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GEOTHERMAL SCALE CONTROL BY CRYSTALLIZATION

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Introduction The deposition of scale in a geothermal power plant is considered a major risk. Unless scaling can be reduced to an acceptable level by an on-line treatment technique, the geothermal plant must be designed with redundant trains to permit the shutdown and off-line cleaning of a portion of the plant while the balance of the plant continues to operate. This approach not only increases capital investment but involves a substantial expenditure for the chemicals and labor required for descaling. This paper reports the development of a crystallization technique to minimize scale formation in a geothermal power plant without the use of acid or scale inhibitors.

Problems Resulting from Scales The seriousness of scale deposition has been amply demonstrated in plants which manufacture industrial chemicals as well as in geothermal plants. The continued deposition of scale leads to obstruction of process equipment, the blockage of pipe lines, and the "freezing" of valves and pump shafts. A layer of scale on metal surfaces occludes stagnant pockets of liquid, causing locallized pitting attack. Several examples are cited here.

Bechtel was directly involved in tests on a large flashed-steam geothermal pilot plant fed with very saline geothermal brine in the Salton Sea area of Southern California. A thin layer of silica/sulfide scale caused serious pitting corrosion in the carbon steel feed line to the plant. Silica scale, which had deposited in some process vessels to a depth of almost two feet, required hand cleaning and hydroblasting for its removal. Scale deposited so rapidly on thermowells and pressure gauge taps as to make the readings meaningless. Valves froze. Pump shafts required replacement every two months. Initially, an injection well was clogged by scale.

As a second example, at a 3-plant geothermal desalination installation at East Mesa, calcium carbonate scale reduced the flow passage in a 10-inch pipe to an opening four inches in diameter after only four months' operation. A barium sulfate deposit reduced the heat transfer of tubing to only a fraction of its initial value.

Techniques of Scale Control Although the list of failures enumerated above appears to be discouraging, there are methods for dealing with at least some of the problems. In this section are discussed Bechtel experiences and the experience of others in scale control:

- Redundancy, while not a scale control technique, provides the plant designer with one alternative in dealing with this problem. As an example, the plant can be designed with three trains, each of 50% of the total plant capacity. The rated output is delivered by two of the trains while the third is shut down for cleaning. Redundancy involves a substantial increase in plant investment. In addition, there is the added cost for the labor and materials required for descaling. The three-train concept contains the tacit assumption that the cleaning of one train can be accomplished before a second train must be shut down. If this assumption is not valid, it may be necessary to provide four or more trains.

- The operation of several geothermal pilot plants presented the opportunity to test another alternative scale control technique. At the East Mesa Test Site of the U.S. Department of the Interior, several additives were tested in three geothermal desalination plants.

The most successful was a compound marketed under the name of Dearborn #8010, which was effective in controlling scaling by calcium carbonate, calcium sulfate, barium sulfate, and strontium sulfate.

In the Niland area of the Imperial Valley of Southern California, on the other hand, the brine chemistry is entirely different. Of all the scale control additives tested there, only one showed any promise against silica and heavy metal sulfides, the principal offenders, and that inhibitor deteriorated rapidly at the elevated brine temperatures.

- An interesting alternative was developed for the control of silica scaling. It was discovered that when the brine became supersaturated in silica as a result of a drop in temperature, the SiO_2 formed submicroscopic micelles. These micelles could be prevented from agglomerating for long periods of time by maintaining the brine at a low pH. For example, a pH value of 3.0 to 3.5 retarded scaling for periods as long as two hours, a sufficient length of time to permit reinjection and migration of the brine into the subterranean formation. To avoid excessive corrosion at such low pH values, however, it would have been necessary to construct, or at least to line the plant and reject brine lines with the more costly corrosion-resistant alloys. Consequently, in spite of the promising laboratory results, brine acidification was not considered for the 10 MWe geothermal power plant operated by the San Diego & Gas Electric Co., where the Niland brine's scaling tendencies severely hampered the functioning of the plant.

