MEMORANDUM REPORT

AGRICULTURAL DRAINAGE TREATMENT TECHNOLOGY REVIEW

Prepared
Under Contract for

San Joaquin Valley Drainage Program

JULY 1990

DISCLAIMER

This report presents a review of agricultural drainage research performed for the Federal-State Interagency San Joaquin Valley Drainage Program. The purpose of the report is to provide the Drainage Program agencies with information for consideration in developing alternatives for agricultural drainage water management. Publication of any finding or recommendations in this report should not be construed as representing the concurrence of the Program agencies. Also, mention of trade names or commercial products does not constitute agency endorsement or recommendation.

The San Joaquin Valley Drainage Program was established in mid-1984 as a cooperative effort of the U.S. Bureau of Reclamation, U.S. Fish and Wildlife Service, U.S. Geological Survey, California Department of Fish and Game, and California Department of Water Resources. The purposes of the Program are to investigate the problems associated with the drainage of irrigated agricultural lands in the San Joaquin Valley and to formulate, evaluate, and recommend alternatives for the immediate and long-term management of those problems. Consistent with these purposes, Program objectives address the following key areas: (1) public health, (2) surface-and ground-water resources, (3) agricultural productivity, and (4) fish and wildlife resources.

Inquiries concerning the San Joaquin Valley Drainage Program may be directed to:

San Joaquin Valley Drainage Program
2800 Cottage Way, Room W-2143
Sacramento, California 95825-1898

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By
George P. Hanna, Jr., Ph.D., P.E.
Jo Anne Kipps
Lawrence P. Owens, P.E.
7389 N. Bond Ave.
Fresno, CA 93710

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AGRICULTURAL DRAINAGE TREATMENT TECHNOLOGY REVIEW

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LIST OF ABBREVIATIONS

AAS	Atomic absorption spectrophotometry
ABSRS	Algal-bacterial selenium removal system
af	acre-feet
af/yr	acre-feet per year
DAF	Dissolved air flotation
DMSe	Dimethyl selenide
DWR	Department of Water Resources
ft^2	Square feet
ft^3	Cubic feet
ft/yr	Feet per year
g/m^3	Grams per cubic meter
$g/d\text{-}m^3$	Grams per day per cubic meter
GC	Gas chromatography
gpd	Gallons per day
gpm	Gallons per minute
HRP	High-rate ponds
ICP	Inductively coupled plasma
IX	Ion exchange
$kg/d\text{-}m^3$	Kilograms per day per cubic meter
kW/af	Kilowatts per acre foot
kWhr	Kilowatt hour
L/hr	Liters per hour
lb	Pound
LBDDF	Los Banos Demonstration Desalting Facility
LBL	Lawrence -Berkeley Laboratory

m^2	Square meters
m^3	Cubic meters
m/h	Meters per hour
mg/kg	Milligrams per kilogram
mg/L	Milligrams per liter
ml/min	milliliters per minute
mmol/L	Milli-moles per liter
MSGP	Methane specific gas production
mV	Milli-volt
NTU	Nephelometric turbidity units
O & M	Operation and maintenance
ppm	Parts per million
psi	Pounds per square inch
PVC	Polyvinyl chloride
RO	Reverse osmosis
SDI	Sludge density index
SJVDP	San Joaquin Valley Drainage Project
TDS	Total dissolved solids
TFC	Thin-film composite
UC	University of California
UCB	University of California, Berkeley
ug/L	Micro-grams per liter
uS/cm	Micro siemens per centimeter
USBR	U.S. Bureau of Reclamation
VSS	Volatile suspended solids

EXECUTIVE SUMMARY

Inadequate subsurface drainage coupled with increasing salt accumulations on the west side of the San Joaquin Valley threaten the productivity of over one million acres of irrigated farmland. In 1983, it was discovered that concentrations of selenium, a trace element found naturally in westside soils, was being leached out in drainwater conveyed to the Kesterson Wildlife Refuge, and was accumulating there in sufficient concentrations to pose a toxic threat to portions of the wildlife population.

