COMPARISON OF CRYSTALLIZER REACTOR CLARIFIER AND pH MOD PROCESS TECHNOLOGIES USED AT THE SALTON SEA GEOTHERMAL FIELD

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ABSTRACT

The Salton Sea Field. located in Imperial County. Ca., is a large water dominated geothermal resource that was not developed until the 1980's because of the high corrosion and scaling tendency of the brine. Two technologies, crystallizer reactor clarifier and pH Modification. have been developed to control scaling. Both of these technologies are being used at commercial power plants located at the Salton Sea Field,

This paper explores the development of these technologies, compares their differences. and evaluates the economic and technical advantages of each. Both technologies continue to undergo improvements to reduce cost and increase competitiveness in the market place.

1. BACKGROUND

The Salton Sea geothermal discovery well. drilled in 1957, encountered temperatures of approximately 290 °C (554 °F) at depths of about 1,432 m (4,700 ft). Subsequent flow tests of this well and later confirmation wells in 1961 through 1972 revealed a geothermal system with prodigious productivity and consistently high temperatures at relatively shallow depths (Signorotti and Hunter. 1992).

The Salton Sea geothermal resource is now considered one of the largest (> 1.000 MW possible) and hottest (250 °C to 370 °C or 480 °F to 700 °F) water dominated fields in the world. However, the brine is characterized as an extremely high salinity liquid with the concentration of total dissolved solids greater than 200,000 ppm. Although the bulk of the dissolved solids is alkali and alkaline earth chlorides, significant concentrations of silica. heavy metals, and various other elements *are* found in the brine. Typically. non-condensable gases compose about 0.2% by weight of the brine and are approximately 95% by weight carbon dioxide with minor but measurable concentrations of hydrogen sulfide. A typical brine analysis is presented in Table 1. The chemistry and high temperature of Salton *Sea* brines have led to the principal challenges to the development of the Salton Sea resource: scaling and corrosion of plant equipment, piping, and injection wells.

Based on encouraging geothermal discoveries and flow-tests by Magma Power Company and others, San Diego Gas and Electric Company and the United States Department of Energy (DOE) constructed and operated the Geothermal Loop Experimental Facility (GLEF) at the Salton Sea Resource from 1975 to 1979. In what can be considered a pioneering research and development effort. this facility studied the technical problems in handling these fluids utilizing a 10 MW equivalent dual flash brine handling system. Extreme scaling at the GLEF necessitated plant shutdowns after approximately 1,000 hours of operation. Also, scaling of injection pumps, piping, well tubulars, and injection well formations resulted in an unacceptably rapid loss of injectivity.

Table 1. Typical analysis of Salton Sea Brine

Element	Concentration (mg/Kg)
Ba	210
Ca	20.600
Cu	2
Fe	540
K	12,000
Li	160
Mg	50
Mn	770
Na	51,200
Pb	70
Sr	360
Zn	300
Cl	119.000
NH_3	350
TDS	214.000

As a result of these problems, a stem turbine power plant was never built at the GLEF. In a summary DOE document published in 1980, it was stated that "the utilization of these fluids, which contain up *to* 300.000 ppm of dissolved solids, remains one of the major unsolved problems in geothermal energy in the United States" (DiPippo, 1980).

2. DEVELOPMENT OF SOLUTIONS

2.1 Crystallizer Reactor Clarifier Technology

During the period in which the GLEF was in operation, Magma Power Company proposed changes to the conventional dual flash direct steam method of processing brines. These changes included: (1) a reactor clarifier to precipitate scaling constituents (mainly iron rich amorphous silica) and to remove suspended particles from the brine before injection; and (2) seeding of the brine in the flash vessels to reduce scale formation. In the seeding process a slurry of seed material is introduced into flash crystallizer vessels along with feed brine. When precipitation occurs, mainly due to cooling and concentrating of the brine. it is more likely to occur on the high surface area seed slurry than on the relatively small, dissimilar metal surfaces of plant equipment.