- In that plant, the reject brine was stabilized by contact with a slurry of suspended scale in a reactor-clarifier which followed the flash chambers, thus protecting the injection well and the surrounding geologic formation. In addition, tests were begun on slurry seeding for scale control upstream in the geothermal flashed steam plant so as to protect the plant equipment and lines from scale.

Of all the alternatives for controlling the scaling of high silica brines, slurry seeding appears to have the best potential. The use of slurry seeding is an old, established process. It has been applied for many years to to the crystallization of salt, fertilizers, and industrial chemicals. In these processes, while concentrating an aqueous solution of the desired materials, undesirable impurities (for example, calcium sulfate) precipitate from the liquor. The precipitated scale particles circulate with the liquor. As additional scale is formed, it deposits on the suspended particles in preference to the walls of the vessels and piping. As a result, the equipment remains clean and free from scale deposits. Improved scale control is achieved by augmenting the self-generated scale particles by addition either of synthetic "seeds" or by a slurry of scale removed from a preceding batch of brine.

This procedure was extended in the early 60's to the desalination of sea water in pilot plant tests at the Office of Saline Water Test Site at Wrightsville Beach, N.C. These tests were directed toward the prevention of calcium carbonate scaling in a vertical tube evaporator without dosing the sea water with acid or a threshold inhibitor. In acid dosed plants in general use at that time, acid accelerated the corrosion of vessels, lines, and heat exchange surfaces. The inhibitors which were then available were ineffective under the conditions prevailing in the evaporator. It was hoped that slurry seeding would successfully replace these older methods of scale control. The equipment was charged with a quantity of "Snow White Filter", a commercial grade of calcium sulfate anhydride. After several hundred hours of operation, the plant was opened and found to be virtually scale free.

<u>Basis of Crystallizer Process</u> In the process described here, a seed slurry is maintained in suspension in each of the two stages, which deliver flashed steam to the high-pressure and intermediate pressure ports, respectively, of the steam turbine. The turbine, in turn, drives a generator. Each stage in the flowsheet of Figure 1 consists of a flasher-crystallizer-separator (FCS). The following steps occur in the FCS:

- As the brine enters each vessel, a fraction of its water content is flashed into steam, which is delivered to the power plant turbine.

- The evolution of steam fron the brine increases the concentration of all dissolved species in the residual liquor, including the scale formers.
- Gases such as carbon dioxide, ammonia, and hydrogen sulfide are released, causing changes in pH and brine chemistry.
- A drop in temperature accompanies the flashing process, resulting in the supersaturation of some of the dissolved species which have a positive temperature coefficient of solubility.

In an attempt to relieve supersaturation, numerous crystal nuclei are rapidly formed unless the flashing zone already contains an adequate population of nuclei. In the latter case, the pre-existing nuclei grow to a size favorable to the subsequent sedimentation and filtration steps. Absence of such nuclei, on the other hand, leads to the formation of many new crystals. The distribution of the precipitating species among this large population results in very small crystals, which are difficult to remove by settling or filtration.

Flasher-crystallizer-separator (FCS) Design

In the design developed under this study, the spontaneous formation of many small nuclei is prevented by contacting the flashing brine promptly with seed crystals of scale which had been generated previously. In the conceptual design shown in Figure 2, geothermal brine is introduced into the bottom of the FCS. The jet of brine entering the throat of the venturi entrains a slurry of previously formed scale. The pressure drop in the throat flashes a portion of the hot fluid into steam. The high vapor-to-liquid ratio in the ascending three-phase fluid results in a very low fluid density.

When the ascending fluid strikes the baffle plate, steam separates while the remaining slurry is deflected downward around the outside of the venturi. The descending slurry is drawn into the bottom of the venturi to repeat its circuit. The self-induced agitation replaces the mechanical turbine-blade stirrers commonly installed in crystallizers, eliminating the attendant equipment cost, power consumption, maintenance problems, and attrition of the crystals (Ref. 1).

Those crystals which have grown to maximum size settle to the bottom of the FCS and are drawn off through the sludge discharge line. A small stream of brine ascends the sludge pipe so as to elutriate the fine particles and recycle them to the recirculating sludge circuit for further crystal growth.