Following this disclosure, and the subsequent plugging of the drains to the Kesterson area, a stepped-up research effort was instituted to manage the selenium problem, attacking it from many directions, including the treatment facet. Research efforts were directed at selenium removal from both agricultural drainage and selenium-laden soils, in which evaporation coupled with biologic conversion contribute to elevated selenium levels. Both biological and physicochemical removal systems were explored. Several contracts were let by the San Joaquin Valley Drainage Program (SJVDP) along with others to research the subject with the objectives of applying state-of-the-art water and soil treatment technologies, or developing new technologies to solve the problem.

This report is a review of the major treatment research efforts undertaken. It addresses to the extent possible both the technical and economic feasibility of each process, and attempts to evaluate research efforts and findings with regard

to process feasibility, short-range and long-range applicability, and relative costs.

Research in treatment technology has emphasized the removal of selenium, primarily because it is reported to be the major cause of the biological damages at Kesterson Reservoir and at several evaporation ponds in the valley. The current status of selenium removal treatment technology reflects research conducted in various progressive stages: bench-scale, field pilot plant, and prototype plant. The Los Banos Demonstration Desalting Facility operated by DWR is the single attempt at testing a treatment technology in a prototype plant.

The biological drainage treatment schemes generally utilize anaerobic/anoxic processes and result in the reduction of soluble selenate to selenite and elemental selenium, which are then removed by proven solids separation technologies. All of the biological processes require amendments of carbon and nutrients to support the biological activity. In one anaerobic research effort carried to pilot plant level by EPOC AG, methanol was utilized as the carbon source; while in an algal-bacterial pilot plant operated by UC Berkeley researchers, algae were grown and harvested to provide the carbon source for the subsequent anaerobic bacterial selenium reduction step. In another study, the kinetics of facultative-bacterial selenate reduction were investigated using bench-scale batch reactors in which selenium removal was demonstrated to be influenced by nutrients, oxygen supply, and temperature. Oxygen stimulated the bacterial growth,

but selenium reduction was most effective at low oxygen concentrations. In another variation of the selenium reduction process, a submerged soil column experiment developed an anoxic biomass on the soil surface which removed both nitrate and selenate as water moved through the column. The projected scale-up of this system would involve growing and harvesting pond biomass to provide the carbon feed, similar to the algal-bacterial process use of algae for carbon feed.

In most of the biological studies, nitrate was identified as an inhibitor to selenate reduction, and a denitrification step would be included in most biological treatment scheme. A major cost item in biological processes is the carbon required, especially for biological denitrification. While methanol may be relatively expensive, the use of alternative "free" carbon sources such as sugarbeet waste may be more costly in the long-run due to the variable carbon content of the feed.

Substantial selenium removals have been achieved with the biological reduction processes, and further exploration involving process design to improve the system efficiency appears to be warranted. In a more recent anaerobic/anoxic reduction study, a sequential batch reactor system was studied at bench-scale, and field studies are now proposed.

A research program to remove selenium from soils by a microbial volatilization process has been developed in the laboratory and field tested on Kesterson area pond sediments, and

on San Luis Drain sediments. The process requires application of soil amendments for the carbon source, and a number of these consisting mostly of natural waste products were tested. Results showed a decrease in the soil selenium inventory of from about 17 to 25 percent in a ten-month testing period. Calculated half-life values, representing the time required to convert half of the residual soil selenium into dimethylselenide (DMSe), range from 2.48 to 12.55 years, with a large number of the soil amendments producing half-life values at the lower end of the scale. The relatively long time required to reach selenium target levels may be considered disadvantageous; however, the process volatilizes selenium from the system leaving no high-selenium sludges requiring costly disposal.

Another application of this process to evaporation pond sediments is currently being supported by the State Water Resources Control Board. Process application to soil sediments containing high concentrations of selenium appears meritorious; evaporation ponds with soil selenium concentrations approaching allowable limits can be recycled for continued use.

Microbial volatilization was also found to occur from pond waters. Field experiments with water columns containing a casein amendment volatilized up to 28 times the selenium evolved from unamended control columns. However, practical application of this technique is questionable because the required amendment addition would undoubtedly result in pond eutrophication.

