

# Ion Exchange for Nitrogen Removal

An extensive review of a project for using continuous ion exchange for removing nitrogen from waste water in a large nitrogen complex.

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Continuous ion exchange appears to be providing satisfactory treatment of liquid waste effluent from the CF Industries nitrogen complex in Hertford County, North Carolina. The process is experimental, and all the questions have yet not been answered. This article is a progress report.

Continuous ion exchange concentrates the dissolved solids (mainly ammonium nitrate) in the waste water. In this manner, it serves as a preconcentrator to return the material to product. In that sense, the unit is a pollutant concentrator and not a water purifier.

Overall cost of this preconcentrator is such that if the AN in the waste water were raised from its normal 0.35% concentration to a 1.10% level, direct evaporation by steam would be competitive. Preconcentration to this level by low heat, which is sometimes available in a nitrogen plant, might be considered a good alternative.

The waste stream is demineralized in the continuous ion exchange plant, and the partially demineralized water is used for cooling tower make-up. The term demineralized water is used here in the vernacular sense; the effluent in fact always has significant residual dissolved solids; e.g., none of the silica is removed. All total dissolved solids remaining in the effluent stream enter the cooling tower and are reconcentrated there.

The continuous ion exchange plant produces a concentrated waste stream, chiefly ammonium nitrate. This weak aqueous stream of ammonium nitrate affects the product distribution of the nitrogen complex, since it has a limited use.

To achieve a fit between the waste water stream from the nitrogen complex and the capacity of the continuous ion exchange plant, the volume of waste water had to be severely curtailed. This reduction created many difficulties in the operation of the nitrogen complex and has caused significant extra costs.

The continuous ion exchange plant recovers 4.8 ton/day average of ammonium nitrate. It is onstream 93.0% of the time and therefore recovers a net amount of 4.5 ton/day of ammonium nitrate. Annual direct costs, which are based on the first nine months of fiscal 1973-74, are \$663,900. In one year, 1,650 ton of ammonium nitrate are recovered at a net cost of \$402/ton.

Figure 1 shows the plant site and the ponds. The CF Industries North Carolina nitrogen complex is on an approximately 1,000-acre tract on the south bank of the Chowan River. The nature of the river is relevant to this discussion in that it led to the severely limited discharge with which the complex is now operating.

The complex is comprised of the following manufacturing units (capacities in ton/day): ammonia, 600; nitric acid, 1,000; ammonium nitrate, 1,250; prilling plant No. 1, 500; prilling plant No. 2, 800; and urea (once-through), 300. In addition, there are conventional facilities to manufacture and store AAN and UAN.

## State government aims for improved water quality

The State of North Carolina has for many years pursued a policy of maintaining and improving the quality of its streams. Particularly in recent years, there has been a very active program in the State of initiating new waste treatment facilities and upgrading existing ones.

The nitrogen complex has received very close attention from its inception in late 1969. The rural setting, the fact that it is the largest single manufacturing complex in the area, and the sensitive nature of the river are all facets that combined to place extreme pressure on the complex to abate its discharge.

In addition, the complex experienced great difficulties in starting up. These difficulties generally increased both the volume and the mineral content of the waste water, thus aggravating the problem.

To achieve zero discharge, the waste stream was to be demineralized with a continuous ion exchange plant. The demineralized water was to be used as boiler feedwater and cooling tower make-up. It should be noted that the demineralized water from the continuous ion exchange plant has never been acceptable as boiler feedwater. This is so because some break-through always occurs. Therefore, the demineralized effluent can be expected to be of lower qual-

