External Treatment of Feed Water for Steam Flood Steamers

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The purpose of this paper is to provide a concentrated review of significant water characteristics and treating methods as related to steam flood boiler operation. In recent years, considerable interest has developed in the direct application of high pressure steam for the purpose of recovering crude oil not obtainable otherwise. With the increasing size and number of steam flood operations, there has been a turn toward higher capacity generators and higher operating pressures. As these pressures increase, water supply characteristics and water treatment methods have increased in importance.

STEAM GENERATOR TYPE

Most of the present steam floods are operating with the boiler pressure in the range of 500-700 psi with some in the range of 1500 psi, both operating and projected. Several installations of even higher pressures, up to 2000 psi are being considered and planned. Practically all of the units being used in this type service are the monotube. single pass boiler which is a type particularly suitable for this service. The generating tube is a huge coil with feedwater pump at one end with a suitable steam-water mixture being removed from the other end of the coil and injected directly to the point of application. No large drums are involved in the design of the units with the result that very high pressures can be developed, in conjunction with high capacities, at relatively low cost. The units are of compact design, readily automated, are lightweight and even the larger capacity units are readily skid-mounted. In comparison with standard designs of water tube units, these boilers are relatively safe because of the use of a single coiled tube and the lack of a large vessel such as in the case of a drum-equipped conventional water tube boiler.

These boilers or "field heaters" are subject to waterside failures which may be traced to deficient water conditioning. Scale formation can develop because of improper treatment practices, external or internal or both. Also, excessive boiler water concentration may develop, leading to scale deposition, when steam quality is allowed to develop to high levels.

The rather standard practice in the industry is to operate these units in order to provide 80 per cent quality steam with an actual mixture of 80 per cent steam and 20 per cent water being supplied to the injection well. On this basis, all of the solids present in the original feedwater are concentrated in the 20 per cent water remaining at the point of exit from the boiler. The feedwater solids have then concentrated five times in the boiler water or the boiler water is said to have "cycled" five times on the basis of the original feedwater.

The actual pressure of operation imposes some limits on the characteristics of the feedwater and if the existing water supplies do not meet the practical maximums, then treatment of the water in some suitable yet simplified manner is required. When considering water treating procedures, it is essential that proper emphasis be pleced upon the type of operators who are going to be available for control of the water treating plant, the locale of the operation and the amount of attention that is expected to be given to the installation.

APPLICATION METHODS OF EXTERNAL TREATMENT

In the water treatment field, those processes which treat or condition water external to the boiler are considered as "external" treatment, while those chemicals which are injected directly to the boiler feedwater or to the boiler itself are considered as part of the "internal" treatment system. Keeping in mind the fact that water treatment procedures should be as safe and trouble free as possible, requiring a minimum of supervision, it is frequently desirable to employ equipment which may be more expensive initially or may be more expensive to operate when these costs are compensated by reduced supervision requirements. Table 1

WATER TREATMENT METHODS AND APPLICATIONS

| Process | Equipment <u>Used</u> | Chemicals | Purpose |
|---|--|--|--|
| Aeration | Forced Draft Aeration Tower | None (Air Only) | Oxidation of Iron. Removal of Carbo dioxide. |
| Degasifying | Forced Draft Tower | Flue Gas | To lower pH, increase efficiency hydrogen sulfide removal. |
| Coagulation | Sludge Contact Clarifier | Lime, soda ash, alum, iron salts, magnesium salts, in any combination | Coagulation of suspended matter precipitate iron, reduce hardnes silica, alkalinity. |
| Filtration | Septum ^T ype Filters | Diatomite Filter Aid | Remove small quantities of oil, su pended solids, precipitated iron. |
| | Sand or Coal Filters, Pressure or Gravity | Usually follow Coagulation | Designed to handle larger quantitie of coagulated material and suspende solids. |
| Sodium Zeolite Softening | Pressure Tank Equipped with Exchange Resin and Supporting Bed | Salt (NaCl) | Exchanges sodium for calcium an magnesium present in raw water Exchanges small amounts of iro also. |
| Sodium Hydrogen Zeolite | Pressure Tanks Equipped with Exchange Resin and Supporting Bed | Salt (NaCL) Acid (66₀Be'H₂SO₄) | Sodium unit as above. Hydrogen un exchanges hydrogen for calcium magnesium, sodium. Reduce alkal nity and total solids. |
| Demineral- ization (Silica Absorption) | Pressure Tanks Equipped with Suitable Resin and Supporting Bed | Acid (660Be'H2SO4) Caustic (NaOH) | Remove all dissolved solids, including SiO2 when strong base anion r sin used. |
| Chlorination | Chlorinator | Chlorine Gas | Oxidize iron, hydrogen sulfide; de troy and control algae, bacteria growths. |

The most commonly used methods of externally treating water supplies and the purpose for which they are used are shown in Table 1.

