptation for an operator. The solid silica, one of the major sources for injector plugging is highly soluble in many high pH fluids. Also, many rock materials are chemicaly not attacked by these fluids, thus eliminating the danger of generating a rock matrix problem. Unfortunately, the native reservoir fluids as well as the injected brine is often highly sensitive to a high pH value. Not the high brine TDS, as frequently assumed, but the high concentration of divalent and trivalent ions in the brines will cause a major secondary problem. The precipitation of hydroxide and basic carbonate scales is the consequence of the chemical reactions between high pH stimulation fluid and reservoir or injection brine. These scales, particularly the hydroxides (e.g. iron, magnesium, manganese, etc.), are extremely fluffy and voluminous in the pores even if their amounts are only very small.

7.1.2 UTILIZATION OF NEUTRAL pH STIMULATION FLUIDS

Stimulation fluids having a neutral pH may also have a potential for injection well stimulations without generating a severe secondary damage. However, these fluids are also not without problems.

There are some neutral pH fluids which could be excellent solvents for certain types of damaging materials. For example, EDTA (e.g. Versene 100) and nitrilotriacetic acid salts are excellent chelating agents for the ions of the alkaline earth metals. Thus, $CaSO_4$, $SrSO_4$ and $BaSO_4$ scales could be removed by solutions of these materials in neutral or near neutral pH water without causing secondary precipitates if properly applied. The major problems is cost. These materials are rather expensive (e.g. on a "per pound" basis) and large amounts would have to be used for most stimulation jobs.

These chelating agents and a number of other complexing agents could find their application in a few rare cases. It may be still more economical to use these agents instead of operating a damaged injection well or drilling of a new injector.

7.1.3 UTILIZATION OF LOW pH STIMULATION FLUIDS (ACID)

Low pH or acid stimulation is probably the potentially best method of repairing or stimulating of a damaged well. Basically, there are two mechanisms by which an acid stimulation can work:

1. Removal of solid flow obstructions (damage material) from the wellbore or from the reservoir in the vicinity

of the wellbore.

2. Dissolving of portions of the reservoir rock, thus creating new flow channels through the damaged portion of the reservoir by leaving the orignal damage material as a new "rock matrix".

Both mechanisms or any combinations of these mechanisms could lead to a successful stimulation of a geothermal injection well.

The literature on various stimulation methods, including acidizing of petroleum wells have been reviewed in a recent report [12]. The number of references on acidizing of oilfield wells (including water injection and disposal wells) is too large to be given again. Only a few references [10,11] describing the general aspects of acidizing are given. A recently prepared report [13] by VR described also the problems associated with transfering the acid stimulation technology from the petroleum industry to geothermal production wells (see also [16]). This latter report [13] also contains some general comments on the feasibility of acidizing geothermal injection wells.

Acidizing of injection wells consists of removing the flow obstructions created by one of the mechanisms desribed in section 6.0. As mentioned in that section, the main categories of materials that can cause damage to geothermal injection wells consist of the following:

1. Sepiolite or other clays
2. Silica
3. Iron compounds (iron hydroxide or iron hydroxychloride)
4. Sulfates of calcium, Barium and Strontium
5. The chemicals and degradation products of various additives in drilling muds and injection waters.
6. Materials specific to a given geothermal operation (e.g. chemicals or chemical reaction products resulting from faulty operations).

Thus, acidizing an injection well involves the selection of acids or acid mixtures which remove these damaging materials without causing problems by secondary deposits of the acid reactions. Among the damaging materials listed above, sepiolite or other clays, silica and others are directly amenable to acidizing. Some other damaging materials may require special chemical methods [9] (see also Sections 7.1.1 and 7.1.2) and the use of mechanical methods.

As mentioned above, the literature on acidizing of low temperature petroleum wells is voluminous and has been reviewed [12]. The only paper describing the high temperature aspects of acidizing (maximum temperature of 400° F) was prepared by Dill and Keeney [14].