The physicochemical processes investigated for selenium removal include attenuation in irrigated soils; adsorption of selenium on iron filings; chemical reduction of selenium (the ferrous hydroxide/selenate reaction); ion exchange; and reverse osmosis. Selenium attenuation in irrigated soils was explored using test columns with simulated agricultural drainwater containing various amendments. Carbon amendments facilitated the transformation of selenate to "organically associated selenium species", suggesting a biological mechanism in the process. The research did not address selenium attenuation under field conditions using actual drainwater.

A patented heavy metal removal process using iron filings is being researched for application in irrigation drainage treatment. Heavy metals and selenium are removed from solution, purportedly by their adsorption on activated iron filing surfaces. The process mechanism(s) are not defined. Further, bed solidification adversely affects permeability and adsorption rates. Currently, the project is being field-tested at the Panoche Drainage District where work is continuing to address the factors related to assessing process feasibility.

Selenium removal by chemical reduction with ferrous hydroxide was researched in the USBR Denver laboratory, and briefly field tested in the Valley. Selenium removal rates for the field test were slower than expected; attributed to inhibiting substances in the drainwater. The inhibitors, mainly oxygen and nitrate, must also be reduced, thus affecting the

technical feasibility and cost effectiveness of the process.

Ion exchange research involved resin identification with preferential selectivity for selenate over sulfate based on relative ion size. Further resin formulation and development will be necessary for ion exchange to be a competitive selenium treatment process.

Reverse osmosis was field tested for selenium removal, and removals of over 97 percent were reported. Drainwater pretreatment is necessary to remove membrane fouling substances. The process is very expensive, but it does generate a water low in TDS. The boron content, however, may remain relatively high. The market value of the treated water for agricultural use will depend on the amount of boron left in solution. If the RO process removes some 50 percent of the boron, the remaining level of some 7-8 ppm or greater would still reduce significantly the resale value of the treated water.

Inhibitory impacts of various drainage constituents can affect the design of treatment processes. Several inhibiting substances to the various processes have been identified. In the biological processes, optimal selenium reduction is associated with conditions of low nitrate and dissolved oxygen. Bicarbonates were also identified as a problem in chemical reduction with ferrous hydroxide. In ion exchange technology, sulfate competes with selenate for available resin sites.

Waste disposal is a major component of treatment strategies. It is necessary to identify the composition of treatment

wastestreams and to quantify the volumes produced by various treatment processes. This is especially important if the wastestream is deemed hazardous, since hazardous waste treatment and disposal constitutes a difficult and expensive problem that must be addressed more thoroughly.

Salt recovery was investigated in the EPOC AG study; but insufficient data were reported to substantiate their claim of recovering salts of marketable high purity. Salt recovery may possibly be a viable option, but additional work is required to develop effective salt recovery methods. The market value and demand for recovered salts also require further evaluation.

The feasibility of discharging treated drainage is largely governed by geographic location. In the San Joaquin River Basin, treated effluent may be discharged to the San Joaquin River provided that water quality objectives for the river are not exceeded. Under adequate freshwater flows, the assimilating capacity of the river may result in realistically attainable treatment goals. However, in the Tulare Lake Basin, drainage is of necessity discharged to evaporation ponds. If such ponds are to provide safe wildlife habitat, then the treated drainage discharge must not contain more than 3 ppb selenium, according to new standards contemplated by the California Department of Fish and Game and the U. S. Fish and Wildlife Service. None of the selenium removal technologies tested under field conditions have been consistently capable of producing effluents with less than 10 ppb selenium.

In the future, large reductions in drainage volume may be expected as irrigation management practices improve water use efficiency. Further substantial reductions may occur through agroforestry programs. The resulting drainage volume reductions will concomitantly result in lower overall treatment costs.

Capital costs and operating and maintenance costs were estimated in a few of the project reports. Wastestream treatment and disposal costs were estimated only in the reverse osmosis feasibility study by CH2M Hill. Other shortcomings of the reports providing cost information were the selection of different cost parameters (i.e., interest rate and design period) and insufficient information to provide a common basis of cost calculation for comparisons. There is a need for developing a set of uniform cost parameters to be applied in future treatment cost analyses. In addition to estimating drainage treatment costs in a uniform manner, there is a need to conduct economic analyses of how drainage treatment costs compare to the costs of other management strategies, and in particular, what constitutes afforadable drainage treatment.