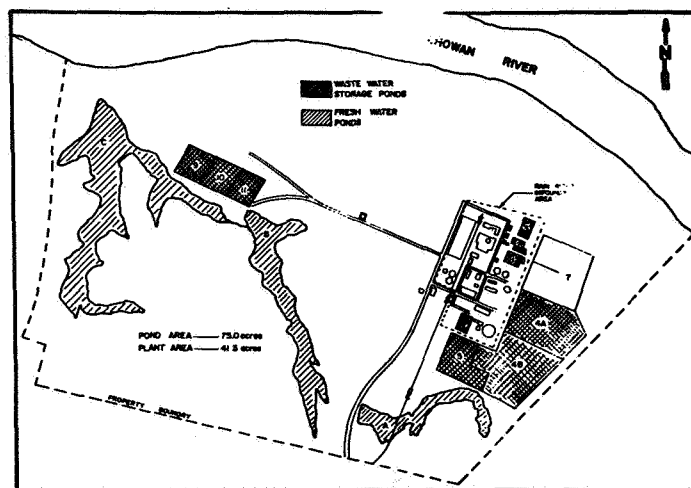


Figure 1. Plant fresh water and waste water storage system.

ity than the available river water. Dissolved solids removed from the waste water along with the regenerants are extracted in concentrated form as 10 to 12% ammonium nitrate. This stream is then concentrated with steam and recycled to product by carefully adding it to special nitrogen solutions.

The continuous ion exchange plant became operational in late 1972. The most pressing problem in December, 1972, was to provide adequate storage for the waste water. The total amount of waste water could be determined by noting the rise in volume, but the individual sources were not well defined at this point.

One of the best ways to establish the rate of progress over a period of time is to take differences in stored waste water and adjust for excess rainfall over evaporation to establish the net outfall from the complex. Between early December, 1972, and early February, 1973, the volume of stored waste water rose from 82 million gal. to 136 million gal., or an average of 586 gal./min. At this point, a maximum volume was reached. Volume then leveled off for a time and began a slow decline.

### How the volume reductions were initiated

On February 1, 1973, CF Industries began operating the plant. During the period after that date, gross changes were made to establish the initial reductions in volume. It is important to note that the 586 gal./min. was an average. When the reduction program was begun, it was much higher. Because the means to measure individual sources were inadequate, no accurate values can be assigned.

Principally, the following items accounted for stemming the increase:

1. Idling the NPK Plant.
2. Reduction of streams such as steam condensate losses and water leaks.
3. Reduced cooling tower blowdown.
4. Improved demineralization and reuse of 1,500-lb./sq.in. gauge boiler blowdown in lower pressure boilers, thereby reducing overall boiler blowdown.
5. Use of the continuous ion exchange plant to treat waste water rather than fresh pond water. Fresh pond water after filtration was sent directly to the cooling tower.

By February 8, 1973, the situation had started to become more stable, and it can be used as a reasonable point of reference. The decrease in waste water volume over one year was found to be 15,460,000 gal., the difference between 130,000,000 at Feb. 8, 1973, and 114,540,000 at Feb. 8, 1974. The decrease then equals 29 gal./min. The water balance for the year examined looks like this: net volume through continuous ion exchange plant, 250 gal./min.; excess rain over evaporation, -48 gal./min.; and decrease in waste water storage, -29 gal./min. Thus, the net contribution from the complex was 250 - 77 = 173 gal./min.

This water balance was achieved by removing several major contributors from the system in 1973. They were demineralizer waste, primary reformer header spray cooling, and ammonia plant process condensate. The demineralizer waste was removed from the system by May 1, 1973, the spray cooling by October 1, 1973, and the process con-

densate by January 1, 1974.

The contribution in 1973 of streams removed by 1974 was calculated as follows: demineralizer waste, 84 days x 143,000 gal./day = 12,012,000 gal.; spray cooling, 264 days x 28,800 gal./day = 7,603,200 gal.; and process condensate, 325 days x 72,000 gal./day = 23,400,000 gal.; and a total of 43,015,200 gal. This amount, 43.01 million gallons, when taken over 365 days averages 82.0 gal./min.

In the net contribution from the complex of 173 gal./min., there were 82 gal./min. now permanently removed. At this writing then, the net contribution from the complex is 173 - 82 = 91 gal./min.

The demineralizer waste stream needs further clarification in the effect that it has on the continuous ion exchange plant. Thus far, this discussion has centered on hydraulic data. However, the true limitation of the continuous ion exchange plant is the total dissolved solids (TDS) in feed stream.