From the various literature citations, it can be recognized that four major types of acids are used in conventional well treatments. These acids are:

1. Hydrofluoric acid.
2. Hydrochloric acid.
3. Formic acid .
4. Acetic acid.
5. Mixtures of the above four acids.

A recent report [15] by Vetter Research on acidizing gives the results of a laboratory study of the reactions of acids with calcium cabonate, kaolin, sepiolite and two formation materials at geothermal temperatures. Only limited data was obtained for the reaction of HCl with these materials. The report provides the basic information for the selection of acids (hydrochloric acid, hydrofluoric acid, acetic acid and formic acid) for the acidizing of geothermal production wells which are damaged by sepiolite clay. However, the report does not give any information on the chemical reactions of sepiolite with hydrochloric acid or mixtures of hydrochloric acid and hydrofluoric acid. In Section 8.0 of this present report, some laboratory studies on the acid reactions between sepiolite and these acids are described.

7.2 GENERAL ASPECTS OF INJECTION WELL STIMULATION FOR THE DESIGN, EXECUTION AND EVALUATION OF AN ACID JOB

Assuming, (a) the damage to geothermal injection well and (b) the acid/rock, acid/fluid and acid/damage-material interactions are all known in sufficient detail a job could be designed and performed in the field. This leaves the opertor still with a major problem: How can he be assured that the job is properly executed? One of the major risks in acidizing of any well is that the acid fluids are not prepared properly or are poorly handled in the field, thus deviating drastically from the job design. This means, execution of the job is equally important.

Assuming, (a) the extent of the damage (type, amount and location of damage) and (b) the acid reactions are not known in all required details, the operator may gain new and critical information during the execution of the "poorly" or wrongly designed job thus demanding special attention to be paid to the execution details of the job.

Finally, a properly designed and executed acid job may or may not result in a desired, assumed and/or expected increase of the injectivity for a number of reasons (see 7.2.3). This calls for a thorough evaluation of the job as outlined later (see Section 7.2.3).

7.2.1 DESIGN OF ACID JOB

Normally, the operator lacks sufficient details on (a) the type, location and amount of damaging materials and (b) all possible chemical and physical reactions between the injected acid solution and the various liquid and solid materials present in the original rock matrix. This lack of information causes major job design problems. In addition, secondary reaction products (see earlier in this report) can cause the precipitation of new materials, thus causing new damage.

Laboratory experiments as those described in this present and another report [15] can be used to somewhat overcome the lack of information on the primary and secondary chemical reactions. However, even these lab tests still leave the operator with the common design problem that he does not know the correct type, location and amount of the damaging materials.

To overcome these design problems, the operator may have to design a pilot acid stimulation job which should be designed, executed and evaluated for nothing else but to gain the required information for a subsequent job. The design of this pilot or experimental job should be quite different from the subsequent routine-type stimulation job based upon the different objectives of the two different jobs.

Quite often, some additional and critical variables required for proper job design are also lacking. As the chemical reactions between the acid and the various plugging and native rock materials proceed, still unreacted particles may be dislodged and may start flowing into the pores. This may generate the often experienced "check valve" effect after an attempted acid stimulation job. This raises the question whether the spent fluids should be forced into the reservoir or should be back-flowed prior to resuming normal injection operations. This question is addressed in the next two sections.

7.2.1.1 DISPERSION OF CHEMICAL REACTION PRODUCTS INTO RESERVOIR

The common assumption is that dislodged and migrating fines should be forced into the reservoir after an acid stimulation job. It is then assumed that the damage caused by these particles through settling in a larger distance from the wellbore will cause only a minor new damage.

Laboratory experiments recently performed [3] indicate that this assumption may be incorrect. Fine particles may flow a considerable distance from the wellbore where they can form permanent damage collars. It may become impossible to remove these damage collars at a later time. Due to the distances and associated pore volume involved in this damage collar removal, the amounts of acid and/or other chemicals may become very large and economically unaffordable. Thus, this damage may become irrepairable and permanent.

