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COMMENCING JUNE 24, 1977, COMMUNITIES THROUGHOUT THE UNITED STATES ARE REQUIRED TO COMPLY WITH THE ENVIRONMENTAL PROTECTION AGENCY NATIONAL INTERIM PRIMARY DRINKING WATER REGULATION DATED 24 DECEMBER 1975. THIS REPORT IS BASED UPON PILOT PLANT EXPERIMENTS AND PLANT DATA WHICH USED GRANULAR F-1 ACTIVATED ALUMINA (MESH SIZE 28 TO 48) MANUFACTURED BY ALUMINUM COMPANY OF AMERICA. THE BASIC PRINCIPLES OF FLUORIDE REMOVAL TECHNOLOGY ARE: (1) OPTIMIZE THE ENVIRONMENT FOR (?)SORBING OF FLUORIDE IONS TO ACTIVATED ALUMINA SURFACES. (2) PREVENT COMPETING IONS FROM OCCUPYING ALUMINA SURFACES WHICH ARE TO BE RESERVED FOR FLUORIDE IONS. (3) UPON REGENERATION OF AN EXPENDED TREATMENT BED, TAKE ALL STEPS NECESSARY TO REMOVE ALL FLUORIDE IONS FROM THE BED PRIOR TO RETURN TO TREATMENT. THERE ARE FOUR MODES OF OPERATION: TREATMENT, BACKWASH, REGENERATION AND NEUTRALIZATION. OPERATIONAL DETAILS FOR EACH MODE ALONG WITH OTHER IMPORTANT CRITERIA ARE PROVIDED IN THIS REPORT.

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Removal of Excess Fluoride from Drinking Water

Rocky Mountain Arsenal
 Information Center
 Commerce City, Colorado



January 1978

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INTRODUCTION

Commencing June 24, 1977, communities throughout the United States are required to comply with the Environmental Protection Agency National Interim Primary Drinking Water Regulations dated 1975 December 24. Maximum contaminant levels in potable water supplies have been established for ten (10) inorganic chemicals, one of which is fluoride. The maximum contaminant level for fluoride varies from 1.4 to 2.4 mg/L depending upon the annual average of the maximum daily air temperatures (see Table I). In order that the prescribed maximum level be enforced, it is imperative that achievement be technically and economically feasible.

TABLE I
MAXIMUM CONTAMINANT LEVELS FOR FLUORIDE

<u>Average Maximum Daily Temperature</u> <u>Temperature</u> <u>Degrees</u> <u>Fahrenheit</u>	<u>Temperature</u> <u>Degrees</u> <u>Celsius</u>	<u>Level</u> <u>Milligrams</u> <u>per Liter</u>
53.7 and Below	12.0 and Below	2.4
53.8 to 58.3	12.1 to 14.6	2.2
58.4 to 63.8	14.7 to 17.6	2.0
63.9 to 70.6	17.7 to 21.4	1.8
70.7 to 79.2	21.5 to 26.2	1.6
79.3 to 90.5	26.3 to 32.5	1.4

Since it became known that excess fluoride in drinking water caused mottled teeth in children,¹ many methods for removing this mineral have been developed. One of the methods which can defluoridate water supplies relies on activated alumina. This method is safe, reliable and simple. Two operating plants have experienced several years of low cost defluoridated water production. The first is the Lake Tamarisk Plant at Desert Center, California with eight years of operation (see Figure 1). The second is the Rincon Water Company Plant at Vail, Arizona with five years of operation (see Figure 2). A third plant is under construction for the town of Gila Bend, Arizona; operational status is planned for March, 1978 (see Figure 3). Development work in pilot plant equipment on a continuing basis has perfected the treatment and regeneration processes at each of these locations (see Figure 4). It was possible to make continuing refinements in the design and operation technique by employing the same alumina technology in all three plants.

Fluoride Removal Technology

This report is based upon pilot plant experiments and plant data which used granular F-1 Activated Alumina (mesh size 28 to 48) manufactured by Aluminum Company of America.

The basic principles of fluoride removal technology are:

- 1) Optimize the environment for sorbing of fluoride ions to activated alumina surfaces.
- 2) Prevent competing ions from occupying alumina surfaces which are to be reserved for fluoride ions.