The ammonia plant produces high-pressure (1,500 lb./sq.in. gauge) steam, therefore all solids must be removed from the boiler feedwater. In this case, the quality of the raw water is such that the anion exchanger is the limiting factor, and 3 ton/day of caustic soda are required for regeneration. The cation exchanger is regenerated with sulfuric acid, and the regeneration is adjusted to yield a slightly alkaline waste when the two waste effluents are combined. Each day, approximately 5-1/3-ton of sodium sulfate are so produced.



When evaluating this stream's impact on the continuous ion exchange plant, it is noted that it would occupy more than its complete capacity.

The continuous ion exchange plant fairly consistently removes 4.8 ton/day of  $NH_4NO_3$ . An equivalent in terms of  $Na_2SO_4$  would be 4.3 ton.

The stream from the demineralizer unit was impounded from August 15, 1972, until May 1, 1973, at which time permission was granted by the State of North Carolina to discharge it back to the surface waters of the State. At all times, it was kept segregated from the stream feeding the continuous ion exchange plant. This highly concentrated waste, amounting to nearly 91 million gal., is stored separately in three ponds and is being blended into the continu-

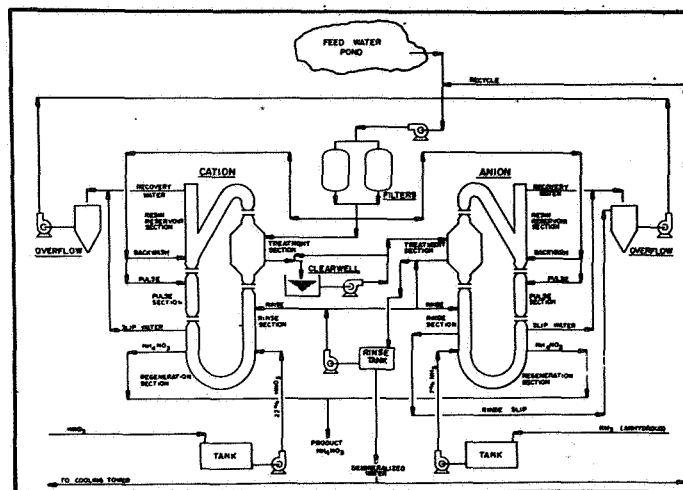


Figure 2. Continuous ion exchange plant flow diagram.

ous ion exchange plant feed stream. If fed directly to the continuous ion exchange plant, it would reduce its normal net throughput from 250 gal./min. to 125 gal./min., or to one-half, because of its nearly double TDS content.

The time required for depleting the 91 million gallons will be 3.1 yr., computed as follows: Continuous ion exchange plant capacity is 250 gal./min., from which is subtracted the excess flow of rain over evaporation (48 gal./min.) and the contribution from the complex (91 gal./min.), giving 111 gal./min., as the excess continuous ion exchange plant capacity.

The stored waste TDS is twice the amount of the normal feed TDS. Therefore, the adjusted excess ion exchange plant capacity is  $0.50 \times 111 = 55.5$  gal./min. Then, the time requirement in years is calculated as follows:

$$\frac{91 \text{ (million gal.)}}{365 \text{ (days)} \times 55.5 \times 1,440 \text{ (min.)}} = 3.1 \text{ yr.}$$

### Most important side is the TDS

One side of the coin, hydraulics, has been examined. The other and really the most important side is TDS. The continuous ion exchange plant can handle hydraulic loads up to 625 gal./min. with the TDS at 2,320 ppm  $\text{CaCO}_3$  (design). The actual case, however, was different. Most streams, except the ammonia plant process condensate and the primary reformer header spray, were very concentrated by removing the less ionized streams only storage room was created.

The only stream involved which was hydraulically significant as well as having a very high TDS content was the demineralizer waste. Removal of the others really only bought time. The real problem was product spills and losses in the plant.