Recommendations are presented for specific project research, wastestream characterizations, integrated treatment, expansion of research scope to other substances of concern, quality control, and economic analysis. It is recommended that an "Expert Syste " approach be developed to assist in decision making regarding the application of specific treatment processes or combinations of processes to meet specific conditions.

Selenium is presently the primary contaminant of concern. However, future research will, in all probability, consider drainage issues other than selenium removal. In particular, the problem of salt accumulation must be considered. Improved irrigation management will reduce salt import into the valley, but will not achieve a salt balance. Currently the scope of salt-management options has been limited by policy decision to consider only in-valley solutions to the drainage problem. However, the continuing salt accumulation in the valley will have to be addressed, ostensibly as a mass-balance problem based on establishing acceptable salt tolerance levels compatible with land use objectives. For example, if agricultural productivity is to be sustained, an economically and politically feasible salt export system will have be developed to remove excess salt from westside soils.

INTRODUCTION

The agricultural productivity of over a million acres of irrigated farmland in the western San Joaquin Valley is threatened by poor drainage and concomitant salt accumulation. One immediate remedy is to drain the saturated root zone through subsurface perforated pipe networks. The irrigation leachate collected by these "tile drains" is generally saline, and sometimes contains high concentrations of toxic and potentially toxic elements.

The contamination of subsurface drainage water by trace elements renders it unsafe for discharge to receiving waters. Consequently, a considerable amount of research has been initiated to develop new treatment technologies to improve the quality of drainage water as one component in the management of the drainage problem.

Research on treatment technology has emphasized the removal of selenium, primarily because it is reported to be the major cause for the biological damages at Kesterson Reservoir and at several evaporation ponds in the valley. Also, it is the one substance of concern that does not have an already established treatment process for removal.

To coordinate drainage-related research efforts, the San Joaquin Valley Drainage Program (SJVDP) was established in mid-1984 as a cooperative Federal-State program. Its primary function is to integrate the drainage-related activities of the

following agencies: California State Department of Water Resources (DWR), California Department of Fish and Game, U.S. Bureau of Reclamation (USBR), U.S. Fish and Wildlife Service, and U.S. Geological Survey. The main purpose of the SJVDP is to identify measures to help solve immediate drainage-related problems on the westside of the San Joaquin Valley and to develop a comprehensive plan for their long-term management.

Drainage treatment research has focused on selenium removal using biological and/or chemical processes. This report reviews the major findings and conclusions to date regarding the engineering aspects of treatment technologies developed as a result of research sponsored by SJVDP, DWR, USBR, U. S. Bureau of Mines, Westlands Water District, and Panoche Drainage District. Comprehensive reports on drainage management include one on irrigation drainage treatment, disposal, and reuse (SJVDP 1988), and another which proposes preliminary planning alternatives for solving the westside's drainage problem (SJVDP 1989).

The scope of work for this review of treatment technologies included the following objectives:

(1) Review work accomplished and the state of development relative to the purpose for each treatment method investigated;

(2) Assess what work remains to be done for each treatment method to be considered available for implementation.

(3) Compare alternative treatment methods, projected to prototype scale, considering accomplishment, cost,

waste disposal, potential environmental impacts, and level of confidence.

The last objective required adjusting pertinent cost data (if provided) such that key cost determining variables were equal. Common variables selected were: design period of 20 years, interest rate of 9-3/8 percent, and average labor cost of $40,000/person-yr, including overtime and benefits.

TREATMENT TECHNOLOGIES

Selenium removal mechanisms are classified either as biological or chemical. A common theme in many systems is the reduction of selenate to less soluble forms which are then removed by proven solids separation technologies. Examples of biological selenate reduction include the Binnie or Biosel Process, the University of California Algal-Bacterial Selenium Removal System (UC ABSRS), and the sequencing batch reactor developed by UC Davis researchers. Reduction of selenate by chemical means (ferrous hydroxide) is the focus of one USBR research team.

A different approach taken by UC Riverside researchers consists of the removal of selenium from soil either by microbial volatilization or selenium attenuation. Another method involves adapting a patented heavy metal removal process using iron filings (the Harza Process) to irrigation drainage treatment. Other treatment technologies include reverse osmosis and ion exchange.