Of the processes listed above, the coagulation process, with or without silica absorption, and the demineralizing process require the most attention. Where the raw water supply is a well water of constant characteristics, all treatment processes are greatly simplified. However, with use of surface supplies of variable characteristics, the coagulation process, using a conventional or compact type clarifying unit requires careful supervision if proper results are to be obtained, particularly in cases where silica absorption is important.

While gravity filters and various types of pressure filters are employed in field operations, the diatomaceous earth filter is readily employed whenever small quantities of iron oxide, oil, colloidal matter or sediment (turbidity) are to be removed. Where turbidities and suspended solids concentrations are high, the more conventional filters, preceded by a clarifier, will be required.

The removal of hardness to a satisfactory de-

gree is probably the most important requirement common to all water supplies. In most cases, the sodium zeolite softener is the most practical way to achieve this end. In some cases, sodium-hydrogen zeolite units have been employed in order to obtain alkalinity reduction as well as softening.

In other instances, demineralizing plants have been installed in order to reduce the total solids, hardness and silica content of the water supply. In most instances, the reduction of alkalinity is not necessary as the handling of concentrated acid and caustic for the regeneration of hydrogen zeolite softeners and demineralizing plants poses extra operating hazards.

SIGNIFICANCE OF SPECIFIC WATER CHARACTERISTICS

In this discussion, the effects of feedwater characteristics are considered only with respect to steam generator operation. Because of widely varying subsurface conditions, it is possible that certain subsurface conditions may impose further restrictions as to water quality. In practically all instances, however, any water suitable for these high pressure steam floods will be compatible with other streams in the injection area.

In Table 2 are listed practical feedwater limits. It should be noted that these limits are based upon operation of the generators at 80 per cent steam quality or less.

<u>Hardness removal</u> is an essential requirement in the operation of the monotube boiler. The degree of hardness reduction required is readily obtained with the employment of sodium zeolite softening, removing the calcium and magnesium constituents of the raw water and substituting sodium. Since the solubility of sodium salts is extremely high even under elevated pH, temperature and pressure conditions, little difficulty is encountered with scale formation or deposition when steam quality is properly controlled

Alkalinity concentrations are of significance in stationary plant operation for reasons which are not pertinent to steam flood operations. Therefore alkalinity reduction is seldom required in staem flood operations. Normally the bicarbonate and carbonate alkalinity which may be present in a given supply will break down under operating conditions to release carbon dioxide in the steam phase allowing hydrate alkalinity to remain in the water phase. Since the water and steam phase are intimately mixed, the pH of the mixture is maintained at a high enough level that carbon dioxide corrosion is seldom encountered in the casing or piping through which the mixture travels. In those isolated cases where some corrosion does develop, the application of a filming amine has proven satisfactory, providing an economical treatment and eliminating the need for alkalinity reduction by externel means.

Silica concentrations shown are higher than those shown by others. Where the total solids content of the boiler water is quite high, and this is the case in most steam floods, the significance of silica as a scaling factor is consider-

| (Generator Operation at 80% Steam, 20% Water) | | | | | | |
|---|-------|-------------|------------|-----------|-----------|--|
| Pressures Up To (psi) | | | 500 | 1000 | 1500 | |
| Constituent | Units | Max. or Min | | | | |
| Hardness (CaCO ₃), | ppm | Max. | 0 - 2 | 0 - 2 | 0 - 1 | |
| Alkalinity (total), | ppm | | No Limits | No Limits | No Limits | |
| Silica (SiO ₂) | ppm | Max. | 100 | 75 | 50 | |
| Iron (Fe), | ppm | Max. | 1.0 | 0.5 | 0.1 | |
| Turbidity, | units | Max. | 5.0 | 3.5 | 3.0 | |
| Suspended Solids, | ppm | Max. | 2.0 | 1.0 | 0.5 | |
| Dissolved Solids, | ppm | | No Limits. | No Limits | No Limits | |
| Dissolved Oxygen, | ppm | Max. | 1.0 | 1.0 | 0.5 | |
| Hydrogen Sulfide, | ppm | Max. | 0.5 | 0.5 | 0.5 | |
| 0i1, | ppm | Max. | 1.0 | 0.5 | 0.5 | |
| ph | | Min. | 9.0 | 9.0 | 9.0 | |

Table 2

| SOME PRACTICAL | STEAM FLOOD |) FEEDWATEF | LIMITS |
|----------------|-------------|-------------|--------|
| | | | |

ably reduced particularly when high sodium concentrations are present. In high pressure stationary practice, silica concentrations are significant since they may form a fair proportion of the solids content of the feedwater unless removed and thus contribute to appreciable scaling. Secondly, silica concentrations must be controlled in such installations because of possible vaporization and resulting turbine blade deposits. Neither situation exists in steam flood applications and, therefore, the normal silica limitations imposed on the conventional system do not apply in this instance and this is the basis of the silica limitations indicated in the above.