The continuous ion exchange plant removes a net of 4.8 ton/day of  $\text{NH}_4\text{NO}_3$ , or its equivalent in other ions. Therefore, the net daily contribution to the continuous ion exchange plant must not exceed 4.8 ton  $\text{NH}_4\text{NO}_3$ . Depletion of the stored waste indicates that spills and losses are being minimized. One year ago, during a rain, the normal nitrogen content of the ditches would be as high as 2,000 ppm total N. This is now 500-600 ppm total N, which shows the magnitude of the reduction.

Reductions in ionic loading were achieved principally by installing pads under areas where spills are likely and frequent.

It was found that:

1. The ammonia plant contributed very little in the way of dissolved solids.

2. The nitric acid plants already had reasonably efficient collection of product spills, which in this case consisted primarily of collecting spills during sampling operations.

3. The ammonium nitrate and AAN solutions area was found to be a very large contributor. A pad was installed under the entire production area as well as the tank car and truck loading areas. Any spills in this area are washed down and recycled to the waste evaporator.

4. The 83% ammonium nitrate storage tank and associated pumps were also heavy contributors. A reclamation pad was installed here.

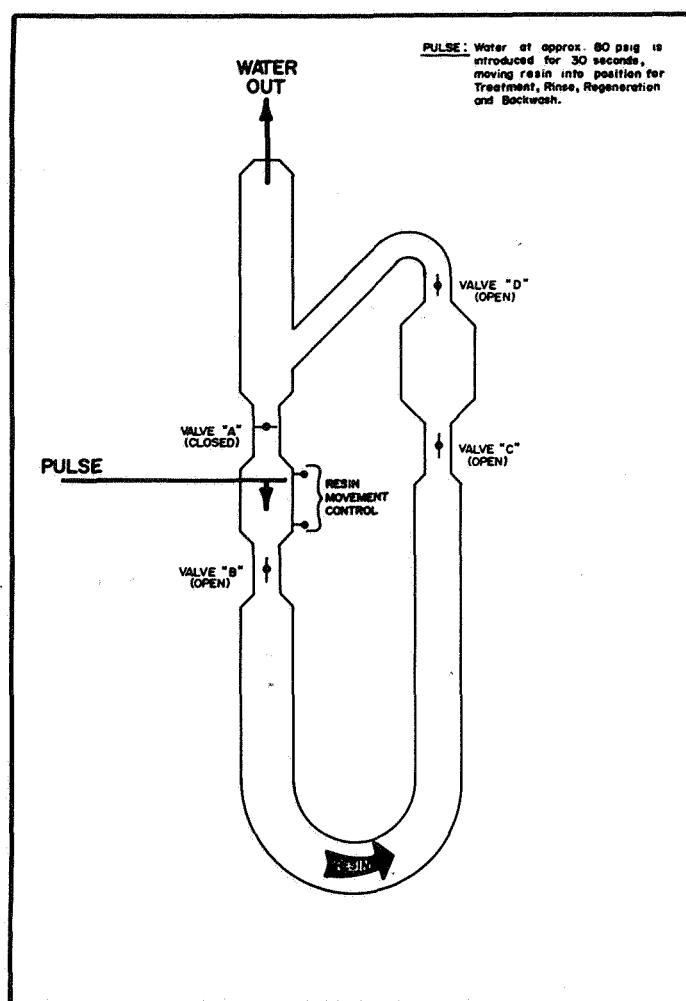


Figure 3. Pulse mode.

5. In the ammonium nitrate bagging and bulk loading areas, most of the problem is centered around making the personnel conscious of the problem. Under the worst circumstances, this can be an area of high contribution.

6. UAN loading is a contributor, but since nearly all tank cars and trucks are top loaded, the product spills are minimal.

At this time then, the continuous ion exchange plant is principally treating: rain run-off from the site, cooling tower blowdown, and depletion of stored waste water.

With product spills under control and the elimination of all unnecessary streams, the continuous ion exchange plant now appears to fit the nitrogen complex. The system is under continuous review, and improvements continue to be made.

### Two exchangers involved in plant operation

Figure 3 outlines the treatment plant. Two exchangers are employed, one filled with strong acid resin and the other with weak base resin. The cation exchanger is regenerated with 22-24% nitric acid, the anion exchanger with 6-8% ammonium hydroxide. The operation of each exchanger is essentially the same.