7.2.1.2 BACK-FLOWING OF WELLS AFTER STIMULATION

Based upon the comments made above, it may be more adviseable to back-flow the well after a stimulation job and before routine injection operations are resumed. Even though this method is safer, it may not be possible to back-flow the well. In most cases, artificial lift will be required for an interim back-flow, thus adding considerable cost to the overall job.

7.2.2 EXECUTION OF THE STIMULATION JOB

The proper execution of an acid stimulation job cannot be overemphasized. Personal experience in supervising or evaluating numerous acid jobs [12,13,15,16,17] showed that the properties of the stimulation fluids delivered to the well site hardly ever agree with the designed fluid properties. However, this is only one of the problems related to a proper job execution.

More important, the execution of an acid job allows the operator to evaluate quickly the relation of wellhead pressure vs acid injection rate as a function of time or cummulative volume of injected acid. This on-site evaluation should always be an integral part of any stimulation job execution. This "quick and dirty" evaluation will rapidly tell whether the injected acid is performing well and will also indicate the timing for (a) acid injection rate increases and decreases and (b) the proper conclusion or shut-down time for the entire stimulation job. Unfortunately, we hardly ever witnessed this portion of an acid stimulation job at any well site.

Finally, there is still another aspect to the job execution as well as job design stimulating of geothermal well through acidification. Field experiments [18,19] showed that the pH of flashed and heat-depleted geothermal fluids can be economically controlled by adding small amounts of acids to these liquids prior to injection into the flashed fluids instead of the conventional injection of acids or acid mixtures into an injection well. Naturally, the duration of such a method would be much longer than the conventional stimulation job. An acid injection rate of the order of a few gallons per minute would be appropriate instead of injection rates on the order of one or two barrels per minute in conventional stimulation job.

Here again proper execution would require a monitoring of the wellhead pressures, acid injection rates and times during this acid injection.

7.2.3 EVALUATION OF THE STIMULATION JOB

The "normal" evaluation method of a stimulation job is based upon the difference of the injectivity before and after the job. Even though this seems to be a logical way to evaluate and/or judge the job, this way has major flaws:

1. The operator normally does not know what the optimum increase of injectivity should be. This means, that any increase of injectivity would be appreciated but could be only a fraction of the theoretically achievable increase of injectivity.

2. If any of the information available (a) for the job design and (b) from the job execution was incorrect or incomplete, this evaluation method would yield rather incomplete information.

3. Any complicating but unknown factors within a given well or reservoir would not be recognized and could not even be realized by using this "normal" evaluation method.

The risk seems to be too large to base the job evaluation solely on the increase of injectivity. It seems to be worthwhile to go to an additional job evaluation method which can be used if the stimulated well is back-flowed after the stimulation job.

The back-flowed (i.e. produced) liquids contain the dissolved products of all chemical reactions taking place during and after the acid job. Using the chemical analyses, flow rates and produced volumes of the back-produced fluids will allow the operator to perform some rather accurate and reliable material balances. These material balances could be used as a valuable aid for the job evaluation.

This method has been used successfully for the evaluation of the acid stimulation of geothermal production wells [17]. The same method could be used for a more accurate and reliable evaluation of acid stimulation jobs on geothermal injection wells and reservoirs.

8.0 LABORATORY EXPERIMENTS ON ACIDIZING

Two types of experiments related to acidification of geothermal injection wells were conducted under this contract. They are:

1. Static Experiments related to the reaction of HCl and

HCl-HF mixtures with sepiolite.

2. Flow Experiments involving the acidizing of Berea sandstone cores damaged by sepiolite particles.

These experiments are described in this section.

8.1 STATIC EXPERIMENTS

The purpose of these static experiments is to quantify the effects of various acid concentrations at two different temperatures on the sepiolite clay particles. Experiments were carried out at 90°C and 150°C using the following acids:

15% HCl, 15%HCl + 1% HF, 15% HCl + 2% HF, and 15% HCl + 3% HF.