¹ L.T., Arnold, F.A., Jr., and Elvove, E., Domestic water dental caries. V. Additional studies of relations of fluoride in domestic waters to dental caries experience in 4,425 white children, age 12 to 14 years, of 13 cities in 4 states. Pub. Health Rep. 57: 1155-1179, Aug. 7, 1942.

FIGURE 1 LAKE TAMARISK WATER TREATMENT PLANT, DESERT CENTER, CA.

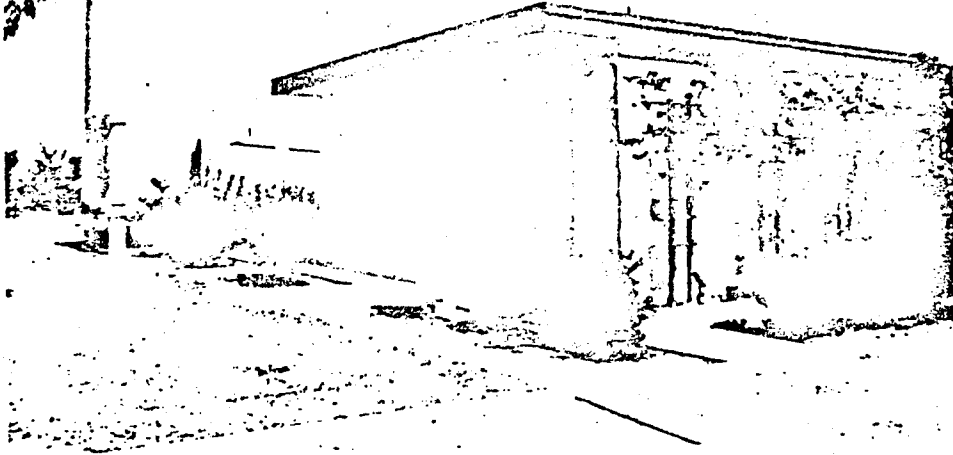


FIGURE 2 RINCON WATER COMPANY TREATMENT PLANT, VAIL, ARIZONA

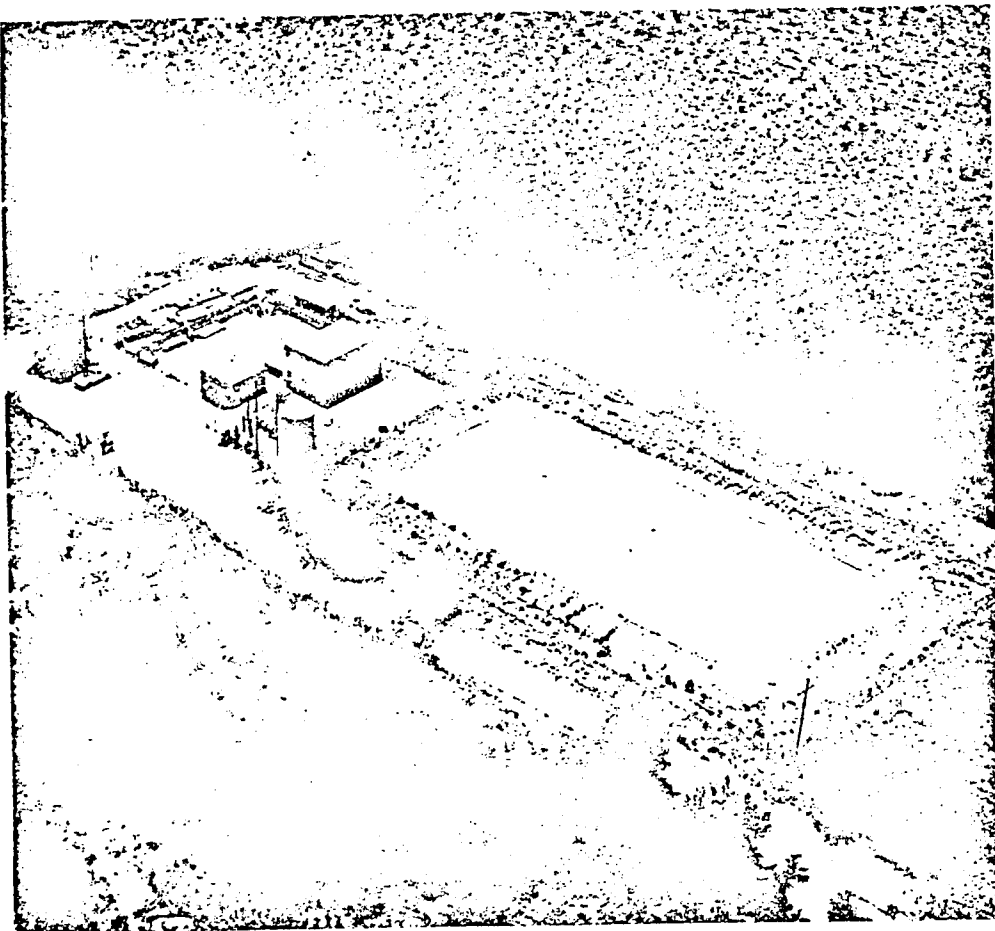


FIGURE 3 GILA BEND FLUORIDE REMOVAL WATER TREATMENT PLANT

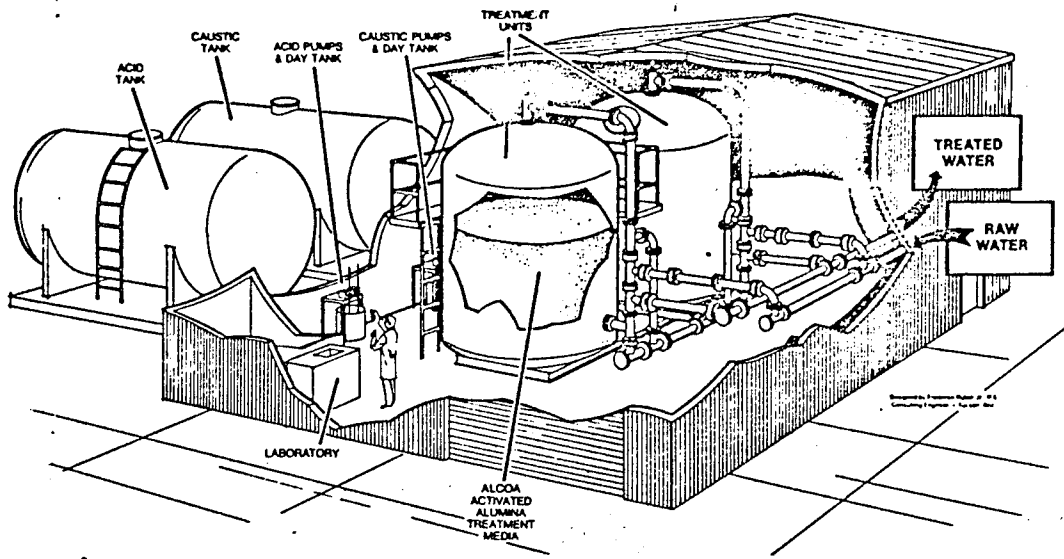
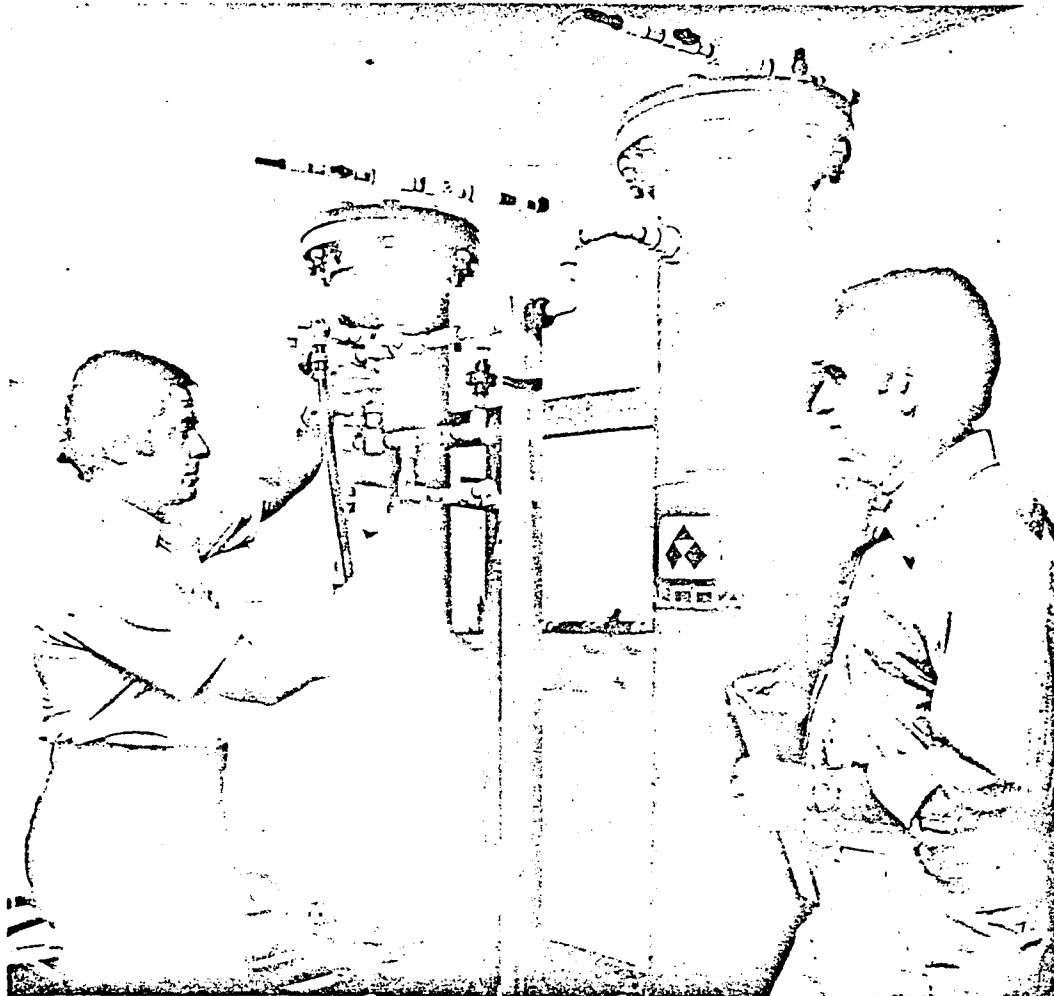