Pulse operation is begun with the "pulse mode" shown in Figure 3. At this time, valve "A" is closed and valves "B", "C", and "D" are open. Water is introduced below valve "A" and the resin in the exchanger is forced down and around the loop.

The pulse mode is controlled by proximity switches

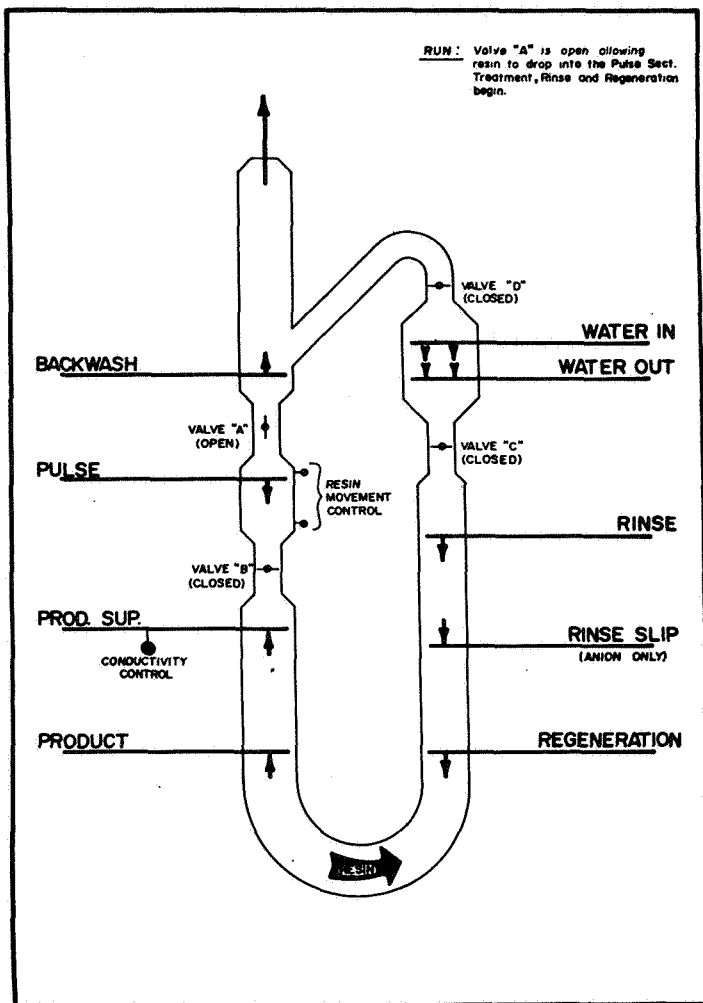


Figure 4. Run mode.

which allow the pulse to continue until the prescribed amount of resin movement is attained. Another stream of water, called secondary pulse, is introduced into the treatment vessel to aid in "fluffing" the resin at this point. The pulse is normally completed in 30 sec.

During the pulse and resin movement, several important things occur which make this process unique:

1. Exhausted resin from the water treatment section is pushed up and over the loop, falling into the resin storage section.

2. Freshly rinsed resin moves into the treatment section.

3. Freshly regenerated resin moves into the rinsing area.

4. Exhausted resin moves into the regeneration area.

Therefore, with the completion of the pulse mode, all resin has been placed in the position for completing the conventional water treatment operations. During the succeeding run cycle, as shown in Figure 4, backwash, regeneration, rinse, and water treatment begin and go to completion simultaneously.

In the "run mode" shown in Figure 4, feed water enters the treatment section where the water with the highest ionic loading contacts virtually depleted resin. This has the advantage of providing the greatest possible driving force and aids in fully "loading" up the resin. As the feed water loses its dissolved solids content moving down through the bed, it encounters resin with more and more capacity until near the exit, freshly regenerated resin is encountered. Thus, the most favorable equilibrium rates throughout the entire bed are provided.