After flashing, the brine rises through the sludge blanket in an annular separator region surrounding the central slurry recycle zone. The added contact with crystals of the sludge blanket helps to stabilize the brine against post-precipitation. The brine rise rate in the separator zone is calculated to achieve the required clarity.

The brine, once its supersaturation is relieved, can move through the remainder of the plant and the injection system without danger of harmful scale deposition. A fraction of the slurry is recycled externally back to each flasher-crystallizer. Those crystals which have grown sufficiently large to permit ready separation are removed and either discarded to waste or delivered to a mineral recovery sub-system. The "seeds" in the slurry may be either self-generated or may be added to the brine from an external source.

Design Guidelines As a practical alternative to pilot plant data, which are not available at present, the designer can rely on scaling experience in geothermal operation supplemented by analogous industrial crystallization experience. For the growth of seed crystals, it had been observed that the growth rate of scale on the lines bringing Magmamax #1 brine from the wellhead to the San Diego Gas & Electric Co.'s geothermal pilot plant was 0.1 mils per hour or 0.0000423 mm. per minute (Ref. 2). If we assume all slurry seeds to be of 10 micron diameter, for example, Table 1 shows that precipitation at 0.1 mils per hour would require a retention time of only 6.6 seconds in the slurry recycle zone of the first crystallizer to relieve supersaturation. Even very large seeds of 300 microns diameter, such as 48 mesh sand, require only about 3 minutes to relieve supersaturation in Stage 1.

Reference 2 shows a scaling rate of roughly 1 mil per hour for the conditions anticipated in the second crystallizer in the present report. This calculates to a required retention time of less than one minute in the slurry recycle zone of the second crystallizer even for the comparatively large sand nuclei.

Weres (Ref. 3) reports tests on the growth of micelles of amorphous silica in which the growth rate is more than an order of magnitude slower than the growth of scale observed on the pilot plant walls and piping. Extensive research on crystal growth, however, has demonstrateda very slow or even zero growth rate on extremely small nuclei.

Another source of uncertainly stems from the fact that the seed crystals will not all be of the same diameter but, instead, will represent a wide (possibly Gaussian) size distribution. R. Bennett provided details concerning industrial experience involving the growth rate of crystals under a variety of conditions (Ref. 4). The crystallizer concept was tested by Imperial Magma on geothermal brines in the Salton Sea area, demonstrating that a flash-crystallizer which circulates a 1% crystal slurry is capable of preventing scale deposition on the plant equipment by brine supersaturated with silica (Reference 5). The results of field and laboratory tests were correlated by Dr. A. Randolph and a correlation of crystal growth rates developed to serve as a basis for the design of the FCS (Ref. 6).

In order to attain a reasonably close approach to equilibrium, the operating conditions shown in Table 2 apply a generous factor of safety to the plant scaling rates of Reference 2. The guidelines of Table 2 form the basis for the material balance in the flowsheet of Figure 1 and the dimensions of the second stage FCS in Figure 2.

The brine effluent from the second stage FCS passes through a dual media gravity filter prior to reinjection. The target purity of the second stage effluent was selected to minimize the frequency of backwashing of the gravity filter.

In contrast to stage #2, the effluent from stage #1 is permitted to contain a much greater load of suspended solids, which will merely combine with the stage #2 slurry crystals in the crystal-growth zone. Consequently, the brine rise rate in the outer annulus may be much greater. This permits the designer to provide a vessel of smaller diameter for stage #1, as shown in Figure 3. Since stage #1 must withstand a working pressure of 1,006 kPa, a decrease in vessel diameter represents a substantial cost reduction.

Conclusion On the basis of the study reported here, a significant reduction in the cost of generating power from a hydrothermal resource may be anticipated. The cost reduction results from the elimination of the redundant train(s) required to permit off-line cleaning of one or more trains, together with the additional piping, valves, and instruments associated with redundancy. A further reduction in plant investment stems from the elimination of the three 55-foot diameter reactor clarifiers required to protect the injection pump and well of a 50 MWe geothermal power plant, an investment of roughly $2,300,000. From the standpoint of operating costs, the cleaning of a redundant train requires the full-time service of a cleaning crew throughout the year. This cost will be eliminated by the FCS design. Finally, the fractionation of low-temperature from high-temperature scale by the dual FCS design may segregate the mineral content of the brine, converting at least a portion of the sludge from a costly disposal problem to a salable material.