The source of the seed material is the reactor clarifier underflow which has basically the same composition as the scale (Featherstone *et al.*, 1979).

Magma's successful pilot testing of reactor clarifiers led to the use of flash crystallizers as flash vessels of a geothermal power plant. The chemical process industry utilizes crystallizers to promote and control product crystal formation. Magma combined the traditional use of crystallizers with the idea of recycling seed material from the reactor clarifier to the crystallizers in a coordinated brine handling system (Featherstone and Powell, 1981). In this way scaling components of the brine precipitated on seed material in vessels designed for precipitation and solids removal. Successful pilot tests of the crystallizer reactor clarifier system were completed in 1980. Magma Power Company was granted a process patent based on the results of the pilot testing (Featherstone, 1984).

The first geothermal power plant utilizing the Crystallizer Reactor Clarifier (CRC) design was built by Unocal's geothermal division in 1982. This was followed over the next eight years by an additional five CRC plants with a total installed capacity of 245 MW.

The successful performance of these plants can be seen in Table 2 where the maximum capacity factor is shown from 1989 to the present. This factor is calculated by dividing the MW-Hr generated in a year by the product of the maximum generation rate times the number of hours in a year. In these calculations no down time for any reason, such as plant overhauls, is assumed. Magma's Unit 3 has just completed a continuous three year run between overhauls, a great improvement in performance and scale control when compared to the GLEF results mentioned earlier.

Table 2. Maximum Capacity Factor for Salton Sea CRC Power Plants

Plant	1989	1990	1991	1992	1993	1994*
Unit 3	92%	86%	98%	91%	99%	98%
Vulcan	92%	92%	86%	92%	94%	96%
Hoch	90%	89%	83%	92%	94%	97%
Elmore	n/a	91%	92%	88%	94%	92%
Leathers	n/a	90%	88%	95%	95%	93%

** data through September 1994*

2.2 pH Modification Technology

As part of the DOE industrial support program for the GLEF, Lawrence Livermore National Laboratory began landmark experiments in which various chemical agents were added to the brine to prevent scaling. This approach keeps scaling components in solution and is conceptually different from the CRC process in which scaling components precipitate in a controlled fashion. The most promising technique found was acidification with hydrochloric acid. Pilot testing with a dual flash unit showed empirically that lowering the pH to 3.5 essentially eliminated scaling except near atmospheric pressure where the high degree of supersaturation of silica renders the acid less effective (Grens and Owens, 1977 and Harrar *et al.*, 1979). Lowering the pH further to 3.0 eliminates the scaling at atmospheric pressure completely, but at the cost of greater corrosion rates and additional expense (Harrar, et al. 1977, 1979).

Unocal further developed the acidification concept through testing at the Salton Sea and at the nearby North Brawley resource. The process was changed in two important ways: (1) the lower limit of pressure was found to be approximately 5.5 to 7 bar at 177 to 185 °C (80 to 100 psig at 350 to 365 °F); and (2) only enough acid was required to lower the pH of the brine about 0.5 pH units. Unocal was granted a patent for the pH Modification process based on these changes (Jost and Gallup, 1985).

Magma's Unit 2 (pH Mod) plant which operates at a final pressure of approximately 7 bar (100 psig) has experienced scaling rates comparable to CRC plants (< 1 inch per year in the most severe scaling areas). The corrosion of plant and well field equipment was the second major challenge to the development of the Salton Sea Field. Through an extensive testing program, Unocal defined the materials of construction necessary to reduce corrosion to within acceptable limits for pH Modification plants. More details in this area will be given in the next several sections.