This configuration permits maximum recovery of dissolved solids with the lowest ratio of regenerant use. Regenerant usage is usually on the order of 100% over stoichiometry, based on  $\text{NH}_4\text{NO}_3$  recovery from the feed stream. In practice, regenerant use fluctuates considerably, due to the large number of variables such as constituents in the feed stream, degree of recycle, etc.

Regenerant is introduced in approximately four minutes, its flow controlled with a timer. It assumes fixed flow and fixed concentration. To introduce more or less regenerant, the time span is either increased or lessened.

Backwash goes on continuously if required. In practice, little backwash is used. It must be noted that the pulse mode, in effect, provides some backwash. Continuous backwash tends to increase resin loss.

#### Most efficient operation centered on more feedwater

Optimizing of the plant has been centered around improving its capacity in terms of amounts of feedwater processed.

Demineralized water quality has been sacrificed to some extent to achieve maximum throughput. The process has two basic operations: 1) resin is regenerated or "stripped" of its absorbed solids load; and 2) regenerated resin is "loaded up" with dissolved solids from the feed stream. Part of the time, these two operations take place simultaneously, but No. 1 must be completed first.

Because maximum capacity is reached only when maximum use is made of the resin, the time increment required to regenerate the resin is the limiting factor. The time required to pulse, regenerate, and rinse the resin is about three minutes. This time period, then, can be approached for the "run" time cycle, but cannot be reduced to less.

It can be said that the "run" cycle may be cut to 3.5-4.0 min. The next important point is that with the treatment time at 3.5-4.0 min., the resin must be loaded to capacity with dissolved solids from the feed stream. However, the flow rate through the unit is not varied and is normally 475-500 gal./min. instantaneously.

With the time and flow rate fixed, loading up of the resin can be controlled by adjusting the TDS of the feed stream. Thus, some "demineralized water" is recycled. This recycle became necessary in 1973 as the complex "dried up." The net result of the drying up was a significant increase in TDS of the waste water.

When it was realized that with recycle the plant could be adjusted better, it was also discovered it could be used as a means to improve its capacity. At this time then, the unit is optimized by: 1) adjusting the run time of the limiting exchanger to just exceeding the regeneration time; and 2) adjusting the TDS of the feed to the point where the limiting exchanger is completely loaded in the given run time.

As discussed previously, some "demineralized water" is recycled to achieve control. However, if Figures 2 and 5 are examined, there is also significant internal recycle. This is where the operation differs sharply from conventional water treatment operation.

The dissolved solids removed from the feed water and the regenerant chemicals ideally are to end up as a "product" stream at the highest possible concentration. However,

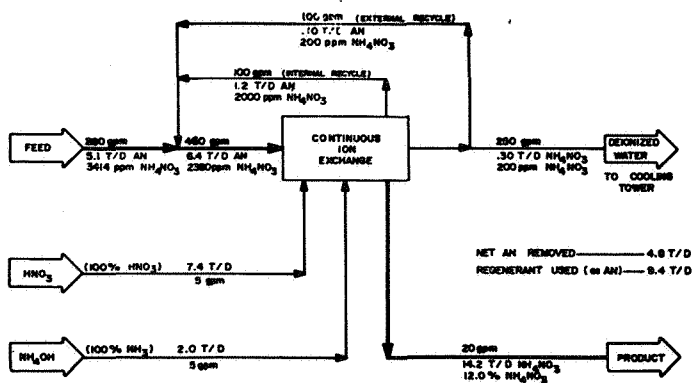


Figure 5. Normal material balance.

in the regeneration and rinse section there is much opportunity for dilution. Some dilution occurs with the pulse mode, the balance with the rinse streams.

The dilute stream is separated from the product stream either by conductivity or pH measurement. These dilute streams, although not concentrated enough to go to product, constitute a significant ionic load when they are recycled. The extra load on the unit so created is usually 20%. Improper adjustment of these streams will cause either extra load for the plant or a more dilute product. In practice, deviations can be spotted fairly quickly by following product concentration.

### Primary problem areas discussed

It is helpful to examine the downtime incurred by equipment failures and discuss the main problem areas. The duration of each shutdown was not necessarily dictated by the item that initiated it. Frequently other work was done that extended the length of the shutdown.