References

1. Ness, J. N. and White, E. T. "Collision Nucleation in an Agitated Crystallizer". Papers presented at AIChE Symposium Series No. 153, Vol. 72, "Analysis and Design of Crystallization Processes". (1976) American Institute of Chemical Engineers, New York, NY.

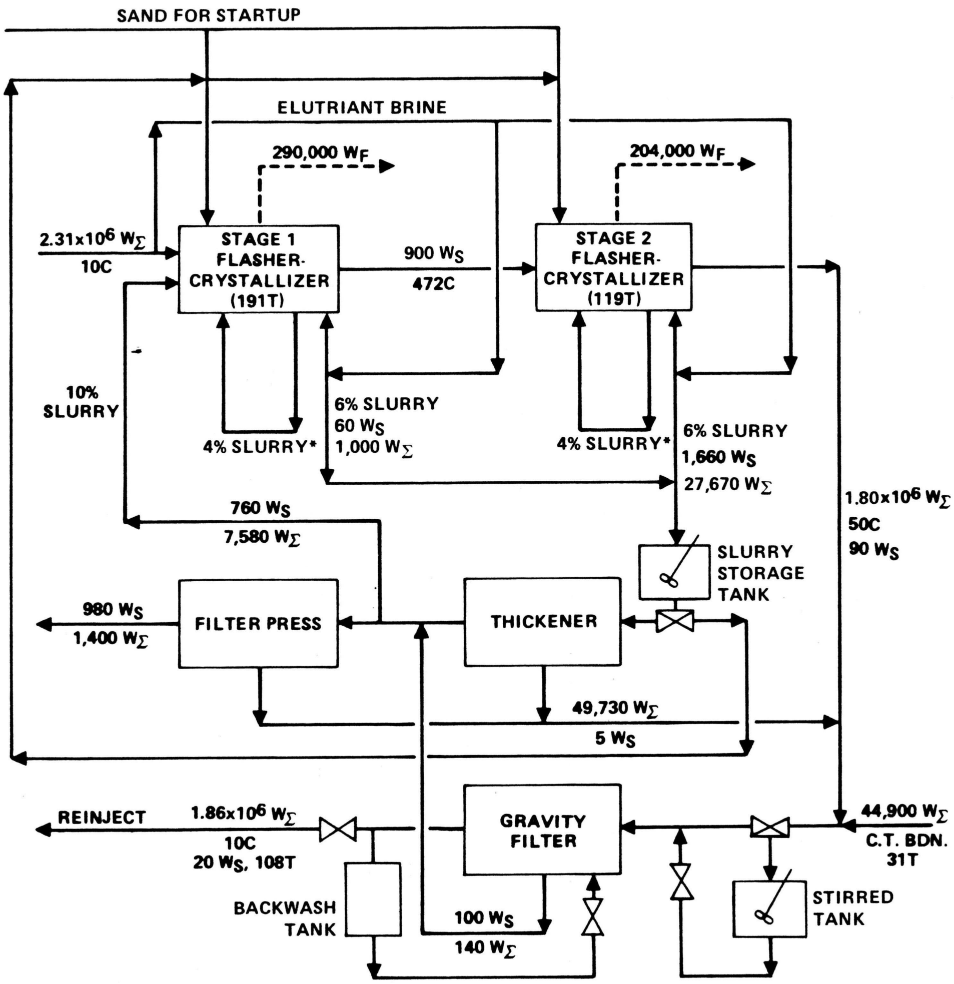
2. San Diego Gas & Electric Co. - Final Report, "Geothermal Loop Experimental Facility", Department of Energy Contract No. DE-AC03-76ET28443 (April 1980).

3. Weres, O., et al. "Kinetics of Silica Polymerization", Report No. LBL-7033 (UC-4), submitted by the Lawrence Berkeley Laboratory, University of California, to the U.S. Dept. of Energy under Contract W-7405-ENG-48 (May 1980).