8.1.1 METHODS

Eight portions of sepiolite (at three-hundred milligrams each) were reacted with twenty milliliter portions of solutions containing various acids at 90°C and 150°C. The reactants were placed in sealed teflon-lined bombs and heated to appropriate temperatures for six hours. The solutions were filtered and analyzed for various ionic species. The solids were analyzed by x-ray diffraction (XRD), scanning electron microscopy (SEM), and energy dispersive x-ray spectrometry (EDXS). XRD, SEM, and EDXS were also performed on an untreated sepiolite sample for comparison. A sample of untreated sepiolite was digested and chemically analyzed to determine its original composition.

The chemical analysis of the solutions and digested samples were done by Inductively Coupled Argon Plasma Spectrometry (ICAP). Dilutions were made when appropriate.

8.1.2 RESULTS

Sepiolite is a hydrated magnesium silicate. Aluminum and iron are the most common substituting ions in the sepiolite structure. The varying composition of the sepiolite demands a precise analyses of all samples.

8.1.2.1 ANALYSIS OF SOLIDS

X-ray diffraction analysis reveal that the sepiolite crystal structure is destroyed in all samples subjected to acidizing. Figure 1 shows the XRD pattern of untreated sepiolite and a typical pattern of an acid treated sample. The XRD pattern of the acid treated sample shows a hump from 17 to 28 degrees. This is characteristic of amorphous material, probably amorphous silica. The quartz peaks derives from minute concentrations of quartz in the original sample and are amplified in the acidized samples because of the absence of other crystalline compounds.

Energy dispersive x-ray analysis of all the acid treated solids indicate that the residual solids are silica. Table 1 shows a EDXS spectrum of untreated sepiolite. Tables 2 and 3 are EDXS spectrum of typical residual solids after acidizing with HCl or HCl/HF mixtures, respectively. These data indicate the removal of magnesium, aluminum, and iron upon acidizing thus leaving only silica in the remaining solid phases.

8.1.2.2 ANALYSIS OF LIQUIDS

The data of the chemical analyses of the various acid solutions are shown in Table 4. From these data, it is evident that increasing the concentration of HF has no effect on the amount of magnesium already leached out by a 15% HCl solution. However, it has a pronounced effect on increasing the dissolution of silica phases (see Figure 2). The effect of increasing the temperature is a slight increase of the amount of magnesium and silica leached into solution. The concentration levels of aluminum and iron leached by a 15% HCl solution remain unchanged by either increasing the concentration of HF or by increasing the temperature.

8.1.2.3 CONCLUSIONS OF STATIC ACIDIZING EXPERIMENTS

From the data presented here the following conclusions can be drawn:

1. At all acid concentrations and at all temperatures used, the sepiolite crystal structure was destroyed. The residual solids after acidizing consisted of amorphous silica and some original quartz.

2. Adding HF to 15% of HCl solution increased the dissolution of silica phases and resulted in decreased amounts of remaining solids.

3. The higher the temperature, the higher is the amount of magnesium and silica leached into solution.

4. Increasing the HF concentration and temperature has no apparent effect on leaching aluminum and iron into solution above that found with 15% HCl solution alone.

8.2 FLOW EXPERIMENTS

The purpose of the flow experiments is to determine the effectiveness of acidizing the zones of a porous media that have been invaded by sepiolite particles. The experiments are done in two stages:

1. The first set of experiments consists of creating a

damage to the porous media by sepiolite injection (in the present experiments, Berea sandstone cores were used).

2. The second set of experiments consisted of acidizing the damaged cores (15% HCl and 15% HCl - 3% HF were used).

The details of these experiments are described in this section.