3. PROCESS DESCRIPTIONS

3.1 CRC Process

A simplified sketch of a typical CRC plant is shown in Figure 1. Two phase flow from geothermal wells is routed through either alloy or cement lined production lines to horizontal separators (operated at approximately 22.8 bar, 227 °C) where brine and high pressure steam are separated. High pressure steam is routed to a centrifugal type scrubber which is designed to remove brine carryover from the steam and from there to the turbine generator. Brine from the separator is flashed into the high pressure crystallizer operating at 8.6 bar and 177 °C. It is at this point in the process that precipitation of scale forming constituents becomes a serious consideration, and it is here that the seeding of the brine to prevent scaling becomes a necessity. Solids from the clarifier underflow are recycled to the high pressure crystallizer where precipitation occurs, mainly on seed particles.

Steam from the high pressure crystallizer is passed through a steam scrubber and then is routed to the turbine. A brine slurry mixture, typically about 2.0% by weight solids, is flashed into the low pressure crystallizer (2.1 bar, 138 °C) where solids contact with scaling materials reduces the scaling tendency of the brine significantly. Low pressure steam flow through a steam scrubber and then to either to a low pressure turbine or to the low pressure side of a dual entry turbine. The brine slurry mixture is flashed to atmospheric pressure in the atmospheric flash tank and then flows into the reactor clarifier.

In the reactor clarifier the scaling constituents precipitate to close to equilibrium values for the various scaling components in solution. The solids are flocculated and settled to the bottom of the tank. Relatively clear brine overflows to a secondary clarifier which removes additional suspended solids from the brine. A flocculent is added to the brine between the two clarifiers to aid in this polishing process. The stable overflow from the secondary clarifier (<20 ppm suspended particles and stable with respect to precipitation) is pumped into injection wells.

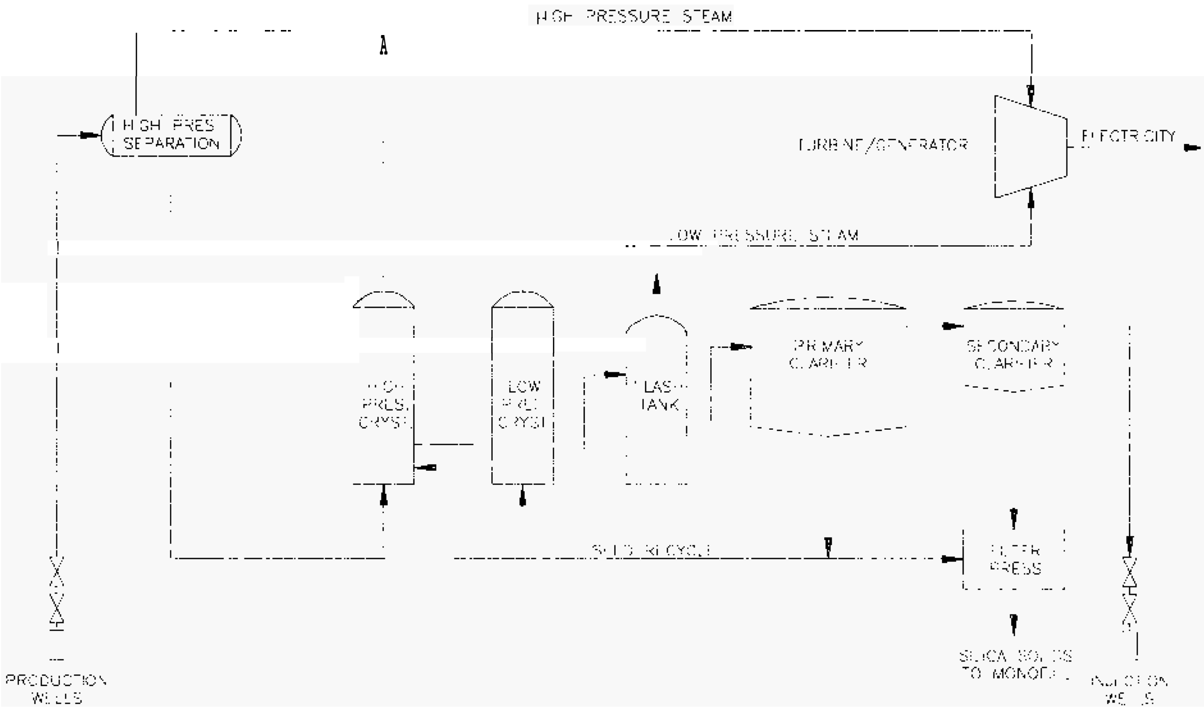

Figure 1. A simplified process diagram for a Crystallizer Reactor Clarifier (CRC) power plant.