FIGURE 4 PILOT PLANT EQUIPMENT USED IN GILA BEND, ARIZONA



- 3) Upon regeneration of an expended treatment bed, take all steps necessary to remove all fluoride ions from the bed prior to return to treatment.

There are a multitude of "common sense" principles that apply to the process which, though important, are not as critical as those listed.

There are four modes of operation: Treatment, Backwash, Regeneration and Neutralization. Operational details for each mode along with other important criteria are provided here.

A. Treatment Mode for virgin or regenerated treatment bed:

The highest fluoride removal environment exists when the raw water pH is adjusted into the range of 5.0 to 6.0 by means of sulfuric acid injection. The best results obtained to date have occurred when the raw water pH has been carefully held at 5.5. In this environment the attraction of the fluoride ion to the activated alumina surface is most favorable and interference with competing ions is minimized. In applications to date, treatment bed capacities consistently exceed 2000 grains/ft³ and some runs have exceeded 3000 grains/ft³.

As raw water pH moves above 6.0 or below 5.0, fluoride removal capacity deteriorates at an increasing rate. For example, from previous experiments it has been shown that at pH 7.0 bed capacity is about 500 grains/ft³. Though efficiency might appear to be the same, breakthrough occurs earlier and treatment runs are shorter. Fluoride removal efficiency approaches 100%, as the treated water fluoride effluent is measured well below 0.1 mg/L during portions of the treatment run at each installation. This efficiency is achieved in waters with divergent chemistry which includes varying fluoride levels (see Table II). Superficial

TABLE II
WATER ANALYSES AT EXISTING OPERATIONS

<u>Facility</u>		<u>Lake Tamarisk</u>	<u>Rincon Water Co.</u>	<u>Town of Gila Bend</u>	<u>RMA</u>
Ca	(mg/L)	11	51	54	100
Mg	(mg/L)	0.5	5.8	2.5	50
Na	(mg/L)	58	151	402	300
SO ₄	(mg/L)	40	261	144	350
Cl	(mg/L)	67	22	582	350
Hardness	(mg/L)	30	152	146	-
Alkalinity	(mg/L)	77	171	52	-
P Alkalinity	(mg/L)	0	0	0	-
Fe	(mg/L)	0.2	<0.05	0.2	<0.05
SiO ₂	(mg/L)	22	55	21	30
F	(mg/L)	7.5	4.5	5.0	4.4
TDS	(mg/L)	409	650	1210	1200
pH		7.9	7.5	8.0	7.5-8.0

residence time (flow time through the bed neglecting the volume of bed material) is also a limiting factor; a five-minute minimum is established as a practical limit for maximum removal efficiency. Best results occur with flow directed down through the bed. Care must be taken to prevent a wall effect or channeling.