The first set of experiments were conducted by pumping a suspension of fine (smaller than 1 micron in diameter) sepiolite particles in water through the Berea sandstone core plugs. The purpose of these experiments was to simulate the damage to porous media by the invasion of sepiolite particles. The second set of experiments were conducted by pumping acid (HCl or HCL-HF mixture) through the damaged cores. The purpose of these latter experiments was to repair the damage by acidizing.

The apparatus used in conducting the flow experiments consists of four reservoirs. Reservoir 1 contains kerosene which is pumped by means of a metering pump at a predetermined rate. Kerosene is used to displace the appropriate fluids to be used in flooding the cores. Reservoir 2 contains deionized water. The purpose of Reservoir 2 is two fold, namely (1) to saturate the core prior to the starting of the experiments using sepiolite particle suspensions and (2) to flush the acid after acidizing. The initial saturation of the core is done by displacing the deionized water using kerosene. This part of the experiment can also be used in determining the initial permeability of the cores used. Reservoir 3 is a slurry vessel and it consists of a cylindrical vessel containing floating a lucite piston. A description of the slurry vessel is given in a separate report [3]. The lower part of Reservoir 3 is filled with sepiolite suspension. The suspension is constantly stirred using a magnetic stirrer to maintain the particles in suspension. Reservoir 3 is used in creating a zone of damage by the invading sepiolite particles. This is done by pumping the particle suspension through the core. During the experiments, the pressure at the input of the core is monitored by means of pressure transducers (see Reference [3]). Reservoir 4 is used to hold acid (either HCl or HCL-HF mixture). Reservoir 4 consists of a stainless steel pressure vessel the inside surface of which is coated with plastic. The acid solution which is displaced by means of kerosene is used in acidizing the cores that were damaged by sepiolite particles.

The core plugs used in all the flow experiments were drilled from a Berea sandstone block. The porosity and permeability of the cores were measured. One of these cores was mounted in the core holder (see Reference [3]). The core was subjected to an overburden pressure of 1000 psia. Initially, the core was saturated by flowing deionized water through it until the inlet pressure reached a constant value. This indicated that the permeability of the core had reached a stable value. Then the sepiolite particle suspension was pumped through the core at a constant flow rate. When the inlet pressure reached a value of 600 psi, the experiment was discontinued and the core was taken out for examination using procedures similar to the ones described in the mentioned report [3]. Another similar core was then mounted and the experiment was repeated until the inlet pressure again reached 600 psi. This second core was subjected to acidizing. The acidizing was done by pumping acid until the pressure reached slightly above 600 psi. Then, the core was shut-in for a short time (usually a minute) to allow the acid to react with the damaged region. This procedure was repeated several times. Eventually the inlet pressure dropped substantially. The core was taken out and examined by SEM.

The above procedure was repeated at four different flow rates with two different acids (HCl and HCl-3% HF). The four rates used are 0.4, 1.0, 5 and 10 ml/min. The core plugs used in all the tests have an average porosity of 20.3% and permeabilities in the range of 100 to 200 md. Using of either of the acids readily restored the damage caused by the sepiolite particles. However, the presence of HF in the acid mixtures result in a severe disintegration of the core material. The cores actually become unconsolidated. This could have a severe impact on the formation through formation collapse.

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TABLE 1

```
   SPECTRUM   UNTREATED                       DEC. 15, 1981

  ACCELERATING VOLTAGE                 20.3 KEV

  INCIDENCE ANGLE                      55.0 DEGREES

  EFFECTIVE TAKE-OFF ANGLE             56.4 DEGREES


                     STANDARDLESS EDS ANALYSIS
                   (ZAF CORRECTIONS VIA MAGIC V)

ELEMENT               WEIGHT    PRECISION    OXIDE      OXIDE
& LINE     K-RATIO    PERCENT    2 SIGMA    FORMULA    PERCENT

 MG KA     0.1442       7.01       0.23      MGO        11.62
 AL KA     0.0142       0.79       0.09      AL2O3       1.50
 SI KA     0.8067      39.66       0.64      SIO2       84.85
 FE KA     0.0348       1.58       0.24      FEO         2.03
 O  *                  50.96

 TOTAL                                                 100.00

   * DETERMINED BY STOICHIOMETRY
```