A portion of the solids **removed** from the reactor clarifier *is* recycled to the high **pressure** crystallizers as seed **material.** Accumulated solids in both the reactor **clarifier** and the secondary **clarifier** are routed to a filter press **were** they are dewatered to approximately 85% by wight solids For **a** 50 MW plant about 27.000 Kg (30 tons') **per** day of filter **cake** are generated.

3.2 pH Mod Process

A simplified **process** flow diagram of **a** typical pH Mod plant is shown **in** Figure 2. **Two phase** fluid from geothernial production wells **flows** into high **pressure** separators operating at approximately 21.4 bar and **223** °C. Baffled, horizontal type, steam brine separators ***are*** normally used **for** this service. Steam flows through **a scrubber** and then to a conventional geothermal **steam** turbine. The **power** conversion technology for both the CRC and pH Mud is similar to geothermal **power** systems found elsewhere in the **world.**

Brine exits the high **pressure** separators **and** is flashed **to a** standard pressure separator operating at about 8.3 bar and 177 °C It is at thir point that scale **control** becomes necessary **because** of iron silicate precipitation. The overall scaling reactinn is thought to be as follows **(Gallup.** 1989):

$$Fe^{+2} + H_2O + Si(OH)_4 \leftrightarrow Fe(OH)_3 \bullet SiO_3 + 2H^+ + \frac{1}{2}H_2$$

Normally, the above reaction proceeds to **the** right, resulting in precipitation of iron silicates and aniorphous silica. The addition of acid drives the reaction to left, keeping the scaling components in solution. As the concentration of iron **in the** brine increases, more **acid** is required to keep iron silicate in solution. At lower pressures and temperatures, the precipitation of amorphous silica alone **becomes** of greater importance. Several investigators **have** shown that lowering the pH of the brine by adding acid **reduced** the scaling rate of silica containing species, indicating that both kinetic **and** thermodynamic (equilibrium) factors are involved in there reactions (Harrar *et ut.,*1977).

In practice. 100 to 120 ppm of hydrochloric acid (pure acid basis) is injected into in-line static **mixers** just **before** the brine flashes **to** standard **pressure** separator conditions. From the point of acid addition high nickel alloys and cement lined steel are the **preferred** materials of construction for brine wetted parts. The pH ofthe brine **is lowered** about 0.5 pH **units** by the additinn of acid

Steam from the standard pressure separator is washed to **remove** trace quantities of HCl vapor and is then routed through a scrubber to a stem turbine. Brine exits the standard pressure separator and is then pumped into nearby injection wells. Injection wellhead **pressure** must be kept above saturation **pressure** of **the brine** to prevent flashing in the injection pipeline which would increase scaling potential. The **general** practice is to **locate** both production and injection wells as close **to** the **plan!** as **possible** but within **the** constraints of good reservoir management principles.

4. ECONOMIC COYSIDEHATIONS

4.1 Power Plant

The pH Mod process has a number of advantages **when** compared to the CRC process. One of the significant differences is that the process **is** less complicated (fewer vessels and associated equipment) thus simpler to operate and maintain. These differences significantly **reduce** the capital. operating, and maintenance ***costs*** fur **a** pH **Mod** plant compared to a CRC plant.