The current status of selenium removal treatment technology reflects research conducted in various progressive stages: bench-scale, field pilot plant, and prototype plant. The Los Banos Demonstration Desalting Facility operated by DWR is the single attempt at testing a treatment technology in a prototype plant.

WATER QUALITY ASPECTS

Treatment technologies for selenium removal from subsurface drainage must operate within a chemically complex matrix dominated by common salt constituents. Another obstacle is the daily and seasonal changes in drainage quality reflecting individual farm managerial practices. Enlarging the drainage catchment area is expected to dampen the daily fluctuations in drainage quality. However, irrigation leachate from large regions will still exhibit significant seasonal quality variation.

Table 1-1 presents a summary of water quality constituents in the San Luis Drain recorded from 1981 to 1984 by DWR and USBR reproduced from Groves (1989). During this period, the ranges reported for drain water temperature and pH were 18°C to 29°C and 8.2 to 8.7, respectively. Because the water percolates through several feet of soil prior to its collection in perforated pipe, it is low in suspended solids as it enters the drain. Predominant saline constituents listed in descending concentration are: sulfate, sodium, chloride, and calcium.

A variety of toxic or potentially toxic elements is present in concentrations several orders of magnitude lower than the

TABLE 1-1: WATER QUALITY SUMMARY--SAN LUIS DRAIN AT MENDOTA FROM 1981 TO 1984 [DATA FROM DWR AND USBR].

Parameter	Minimum (mg/L)	Maximum (mg/L)
Sodium	2190	2700
Potassium	7	10
Calcium	555	710
Magnesium	270	300
Alkalinity	195	218
Sulfate	4650	5600
Chloride	1550	2000
Nitrate	48	60
Silicate	37	42
TDS	9850	11600
Suspended Solids	10	20
TOC	9.5	16
COD	30	52
BOD	3	5.8
Boron	15	19
Selenium	0.23	0.35
Strontium	6.4	7.2
Iron	0.15	0.5
Cadmium	0.001	0.02
Chromium	0.02	0.036
Copper	0.01	0.03
Lead	0.001	0.006
Manganese	0.01	0.02
Mercury	0.0001	0.0002
Nickel	0.02	0.06
Silver	0.001	0.001
Zinc	0.01	0.02

major saline constituents. Of these, three which pose the greatest threat to overall drain water quality are selenium, boron, and molybdenum. Other substances of concern are chromium, mercury, manganese, nickel and zinc (SWRCB 1987). High levels of

arsenic have been observed in agricultural drainage, particularly in the south valley (DWR 1989), an area in which there appears to be an emerging concern with elevated uranium levels in subsurface water. Because this report focuses on selenium removal technologies, only selenium chemistry will be reviewed.

SELENIUM

The following discussion on the chemistry of selenium is abstracted from an article by McKeown and Marinas (1986). Selenium occurs in four oxidation states (+6, +4, 0, -2). In the subsurface drainage water of the western San Joaquin valley, selenium predominately occurs as highly soluble selenate (+6). Concentrations of selenate found in drainage water on the westside vary from less than 100 to over 1000 ug/L (DWR 1989).

The natural cycle of selenium involves the uptake of selenium by microorganisms and plants and the subsequent transformation into various inorganic and/or organic compounds. One example of microbial selenium conversion is the substitution of selenate for sulfate as a terminal electron acceptor for obligate anaerobic sulfate-reducing bacteria. The end product, hydrogen selenide, is about 100 times more toxic than hydrogen sulfide, but is very reactive and will covert quickly to a more oxidized form.

Because the chemistry of selenium is similar to that of sulfur, selenium can substitute for sulfur in numerous organic molecules. Microorganisms employ enzymes which normally catalyze sulfur reactions to process analogous selenium compounds. In

general, microbial toxicity occurs because such selenium analogs to molecules containing sulfur produced in the cell are less stable than their sulfur counterparts. Their subsequent inevitable breakdown causes malfunctions of cellular physiology.

Many common bacteria are capable of reducing selenate and selenite to methylated selenium species or elemental selenium. This process constitutes a metabolic detoxification of selenium and provides a pathway for the return of selenium from the microbial cell to the environment. Completing the microbial selenium cycle is the oxidation by heterotrophic bacteria of elemental selenium to selenite.