TABLE 2

```
  SPECTRUM   90,HCL                          DEC. 15, 1981

 ACCELERATING VOLTAGE                  20.3 KEV

 INCIDENCE ANGLE                       55.0 DEGREES

 EFFECTIVE TAKE-OFF ANGLE              56.4 DEGREES


                  STANDARDLESS EDS ANALYSIS
                (ZAF CORRECTIONS VIA MAGIC V)

ELEMENT                  WEIGHT    PRECISION    OXIDE     OXIDE
& LINE       K-RATIO     PERCENT    2 SIGMA    FORMULA   PERCENT

 MG KA       0.0104        0.54       0.07      MGO        0.90
 AL KA       0.0035        0.17       0.04      AL2O3      0.32
 SI KA       0.9393       44.61       0.70      SIO2      95.44
 CL KA       0.0374        2.71       0.24      CL         2.71
 FE KA       0.0094        0.49       0.15      FEO        0.63
 O  *                     51.47

 TOTAL                                                   100.00

    * DETERMINED BY STOICHIOMETRY
```

TABLE 3

```
   SPECTRUM    90,HCL,HF2                  DEC. 16, 1981

  ACCELERATING VOLTAGE               20.3 KEV

  INCIDENCE ANGLE                    55.0 DEGREES

  EFFECTIVE TAKE-OFF ANGLE           39.0 DEGREES


                  STANDARDLESS EDS ANALYSIS
                 (ZAF CORRECTIONS VIA MAGIC V)

ELEMENT                WEIGHT   PRECISION   OXIDE    OXIDE
& LINE     K-RATIO    PERCENT    2 SIGMA   FORMULA  PERCENT

 SI KA     1.0000      46.74      0.73      SIO2     100.00
 O  *                  53.26

 TOTAL                                               100.00

   * DETERMINED BY STOICHIOMETRY
```

TABLE 4

CHEMICAL ANALYSIS OF REACTED ACIDS

$T = 90^{\circ}C$

ACID CONCENTRATION	Mg(ppm)	Al(ppm)	SiO_2(ppm)	Fe(ppm)
15% HCl	2060	92.3	63.7	43.5
15% HCl +1%HF	2070	134	7700	45.0
15% HCl +2%HF	2040	147	8900	45.8
15% HCl +3%HF	2090	91.6	9830	49.1

$T = 150^{\circ}C$

ACID CONCENTRATION	Mg(ppm)	Al(ppm)	SiO_2(ppm)	Fe(ppm)
15% HCl	2180	131	168	48.3
15% HCl +1%HF	2130	148	8600	46.5
15% HCl +2%HF	2160	145	10,500	46.2
15% HCl +3%HF	2140	124	10,900	46.9