The initial effluent pH will be high with no fluoride removal. (See also neutralization mode below.) After a short period both pH level and residual fluoride will drop to acceptable levels. At that point usable water can be directed to storage and/or distribution. Fluoride level will drop rapidly to a very low level and will stay there until breakthrough begins at which point the level will gradually increase until the treatment run is terminated.

Finished water pH will drop to 6; or possibly lower. Since water in this range will be corrosive, the treated water pH must be adjusted to a desirable level (say 7.3); pH adjustment is achieved by injection of sodium hydroxide, or as explained later, by blending.

B. Backwash Mode:

It is important for two reasons to backwash the bed with raw water prior to each regeneration. First, any suspended solids which have been filtered from the raw water by the treatment bed tend to blind the bed and must be removed. Secondly, even though the above filtration may not have taken place the downward flow tends to pack the bed. Therefore, an upflow backwash expands the bed, breaking up any tendency towards wall effects or channeling. A backwash rate of 8-9 gpm/ft² of treatment bed surface area will expand the bed about fifty percent, which is adequate. Care must be exercised to avoid backwashing granular bed material

out of the treatment unit. Normally, backwash is completed within ten minutes.

C. Regeneration Mode:

The object of regeneration is to remove all the fluoride ions from the bed prior to return of any part of the bed to the treatment mode. The most successful regeneration is accomplished by a two-step process. The first regeneration step is upflow immediately following backwash while the bed is still expanded. This is followed by an upflow rinse. The unit then is drained down to the top of the treatment bed. The second regeneration step is downflow and is immediately followed by the neutralization mode. Regeneration steps employ one percent (by weight) sodium hydroxide solution which flows at a 2-1/2 gallon/minute per ft² of treatment bed area. With a standard treatment bed depth of five feet, each regeneration step takes thirty-five minutes. The intermediate upflow rinse flows at 5 gallon/minute per ft² of treatment bed area for a period of thirty minutes. If the treatment bed depth varies from this standard, flow rates and times must be adjusted. The regenerant solution is usually an in-line dilution of 50% sodium hydroxide with raw water. The temperature of 50% sodium hydroxide must be maintained at 70°F or higher to prevent freezing.