METHODS OF SELENIUM DETERMINATION

An overview of selenium detection methodologies is presented by Gump (1986). Among the methods employed by those engaged in selenium removal research are: ion chromatography, fluorometry, graphite furnace atomic absorption spectrometry (AAS), gas chromatography and inductively coupled argon plasma emission spectrometry. The method of choice for many researchers, however, is AAS of gaseous selenium hydride. This method is currently used to determine various species of organic and inorganic selenium at the part per trillion level (Gump 1986).

In many of these methods, the active species for analysis is selenite. Selenate is determined by running duplicate samples, one of which is subjected to a selenate to selenite reduction step in the analytical procedure. Determination of total

selenium is obtained by oxidizing selenium to its highest oxidation state, then reducing this to selenite for measurement.

For many treatment schemes, understanding the mechanism(s) responsible for selenium removal requires that the various forms of selenium be monitored throughout the treatment process. Speciation determination is a function of sample preparation. While the analysis for selenate/selenite speciation is relatively straightforward, the determination of organic species and elemental selenium is not. Many researchers have assumed that the difference between total selenium and selenium as selenate or selenite is exclusively indicative of the presence of organic selenium compounds. However, the oxidizing step in the sample preparation will transform all forms of selenium to selenate. The determination of organic selenium species requires additional sample preparation.

Frequently, a distinction is made between soluble and total selenium. While the latter is simply a measurement of selenium in an unfiltered sample, the former is obtained by passing the sample through a filter of specified porosity, and measuring the selenium in the filtrate. Instrumental conditions often require that samples be devoid of particulate matter, thus filtration may be a necessary pretreatment step. Removal efficiencies of treatment technologies which rely on selenium determinations of **filtered** effluent samples do not reflect actual efficiencies. For this reason, it is important to note whether the sample is subjected to filtration to assess the performance of the process

under investigation.

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REMOVAL OF SELENIUM FROM SUBSURFACE AGRICULTURAL DRAINAGE BY AN ANAEROBIC BACTERIAL PROCESS (THE BINNIE PROCESS)

In January 1985, the engineering firm EPOC Agricultural Corporation (EPOC AG) began researching methods for removing selenium from agricultural drainage water. After several months of preliminary laboratory analyses, EPOC AG began operating a pilot treatment plant south of Mendota. Results of laboratory and field studies are contained in a report and supporting documentation submitted to the California State Department of Water Resources (DWR) (EPOC AG 1987; Binnie 1988).

EPOC AG was established by the London-based firm, Binnie & Partners, Incorporated, to research the application of crossflow microfiltration in agricultural drainage treatment. Their patented process to remove selenium from water (Downing et al. 1988), developed partly as a result of research sponsored by DWR and Westlands Water District, is commonly known as the "Binnie Process" or more recently, the "Biosel Process" (Groves 1989).

EARLY DEVELOPMENT OF THE BINNIE PROCESS

Because the predominant form of soluble selenium in subsurface drainage water is selenate, initial laboratory research explored a variety of methods to reduce selenate to less soluble species which could be removed by solids separation techniques. Early analyses conducted in London utilized both actual and simulated subsurface agricultural drainage water and included the following physical/chemical tests: electrolysis, direct coagulation, adsorption, ion-exchange, pure chemical

tests, and inhibitors.

The electrolysis was sensitive to drainage quality and pH. Direct coagulation with iron salts required substantial pH adjustments and chemical dosages to achieve good selenium removal. Adsorption test trials using packed beds of iron filings revealed that nitrate was a potential inhibitor to selenium reduction. Ion-exchange removed up to 60% of the selenate, but the regeneration frequency was very high. The pure chemical reduction tests proved to be impractical at the scale required for agricultural drainage water treatment. The tests focusing on isolating compounds or elements which inhibit selenate removal by coagulation revealed that nitrate, and to a lesser degree, hardness, had significant inhibiting effects.

One significant conclusion of these physical/chemical tests was that denitrification was a necessary pretreatment step for optimizing selenate reduction and removal.