CRC power plants are **also** less flexible with respect to changes in generation. **To** increase generatinn. more **brine must** be **flowed** into **the** plant. 'This **increase in** flowrate **results** in a

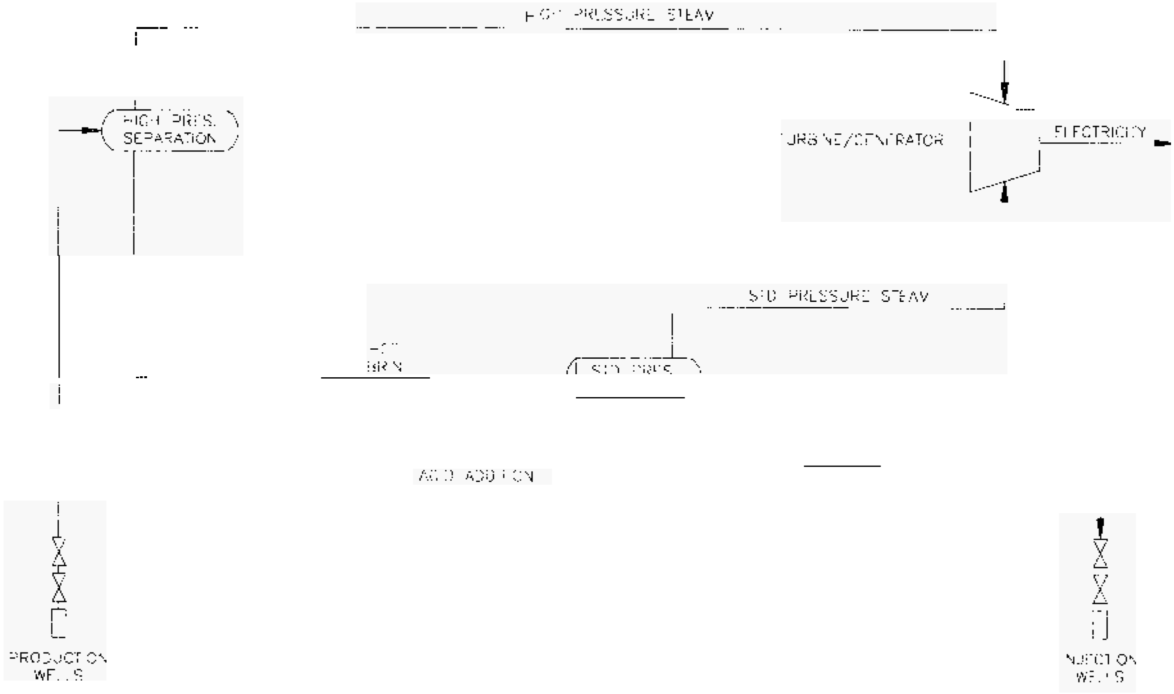

Figure 2. A simplified process diagram for a pH Mod power plant

temporary upset of the clarifiers. In the pH Mod process, the flowrates can be quickly changed requiring only a change in the acid injection rate. This acid injection rate can be automated to further simplify operations.

The pH Mod process, with minimum waste products, has significant environmental advantage over the CRC process. In the CRC process large quantities of filter cake are produced each day. The current practice is to transport the filter cake to a nearby geothermal landfill. In the pH Mod process no filter cake is produced. In addition. less scale is obtained during pH Mod plant overhauls due to the smaller number and reduced size of the vessels incorporated in the design.

4.2 Materials of Construction

One of the major obstacles in the early development of the Salton Sea Geothermal resource was corrosion. High corrosion rates in equipment. constructed from carbon steel. prompted the investigation into new materials of construction. The current solution to this problem is to: (1) line the high pressure separators with alloys such as Inconel 625 or Hastelloy C-276; (2) line the production and injection pipelines with cement; and (3) use alloy tubulars in the production and injection wells.

In the CRC process. observed corrosion rates down stream of the high pressure separator have shown that carbon steel is an acceptable material of construction. In the pH Mod process the standard pressure separator is alloy lined due to the addition of HCl to the process stream.