D. Neutralization Mode:

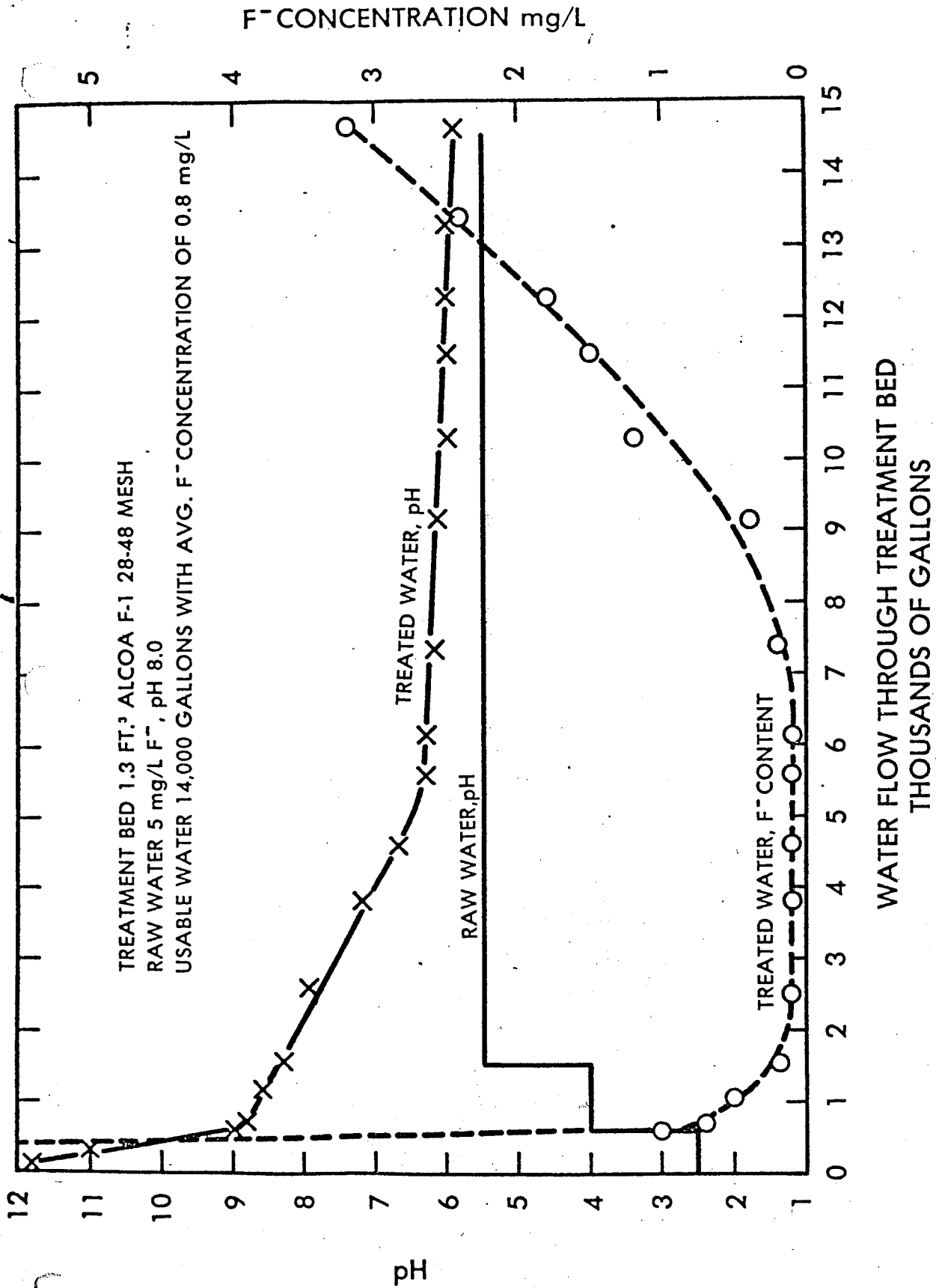
The object of this step is to return the bed to the treatment mode as rapidly as possible without dissolving the treatment media. As soon as the second (or downflow) regeneration step has been completed all of the fluoride should have been

removed from the bed. At this point the bed is drained down to the top of the treatment media again. Raw water with pH adjusted to 2.5 is then fed downflow at the normal treatment flow rate (see Figure 5). The entire bed is in the pH range of 12.5 to 13.0 and the top of the bed is starting to neutralize and enter a treatment mode. As that takes place, the fluoride level in the treated water starts to drop below that of the raw water. Treated water pH also begins to drop. As the fluoride level drops below the mandatory limit the water becomes usable and can be directed to storage and/or distribution. pH may still be high in the treated water (9.0-9.5); however this water can be blended with lower pH treated water from other treatment units as explained later.

When the pH is 9.0 to 9.5, the raw water pH is adjusted to 4 as the bed is rapidly neutralizing. When the treated water pH drops to 8.5, the raw water pH is adjusted to 5.5 where it is maintained throughout the remainder of the run.

Initial Start-up Procedures

When initially placing the bed material into the treatment unit, the vessel should be half filled with water. As the activated alumina is poured into the bed from above, the water dissipates the heat generated by the heat of wetting of the activated alumina thereby preventing cementing of the bed, aids in separating fines from the granular material, protects the underdrain assembly from impact, and initiates stratification of bed material. Once the bed is in place, it must be backwashed for an extended period until all of the alumina fines are flushed



TYPICAL PILOT PLANT RUN - GILA BEND, ARIZONA

FIGURE 5

from the virgin bed. The flow is then reversed and downflow treatment begins for the virgin run.