The polyvinyl chloride (PVC) liners in the treatment vessels began failing early in 1973, and were then replaced with glass. The present liner material has the advantage that it can be patched.

Problems with the large "squeegee" type Crane valves have been with liner failures and failures of the stop block. Failures of the stop block can be very serious, particularly with the "A" valve, because it causes resin to be pulsed out of the vessel. The valves must seat tight for good operation. If a liner becomes rough or abraded, it has to be changed.

The high frequency of "A" valve failures was related to its operation during the run cycle. At this time, resin is dropping into the pulse section, and the "A" valve will frequently open and close when resin alternately floats and settles around the upper proximity switch. A change was made to permit this valve to stay open longer, and the frequency of cycling has been reduced.

The extensive hydraulic system repairs were caused by poor installation of the tubing. The tubing has since been properly supported and flexible pieces are used in problem areas. Very little problem is experienced with the hydraulic system now.

Nozzle repairs in the vessel have been frequent. The failures have been caused by cracking of the light schedule pipe at the weld. Due to its mode of operation, the entire plant is susceptible to failures from water hammer.

In general, emergency maintenance is lower because the unit is shut down approximately every two months for a

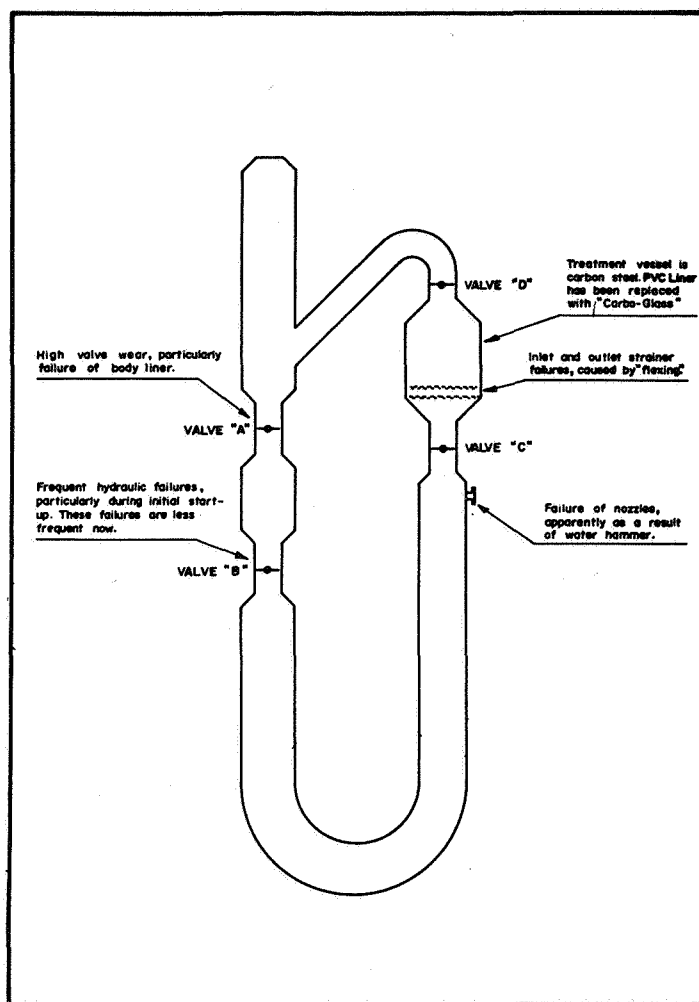


Figure 6. Major maintenance problems.

good inspection. This is particularly important to prevent serious failures of the internal screens. The screens are wound stainless steel wire, and no successful repairs have been made. Areas that have opened up are banded with stainless straps.

Less maintenance is anticipated in the future, and this cost should be reduced.

### Cooling tower a critical element in the project

The cooling tower in this system serves the purpose of evaporating the "demineralized water." It therefore becomes a critical part of the effluent abatement program; in fact, the complex could not operate without a nitrogen-bearing waste stream if the cooling tower was not used for this purpose. In this case, there is a "fit" between the water produced and the cooling tower requirement; also the solids contribution is manageable but barely so.