4.3 Well Field

One of the primary differences between the CRC and pH Mod processes is the quantity of steam produced per unit of brine. In the CRC process, the last flash. before the atmospheric flash, is at 0.7 to 1.4 bar (10 to 20 psig). In the pH Mod process the brine is flashed to only 6.8 to 8.2 bar (100 to 120 psig) before injection. With typical Salton Sea brine. this higher final flash pressure results in about one third less steam per unit of brine for the pH Mod than the CRC process.

Therefore. a pH Mod plant having the same power output as a CRC plant would require about one third more production capacity. However, a pH Mod can take advantage of this higher steam pressure. Utilizing a dual inlet geothermal turbine, designed for higher pressure 18.6/6.9 bar (270/100 psig) steam, the brine requirement per unit of generation can be reduced to 111% of brine required at the five current Salton Sea CRC plants. At these five CRC plants lower pressure 6.9/1.4 bar (100/20 psig) dual inlet turbines are installed.

In the pH Mod process, the higher brine requirements and less flash per unit of brine result in a significantly larger volume of spent brine to be injected when compared to the CRC process. Depending on process efficiency. the pH Mod process produces between 120% and 160% more injectate when compared to the CRC process.

The apparent injectivity (injection rate *vs.* injection pressure) of pH Mod spent brine is also lower, compared to the CRC process. due to the lower density of the injectate. The density difference between the injectate from these two processes is close to 200 Kg/m^3 (sg 0.2). Using a nominal injection depth of 1,000 m (3,281 feet). the wellhead pressure at a pH Mod injection well will be about 19.6 bar (284 psi) higher than a CRC injection well in order to yield the same downhole pressure.

4.4 Reservoir Response

To study the response of the reservoir to CRC and pH Mod developments, a simulation model of the southwest portion of the Salton Sea Field was constructed (Butler. 1992). Modeling results indicated little difference in the predicted response for both processes.

Closer examination showed that net heat removed from the reservoir (primarily the steam to the turbine) is similar for both processes. The net mass withdrawn from the reservoir. due to the evaporation of condensate used for cooling tower makeup, is also essentially the same for both processes. Therefore, long term pressure and temperature depletion of the resource, which is strongly dependent on development size, is only slightly dependent on the process technology used.

Since only part of the produced water is injected (due to evaporation losses in the cooling tower) and essentially all of the produced salt fraction is being injected, the concentration of the brine in the reservoir should increase over time. Modeling results indicate that diluent may need to be added to the injectate from the CRC plants, during their project life, to keep the salt in solution. Projected increase in reservoir salt concentration will not affect the pH Mod process, as much as the CRC process, due in part to the higher injection temperature (Butler, 1991).

4.5 Capital Cost

To study the differences in capital cost between the CRC and pH Mod technology a comprehensive production facility equipment sizing and cost estimation program was developed (Kelley, 1992). The vessel sizing routines in this program follow the same logic as used in the design of Unit 2 (pH Mod) and Unit 3 (CRC). This sizing and cost estimation program was then used to develop cost for plants in the range of 50 to 150 MW.

In development of the resource, large diameter alloy cased production and injection wells were utilized for both CRC and pH Mod processes. As the size of the development was increased, the number of wells and the length of the pipelines were also increased based on a unit area of 8 acres/MW.

Costs estimations for development of the well field were made based on production and injection requirements for CRC and pH Mod power plants. The resulting overall cost (power plant and well field) clearly demonstrates the cost advantage that pH Mod technology has compared to the CRC technology (Hildebrand, 1993). These results are shown in Figure 3.