Subsequent laboratory research focused on biological methods of selenate reduction. Denitrified subsurface agricultural drainage water contacted with anaerobic digester sludge resulted in the reduction of selenate. To investigate this phenomenon, two biological reactor types were tested: sludge bed and fixed film. The inhibiting effect of nitrate was also demonstrated for bacterial reduction of selenate. Anoxic/anaerobic environmental conditions similar to those required for denitrification also favored selenate reduction.

The kinetics of bacterial selenate reduction were studied in continuously-stirred batch reactor experiments. The removal of reduced insoluble selenium particles from biological reactor effluent was investigated in laboratory test runs using ion exchange and a proprietary crossflow microfilter.

FIELD TESTING OF THE BINNIE PROCESS

The process chain judged to be the most successful on the basis of laboratory research consisted of fixed-film reactors operating in series for denitrification and selenate reduction, followed by crossflow microfiltration and ion exchange. This treatment train was field tested at a pilot plant (3-10 gpm) located on Murrieta Farms south of Mendota. The field testing of the Binnie Process occurred in 1985 from July to September. The feedwater was typical of westside subsurface drainage water (see Table 1-1) with the exception of higher than average nitrate, selenium, and chromium levels (100 mg/L as N, 360 ug/L, and 60 ug/L, respectively) and lower than average sulfate levels (3250 mg/L). Daily determinations of influent nitrate and selenium concentrations reflected substantial variability in the "quality" of subsurface drainage water at the pilot plant site.

A flow diagram of the pilot plant is presented in Figure 2-1. At the beginning of the process train, subsurface agricultural drainage water is dosed with methanol prior to entering the bottom of the first fixed-film, rock-filled reactor for biological denitrification and some selenate reduction.