4. Bennett, R. C., Swenson Division of the Whiting Corp. Private Communication. (April 15, 1981).

5. Hoch, A. W., Magma Power Co. Private Communication. (May 6, 1981).

6. Randolph, A. D. Private Communication. (May 15, 1981).



NOTES:

W = FLOW, IN KG/HR, OF BRINE
W_S = FLOW OF SOLIDS (SUSPENDED)
W_Σ = FLOW OF SOLIDS + BRINE
C = CONCENTRATION IN PPM BY WEIGHT
W_F = FLOW OF FLASHED STEAM
T = TEMPERATURE IN °C
* = INTERNAL CIRCULATION
--- = VAPOR FLOW

Figure 1 MATERIAL BALANCE: FLASHER-CRYSTALLIZER-SEPARATOR SECTION

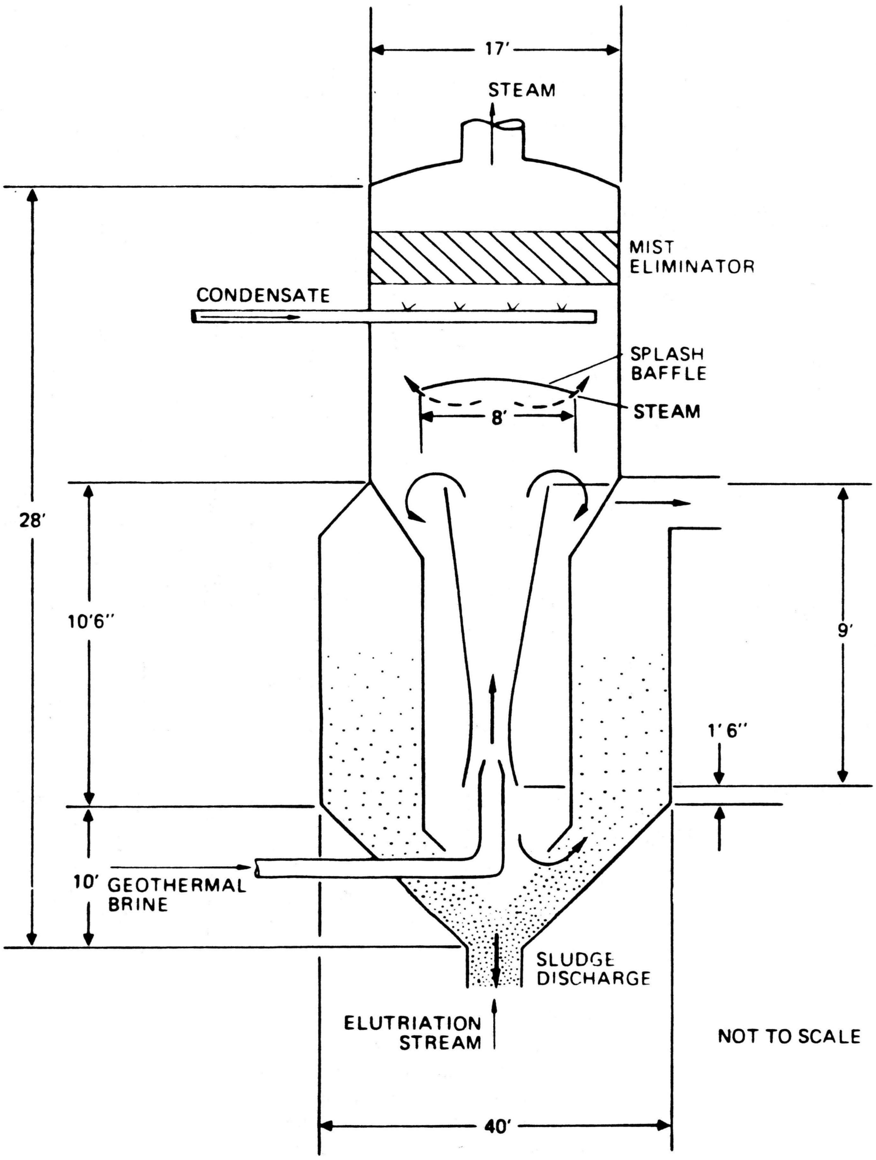