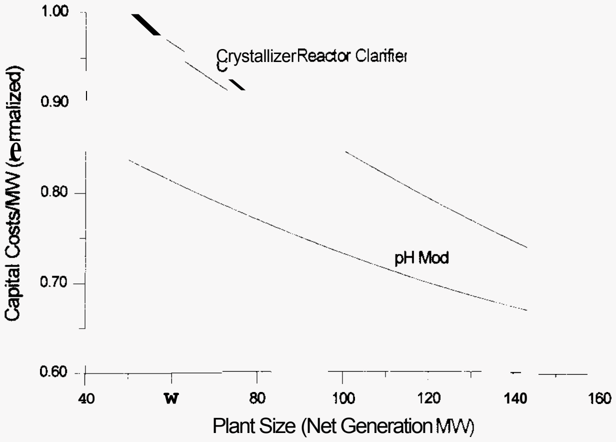

Figure 3 *Plot of* ***capital costs (powerplant and well field) per net MW generated.***

As shown above, CRC developments respond favorably to economy of scale. Developments based on pH Mod technology do not respond as favorably This is because the wells and major equipment are already close to their maximum economical size.

4.5 Operating Cost

Using operating costs for existing pH Mod and CRC power plants, costs were projected for larger developments. These operating costs, shown in Figure 4, include plant overhauls every two years and well workover cost.

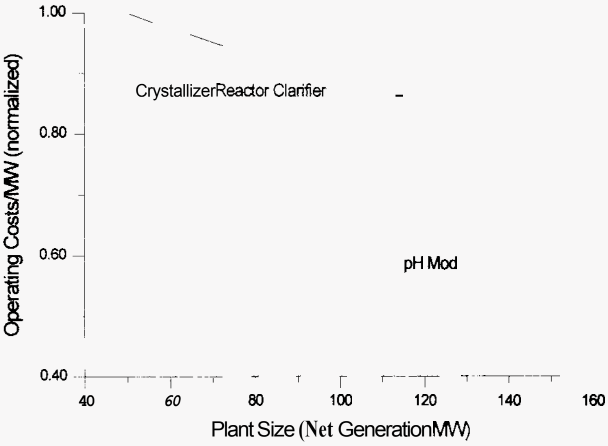

Figure 4. Plot of ***operating costs (power plant and well field) per net MW generated.***

As with capital cost, CRC operating costs respond favorably to economy of scale. Over the range of 50-150 MW, the cost of operating a pH Mod plant is approximately two thirds that of a CRC plant.

5. CONTINUING IMPROVEMENTS

Both the pH Mod and the CRC processes have been improved over the past 15 years. Possibly the most significant improvement to the operability of CRC plants was the incorporation of secondary clarifiers in place of dual media filters as a final polishing step for injected brine. Secondary clarifiers have proven to be far less costly to operate and generally do a better job at removal of suspended particles from the spent injectate, resulting in improvement in long term injection well performance (Featherstone *et al.*, 1988).

The use of chemicals for the prevention of foaming in flashing brine, particularly in crystallizers, was an important improvement. Before the role of foam in the carryover of brine in the steam was recognized, it was necessary to operate crystallizers at very low liquid levels to the detriment of internal recirulation and scale control. With the use of defoaming chemicals, normal liquid levels and good scale control are achieved without significant carryover problems (Gritters *et al.*, 1988). The use of baffle plates in the vapor zones of crystallizers is another important improvement that has reduced brine carryover (Bonham, 1990).

For the pH Mod system, the greatest improvements have come in defining materials of construction which balance corrosion resistance against economics. Some of the details of this work have been mentioned earlier in this paper.

Continuing opportunities for improvement exist for both systems. For the CRC system, the possibilities of mineral recovery promise to improve the overall economics of this process. Mining companies are investigating ion exchange techniques for recovery of zinc, lithium, boron, and manganese (Duyvesteyn, 1992). The results thus far have been encouraging.

For the pH Mod system, a more in depth knowledge of the chemistry of scale inhibition might aid in finding a way to operate at lower pressures without high scaling rates. Operating at lower pressures would lessen the brine production and injection requirements of the process and improve the economics. Extensive work on the fundamental chemistry of iron silicate precipitation is in progress (Freiser, 1994). Both processes would benefit from the discovery of a low cost high temperature corrosion and scaling resistant coating for carbon steel which will withstand the severe requirements of Salton Sea brines.

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