<u>Iron concentrations</u> are of significance since the presence of iron oxide can contribute significantly to scale accumulations. Fortunately, in many waters, the iron contents are naturally low and meet the requirements indicated.

<u>Turbidity</u> is a measure of the optical obstruction of light when passed through a water sample. Colloidal suspensions and suspended solids contribute to the turbidity of a water. Usually, when turbidity is high and above the maximum limits, iron, or suspended solids or other filterable materials are also present in large amounts and the correction of these factors results in a reduction in turbidity.

Suspended solids are usually represented by precipitated iron, mud or silt, sand and the like and it is necessary to maintain these solids at very low values in the type unit involved as in any steam generation unit. Appreciable scaling can develop with large accumulations of these undesirable materials which make up sus-

Dissolved solids are of no great significance in steam flood operations. As pointed out above, practically all the dissolved solids will be in the form of highly soluble sodium salts and should not deposit under the indicated conditions. Dissolved solids limitations are imposed in the operation of standard stationary boilers in order to prevent excessive concentration or solids which are recirculating constantly in such boilers and, also, as further assurance that steam purity guarantees will be met and maximum quality steam generated. None of these conditions pertain to steam flood operations. In many instances where dissolved solids conceivably? could develop to excessive values, other constituents will provide overriding limits and require methods of treatment which will reduce the dissolved solids content in conjunction with a reduction in the other constituents.

Dissolved oxygen content of the feedwater should be maintained as low as possible. Some equipments have been installed with deaerating heaters although, in general, the average installation has relied upon a catalyzed sulfite for control of dissolved oxygen in the range indicated. Above 1000 psi, it is sometimes necessary to employ hydrazine because of the possible breakdown of sodium sulfite to sulfides and sulfur dioxide. Where there is doubt, it is well to check out the use of sodium sulfite first because the catalyzed sodium sulfide will react rapidly with the oxygen and reduce the oxygen content to a satisfactory level before entry into the boiler. Hy-

| | | 4 | | | |
|--------------------------------------|-----------------|--------------|---------|------|------------|
| | Typical Permian | Supplies | | | |
| | | 1 Water | 2 | 3 | 4 |
| Source | Units | Flood | Lake | Well | Potable |
| Total Hardness (CaCO ₃), | ppm | 1840 | 540 | 364 | 266 |
| Calcium (CacO ₃), | ppm | 500 | 230 | 140 | 160 |
| Magnesium (CaCO3), | ppm | 1340 | 310 | 224 | 106 |
| "P" Alkalinity (CaCO ₃), | ppm | 0 | 0 | 0 | 0 |
| "M" Alkalinity (CaCO ₃), | ppm | 246 | 202 | 200 | 324 |
| Sulfate (SO ₄), | ppm | 3360 | 288 | 165 | 41 |
| Chloride (Cl)), | ppm | 920 | 244 | 74 | 48 |
| Silica (SiO2), | ppm | 72 | 47 · | 10 | 14 |
| pH, | | 7.5 | 7.8 | 7.6 | 7.8 |
| Conductivity, | Micromhos | 650 0 | 1500 | 1600 | 525 |
| Total Iron (Fe) | ppm | 0.25 | 0.2 | 4.0 | 0.2 |
| Turbidity | Units | 2 | 2 - 150 | 10 | 1 |
| | | | | | |

drazine reacts slowly and, unless adequate deaeration facilities are provided, some corrosion can be expected even though hydrazine may be used.

Oil contamination is to be avoided if at all possible because of the interference of oil films with heat transfer efficiency and the tendency, in severe cases, to cause overheating of the tube metal.

<u>pH of the feedwater</u> should be adjusted, where necessary, with a material such as caustic soda in order to develop a pH of at least 9.0. Maintenance of minimum pH helps to prevent corrosion of the feed lines and initial coils of the boiler and assures the proper pH level throughout the steamwater system.

<u>Hydrogen sulfide</u>, when present in significant amounts, requires removal. Depending upon the amount of material present, the removal process can be either relatively simple or quite complex. Methods of treatment can vary between simple chlorination to complex pH adjustment and flue gas stripping operations followed by chlorination.