Blending of Treated Water

Another feature which plays a role in plant operation is blending. Blending can take place either in large reservoirs or in the treated water main. During a treatment run there is a long period when the treated water fluoride level is well below desired levels. Then as breakthrough occurs there is a long period of slowly increasing fluoride in the treated water. It is found that treated water can continue to flow to storage and/or distribution until it is 1-1/2 to 2 times the maximum allowable level with the resulting total water average fluoride level meeting a prescribed level (1/2 the maximum allowable level). When there is a large reservoir in which the major portion of a treatment run can be stored, the blending takes place there. At locations where the reservoir is not large and there are two or more treatment units, staggered regenerations accomplish the same result. That is, a regenerated treatment unit will produce very low fluoride water while a second unit in later stages of its treatment run may be producing a higher fluoride level. By mixing the effluent from the two units in the treated water main an average fluoride near the prescribed level can be maintained. Similarly, the high pH treated water occurring early in the run for one unit can be blended with the low pH effluent of another unit which is in a later stage. The benefit of this blending is short lived; soon the pH of the blended streams will have to be adjusted to an acceptable level.

Disposal of Waste Water

The waste water resulting from backwash, regeneration, and the early part of neutralization are not suitable for consumption and must be discarded. The backwash water, composed only of raw water, can be discharged to existing storm water disposal systems. The only objectionable feature of the regeneration waste is the high concentration of fluoride ions which cannot be returned to the ground water aquifer. The high pH can be neutralized. Disposal of high fluoride waste must comply with local waste water discharge standards which do vary. Existing plants concentrate the waste in lined evaporation ponds. Eventually the concentrated waste will be transferred to an acceptable disposal site, or the fluoride will be reclaimed.

The volume of waste water is approximately 4% of the total plant throughput.

Materials of Construction

The cost of the treatment plant is a function of the quality of the materials of construction employed in the design. However, trouble-free, low-cost plant operation can only be achieved by proper selection of materials to meet the service requirements of the process. First, excluding materials for concentrated acid and caustic systems, the treatment system materials shall be suitable for service in the following conditions:

- 1) Potable Water System
- 2) Ambient Temperatures (Provision for Thermal Expansion)

- 3) Exposure to Sunlight (or Protected)
- 4) ph 2-13
- 5) Ease of Maintenance (Remove and Replace with Minimum Logistics)

Materials of construction for the chemical storage and handling systems excluded above shall comply with chemical manufacturers' guidelines.

Operator Requirements

A qualified operator for a Fluoride Removal Water Treatment Plant requires thorough fluoride removal process training, preferably at an existing treatment plant. The operator must be able to service pumps, piping systems, instrumentation, and electrical accessories. The operator must be totally informed about the characteristics of sulfuric acid (in all concentrations) and sodium hydroxide (in all concentrations). Safety requirements including clothing, equipment, antidotes, etc., must be thoroughly understood and executed. The operator must be trained to run routine water analyses including at least two methods for determining fluoride levels. The operator needs simple mathematics for use in record keeping during a treatment run and operation cost accounting. The operator above all, must be dependable and conscientious.

COST OF OPERATION

The cost of operation including chemicals, electricity, bed replacement, replacement parts, and labor currently falls in the range of 8-20¢/thousand gallons of treated water. Individual plant operational cost will vary due to the difference of

fluoride level, plant capacity, treated water consumption, electric utility rate, labor rate, delivered chemical costs, etc.

An example of the low operating costs that may be realized with an activated alumina system is the Gila Bend plant estimate of 15¢/1000 gal of treated water. Based upon the Rincon Water Company and Lake Tamarisk plant years of experience and 1977 data from the Gila Bend pilot plant studies, projected operating costs for the Gila Bend plant are:

1) Chemicals (66° B' H ₂ SO ₄ @ 20¢/gal and 50% NaOH @ 68¢/gal)	- 6¢
2) Electric Utility @ 4¢/kwh	- 1¢
3) Treatment Media Replacement (3%/year @ 30¢/lb)	- 1¢
4) Replacement Parts	- 1¢
5) Miscellaneous Supplies and Services	- 1¢
6) Operator (full time @ \$10,000/year)	- 5¢
TOTAL	15¢/1000 gal

*10 d / 1000 gal x 100 = 10.00/d
370 50 / 4 x
+ Media Replacement
+ Operator*

The 1977-78 materials and construction cost for the plant capable of treating Gila Bend water at the rate of 750,000 gal/day is less than \$200,000.

CONCLUSION

Low operating costs for removal of fluoride from potable water are achieved with the F-1 activated alumina system. Reliability of plant equipment, materials and operational costs have been documented through eight years of commercial field experience. Installation and operating costs are compatible with limited public budgets and funding program. All materials

and equipment are available in today's market and there is existing technology to assist any community in designing a plant to meet their water requirements.

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