FIGURE 1

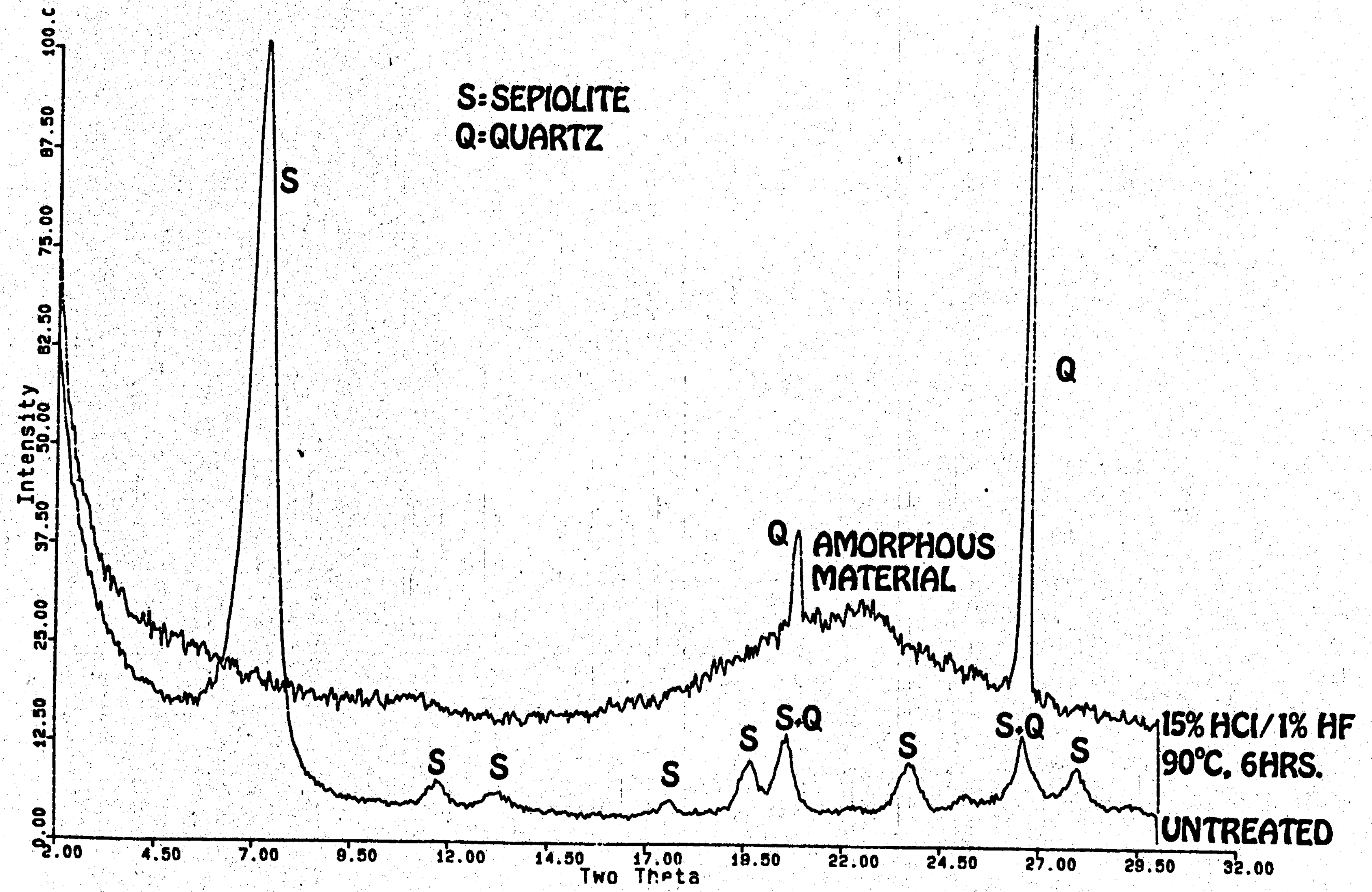
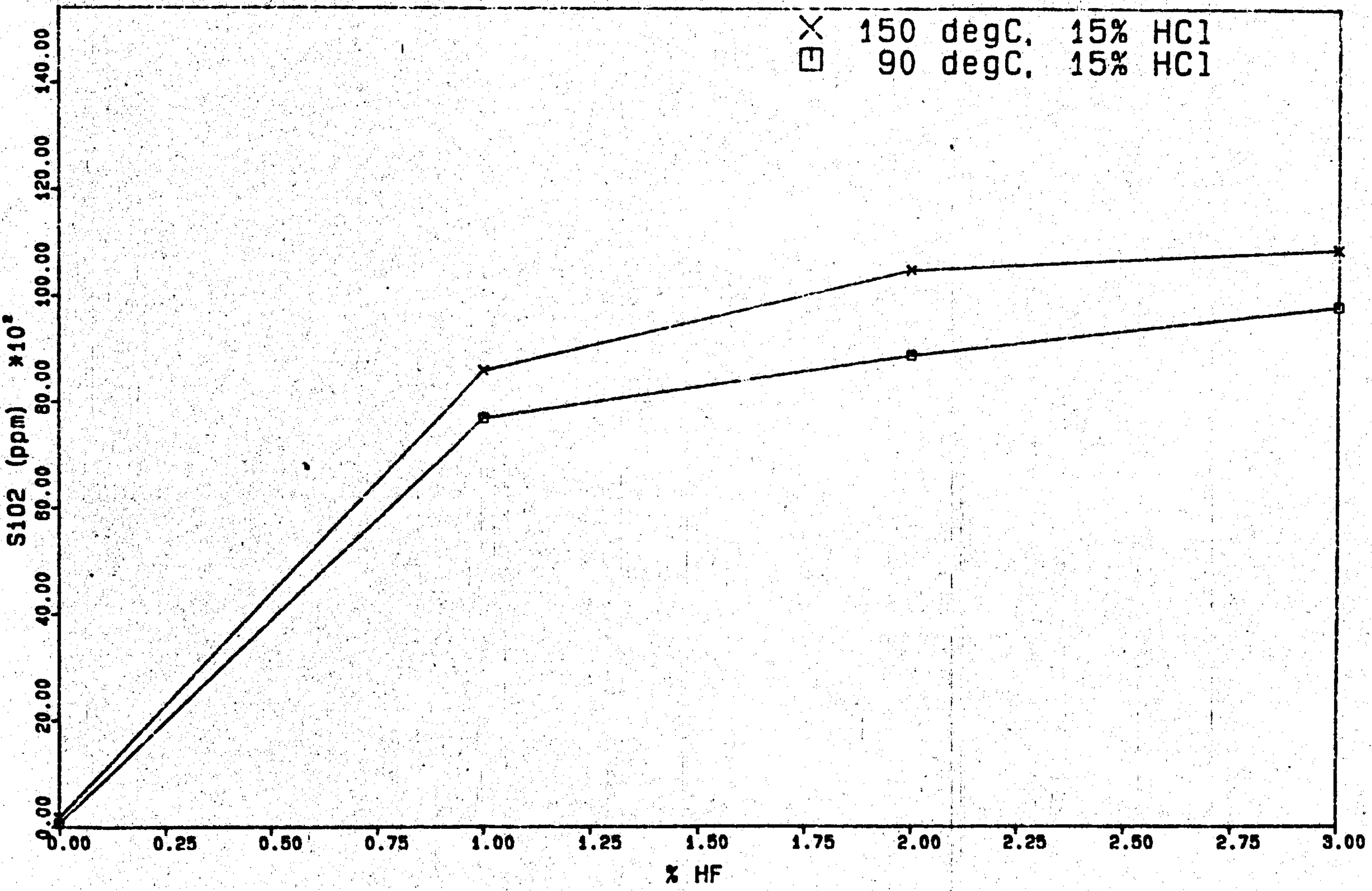

S: SEPIOLITE
Q: QUARTZ
S
Q
Q
AMORPHOUS MATERIAL
S
S
S
S
S.Q
S
S.Q
S
15% HCl/1% HF 90°C, 6HRS.
UNTREATED
Intensity
100.0
87.50
75.00
62.50
50.00
37.50
25.00
12.50
0.00
2.00
4.50
7.00
9.50
12.00
14.50
17.00
19.50
22.00
24.50
27.00
29.50
32.00
Two Theta

FIGURE 2



× 150 degC, 15% HCl
☐ 90 degC, 15% HCl
SiO2 (ppm) *10²
0.00
20.00
40.00
60.00
80.00
100.00
120.00
140.00
0.00
0.25
0.50
0.75
1.00
1.25
1.50
1.75
2.00
2.25
2.50
2.75
3.00
% HF