TYPICAL PERMIAN BASIN WATER SUPPLIES

In Table 3, we have shown four typical water supplies in the subject area.

Methods of treatment required in order to meet the specifications outlined in Table 2 are outlined in Table 4.

Table 5 shows the expected boiler water characteristics upon using the treated Permian basin waters, cycled 5 times (80 per cent quality steam.

INTERNAL TREATMENT

In the above discussion, we have touched upon the occasional requirement for a filming amine treatment in order to reduce downhole corrosion

TABLE 4

Treatment To Be Applied

Water No. 1 (Water Flood)

- 1. Sodium zeolite softener to eliminate hardness, iron
 - 2. For 1500 psi, pretreat with lime softener to provide preliminary softening and silica, iron removal, followed by filtration

Water No. 2 (Lake)

- 1. Clarifier to control turbidity, precipitate iron
- 2. Filtration
- 3. Sodium zeolite softener to eliminate hardness.

Water No. 3 (Well)

- 1. Aeration and filtration to remove iron, turbidity
- 2. Sodium zeolite softener to remove hardness and any other remaining iron.

Water No. 4 (Potable)

1. Sodium zeolite softener to eliminate hardness and iron.

when such corrosion is a problem. In some cases, neutralizing amine treatment has been applied in an attempt to further adjust the pH of the stream but this treatment is extremely expensive when considering the high amount of carbon dioxide present in many instances. For that reason, neutralizing amines have been abandoned for all practical purposes.

The application of catalyzed sodium sulfite and also of hydrazine for oxygen control has been discussed. For alkalinity adjustment, caustic soda is generally employed. With liquid solutions readily available, the material is in a convenient form for use whenever the feedwater pH requires adjustment.

| Т | 'A | B | L | \mathbf{E} | 5 |
|---|----|---|---|--------------|---|
| - | - | | | _ | _ |

| Appro | oximate | e Charact | eristic | s of Pe | rmian | <u>Basin</u> |
|--------|---------|-----------|---------|---------|-------|--------------|
| Water. | After | Treatmen | nt and | cycled | 5 tim | es |

| | - | | | | |
|--|-------|--------|--------------|------|------------|
| Water Source | | 1 | 2 | 3 | 4 |
| | Units | | | | |
| Total Hardness (CaCO ₃), | ppm | 0 - 2 | 0 - 2 | 0-2 | 0 - 2 |
| Total Alkalinity (CaCO ₃), | ppm | 1230 | 1010 | 1000 | : 1620 |
| Total Solids, | ppm | 26,000 | 6000 | 6400 | 2100 |
| Silica (SiO2), | ppm | 360 | 235 | 50 | 7 0 |
| Turbidity, | Units | 10 | 10 | 10 | 5.0 |
| Iron (FE), | ppm | | | | |

Chelating agents have found considerable application in the treatment of the feed and boiler waters for the purpose of sequestering the remaining hardness present in the feedwater, thus preventing deposition of calcium and magnesium scales and maintaining these materials in a solubilized form during passage through the steam generator. The basic chelant employed is the tetrasodium salt of EDTA (ethylenediaminetetraacetic acid). Precipitating agents, such as phosphates, are not employed in monotube boilers because of the high rate of heat transfer and the tendency to deposit in the hotter sections of the coil, creating failure conditions. A suitably designed internal treating system, following satisiactory external treatment, will maintain these boilers relatively free of scale and corrosion problems even under rather severe service conditions.

CONCLUSIONS

As noted above, the trend is toward higher boiler pressures in order to obtain higher heat values in the steam. As part of the process, it is desirable to obtain the maximum BTU's in the shortest possible time and, where crude oil characteristics are suitable, economic advantages are obtainable. The trend toward higher pressures will require increasing attention to water conditions, both external and internal to the boiler. To increase field reliability, some manufacturers are studying design changes which would permit ready removal and repair of damaged coils and the replacement of sections. The design changes are being made to reduce downtime to a minimum when repairs must be made.

Some recent developments have involved the application of superheated steam for the purpose of atomizing crude oil, operating the units, there fore, on the crude oil readily available. This process appears to be economically feasible only where gas is not readily available or is quite ex pensive. It should be noted, also, that steam flood generators are not particularly designed to produce extremely high purity steam even with the installation of separators and accumulators. Passage of such steam, even though the quality may be high, through superheated tubes could lead to considerable maintenance problems due to the deposition of salts in the superheaters at the high total temperature involved, approximately 700°--800° F.

The success of a steam flood operation depends upon many factors. Satisfactory operation of the generator is the first consideration and, for that reason, water characteristics and water requirements assume considerable importance.