Figure 2 STAGE 2 FLASHER-CRYSTALLIZER-SEPARATOR

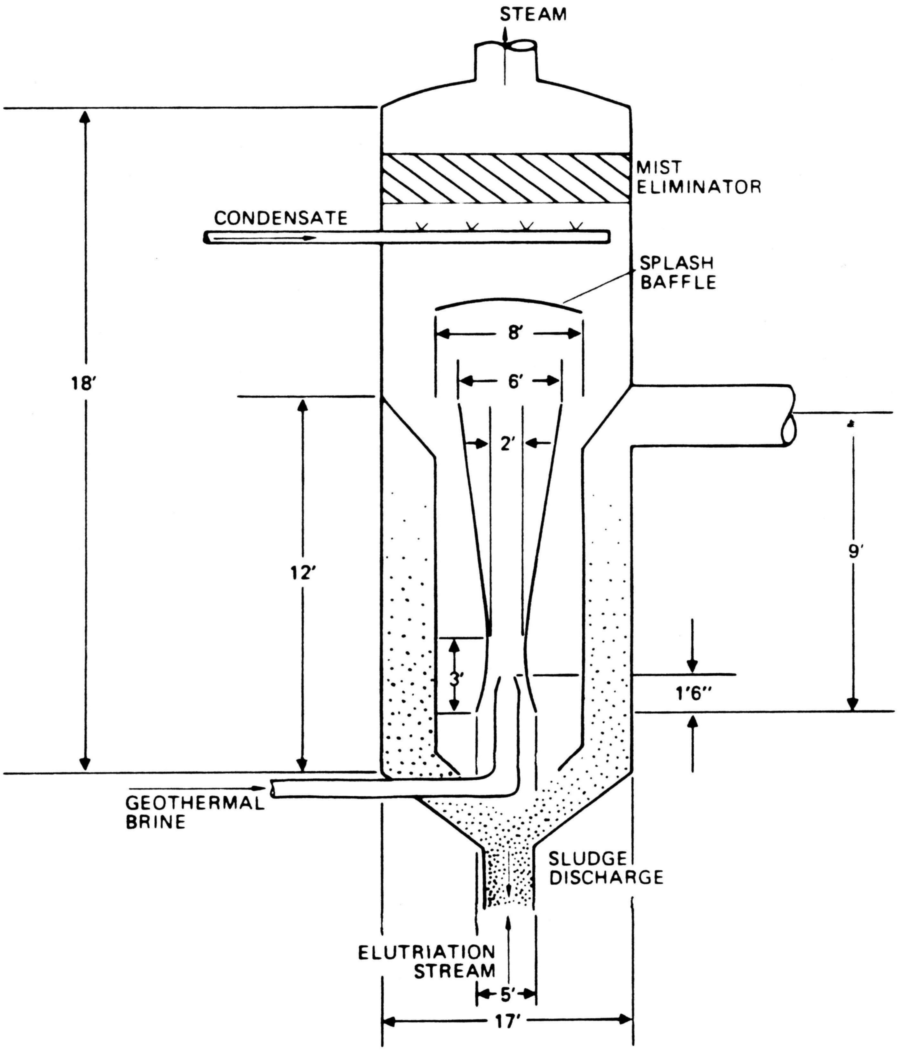


Figure 3 STAGE 1 FLASHER-CRYSTALLIZER-SEPARATOR TEST UNIT

Table 1

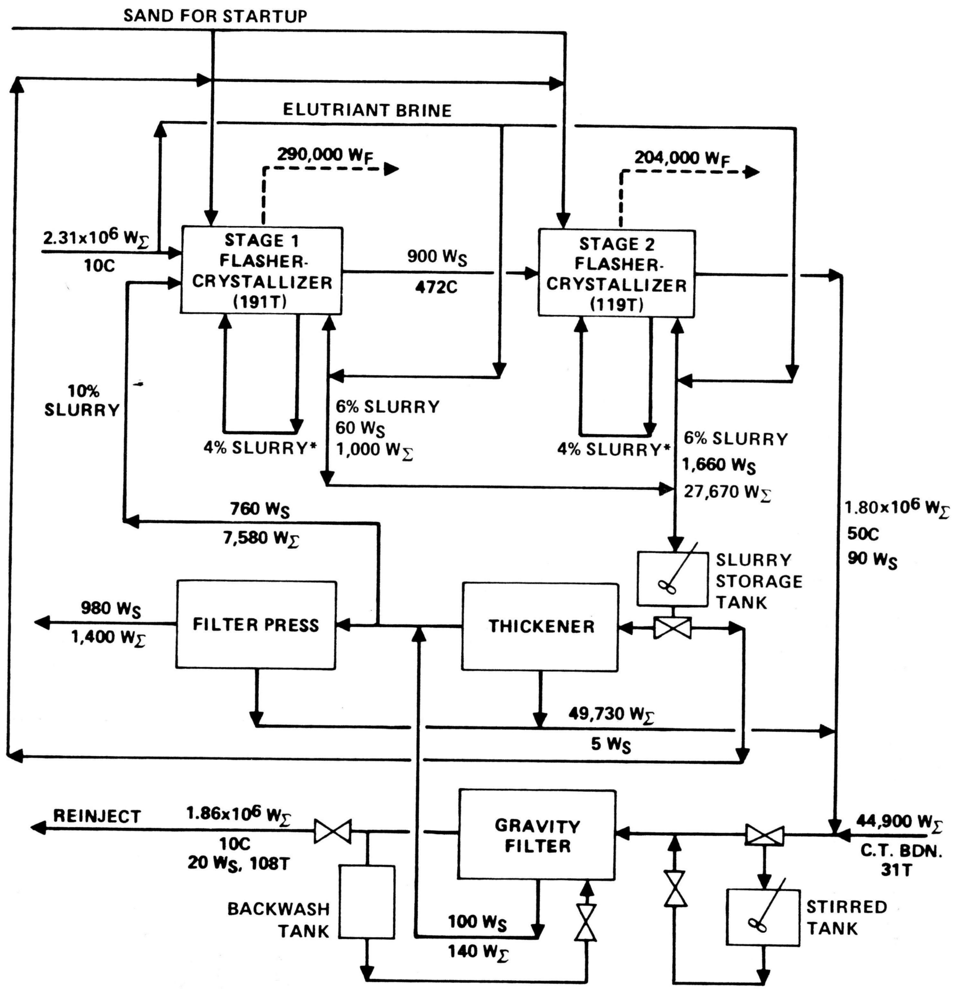
RESIDENCE OF CRYSTALS REQUIRED
TO RELIEVE SUPERSATURATION

Initial Diameter of seed particle (microns)	Residence Time required (minutes)	
	Stage 1	Stage 2
10	0.11	0.02
20	0.21	0.03
50	0.53	0.09
75	0.79	0.13
300	3.17	0.53

Table 2

GUIDELINES FOR CRYSTALLIZER DESIGN

	Flasher-Crystallizers		
	Stage 1	Stage 2	General
Number of trains	-----	-----	1
Mean seed crystal size (microns)	-----	-----	300
Brine feed to vessel (kg/hr)	2.31×10^6	2.02×10^6	-----
Brine leaving vessel (kg/hr)	2.02×10^6	1.82×10^6	-----
TDS in leaving brine (ppm)	257,000	286,000	-----
Internal recycle slurry concentration (wt. %)	-----	-----	4.0
Brine residence time (minutes)	3.0	21.0	-----
Slurry crystal residence time (minutes)	45	27	-----
Brine rise rate in the separating zone			
(gpm/sq. ft.)	48	5.8	-----
(cm/sec.)	3.3	0.4	-----
Flashed steam - Pressure (kPa)	1,006	145	-----
Temperature (°C)	191.1	119.4	-----
Velocity during droplet disengaging (cm/sec.)	58	244	-----



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