The continuous ion exchange plant contributes nitrogen to the cooling tower to the extent of 0.30 ton/day of  $\text{NH}_4\text{NO}_3$ . However, there are several other contributors of nitrogen, for example the fresh water ponds; therefore, the problem caused by high nitrogen levels, is not completely attributable to the continuous ion exchange plant.

Silica content of the Chohan River averages 20 ppm., and the normal river water make-up to the cooling tower is 1,000 gpm. Each day, therefore, 229 lb. of silica is brought in. The continuous ion exchange plant does not remove silica, because weak base resin is used in the anion exchanger.

In theory then, because cooling tower blowdown is directed to the continuous ion exchange plant and silica is not removed, it should concentrate to very high levels in the cooling tower. In practice, it does not. The level of silica builds up to 80-100 ppm. in the cooling water and remains there.

To date, no evidence has been seen of silica deposits in any heat exchange equipment. The evidence is that the silica precipitates out with aluminum, attaches to suspended solids, and is lost anywhere low velocities allow it to. When foam forms on the surface of the cooling tower basin, it has been found to be 2½% silica.

Although silica appears to pose no heat exchange problem, there is reason for concern. It is always possible that some change in cooling water chemistry may cause the silica to deposit on heat exchange surfaces; therefore, a strong effort is being made to determine precisely what is happening. If depositing should begin to occur in heat exchange equipment, the plant would be faced with very serious problems.

Nearly 40 tons of silica can be expected to come into the plant each year, and it must remain somewhere on the site.

Each day the continuous ion exchange plant produces 28,800 gal. of product. It would require a great deal of storage space to store the product as it leaves the unit. For example, five days of production would require a 150,000-gal. tank. The design concept was that the product at 20% AN would be blended to produce UAN 30.

UAN 30 at this plant is produced by design from 83.0% AN and 80.0% urea solution. Under these conditions, the dilute stream from the continuous ion exchange plant would not have been a serious problem. However, it still would have provided 57.0 ton/day of water. UAN 30 contains 25% water. When this is prepared with 83% AN and 80% urea, approximately 30% of the needed water must be added. If we consider the 57 tons of water in the continuous ion exchange plant product being blended into UAN 30, a minimum UAN 30 production of 712 tons is required.

In practice, the situation is much worse because the continuous ion exchange plant product is 12% and the daily water contribution is 118 tons. On this basis, 1,475 ton of UAN 30 production would be required. The latter exceeds the maximum possible UAN production by some 550 ton.

From this it can be seen that the continuous ion exchange plant product must be concentrated. For safety reasons, because the continuous ion exchange plant product is highly contaminated with other ions, it is concentrated to 60-65%. At that level, it can be blended fairly readily with UAN 30. At 60% AN, the water contribution is 9.5 ton/

**Table 1. Annual operating costs  
(based on 9 months run)**

Item	\$
Power .....	13,500
Supervision .....	18,000
Operating labor .....	64,100
Maintenance labor .....	33,000
Payroll added costs .....	22,300
Operating supplies (mainly resin) .....	52,800
Maintenance materials .....	51,000
Rent .....	51,000
Depreciation .....	86,000
Laboratory .....	26,000
Concentrating cost .....	246,206
<b>TOTAL .....</b>	<b>\$663,900</b>

day, and a minimum production of 120 ton of UAN is required.

Thus, to run the continuous ion exchange plant, UAN 30 must be produced continuously all year. Also, continuous ion exchange plant operation and UAN production are interdependent. The minimum production of UAN becomes a factor in sales and product storage.

Safety considerations effectively block the use of recovered AN in the production of either prilled AN or AAN solutions.

The annual operating costs are based on nine months operation, July 1, 1973 through March 31, 1974. The costs shown in Table 1 are those incurred directly and do not include any general operating costs. A total of 1,650 ton of ammonium nitrate are recovered annually,

$$\frac{663,900}{1650} = \$402.40/\text{ton.}$$

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