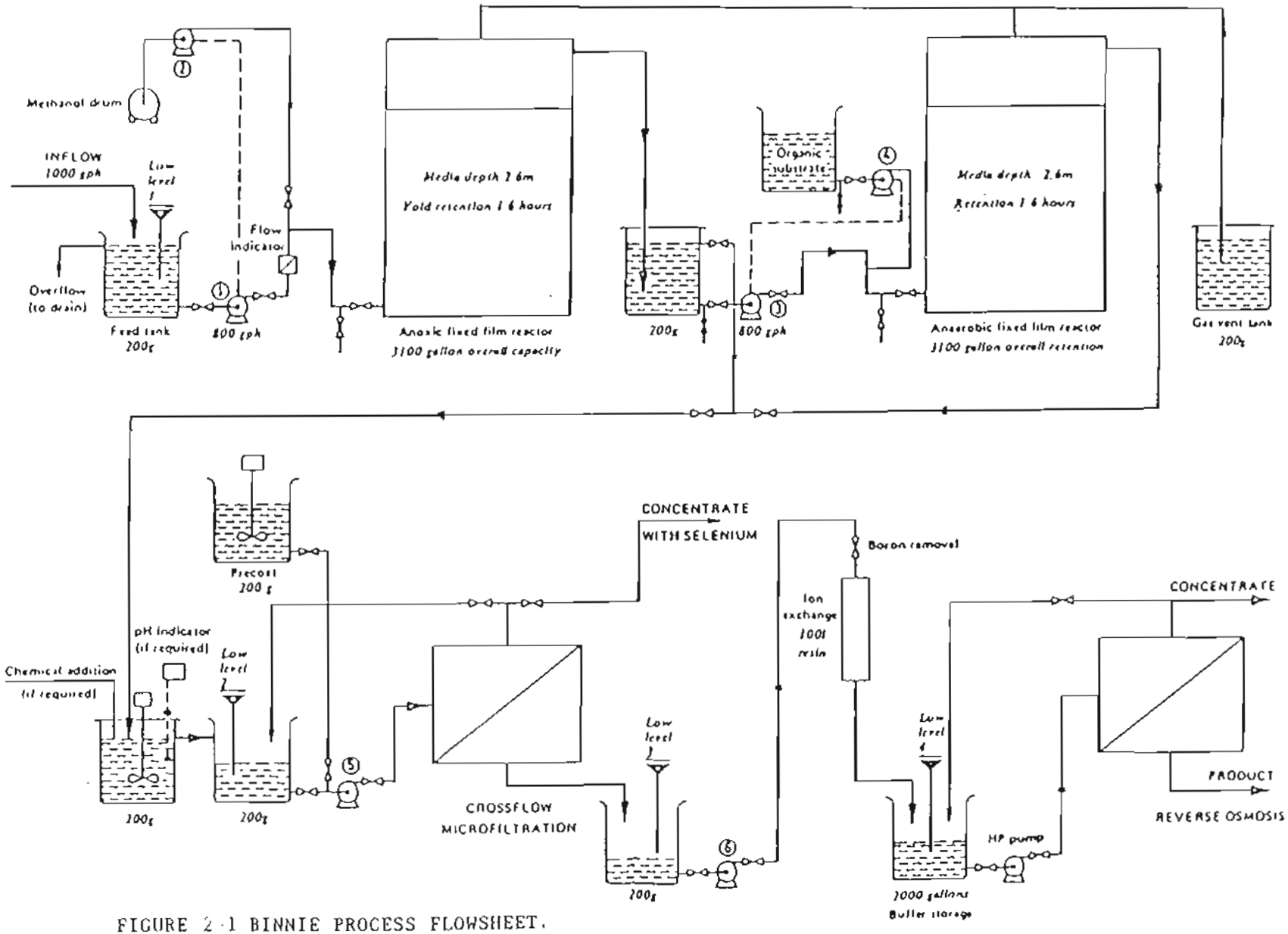

FIGURE 2-1 BINNIE PROCESS FLOWSHEET.

From EPOC AG (1987:22).

After denitrification, the flow is pumped to the second fixed-film reactor for additional selenate reduction. The pilot plant's microbial phase lowered selenium levels to 100 to 150 ug/L from feedwater concentrations of 300 to 550 ug/L. Nitrates were reduced from over 100 mg/L to below 5 mg/L, as N.

The effluent from the second reactor is coagulated, flocculated, then clarified through the crossflow microfilter, a pressure filter which operates at 30 to 45 psi and consists of a fabric tube internally precoated with a metal hydroxide. The membrane filter reportedly removes colloidal solids (0.10 micron), and generates a product water with selenium concentrations of 12 to 40 ug/L. The microfilter permeate enters an ion exchange unit for boron removal. This final "polishing" step reduced selenium levels to below 5 ug/L.

OPTIMIZING THE BINNIE PROCESS

At the end of the three-month field test period, the pilot plant demonstrated that the Binnie Process could reduce selenium concentrations to residual levels. The second phase, lasting from October 1985 to May 1986, focused on optimizing removal efficiencies and cost reduction research. For the fixed-film biological reactors, this involved varying operating parameters such as flowrate, recycle ratio, redox potential and selenium loading. Experimentation with the crossflow microfilter consisted of testing alternative membranes, varying flow rates and pressures, and determining the optimum production flux. Operation of the ion exchange polishing step focused on

establishing removal rates and regeneration intervals.

Various packing media were tested in fixed-film reactors, partly with the aim of increasing bed porosity. Notable among these was one packed with iron filings which was positioned to receive the effluent from the second fixed-film reactor. The effluent leaving this reactor was reportedly "excellent" during the first six months, after which its selenium removal performance fell rapidly until it was negligible. In addition, other biological reactor types were tested, primarily fluidized bed and sludge blanket reactors. Furthermore, the Binnie Process was tested for its applicability in reducing high selenium levels in brine generated from reverse osmosis treatment of agricultural drain water.

Two carbon sources were tested: methanol and Steffens waste, a by-product of sugarbeet processing. During most of the field operation, only methanol was used. Carbon dosages were calculated and expressed as mg/L carbon. Initial dosages ranged from 400 to over 450 mg/L, then dropped to a steady 225 mg/L during the fall of 1985. During the winter and into the next year, the carbon dose fluctuated significantly from a high of around 275 mg/L to zero during periods of equipment failure.

The price of methanol constitutes the major cost item in the Binnie Process. If the carbon source could be obtained for free, (e.g., Steffens waste from a nearby sugarbeet processing facility), then overall treatment costs would drop substantially.

The feasibility of using this free supply was tested when Steffens waste supplemented, then supplanted methanol in the biological reactors. However, while the carbon content in methanol is constant, it is highly variable in Steffens waste due to the process from which it is generated. The waste also contains fluctuating quantities of potentially inhibiting substances, plus innocuous ingredients such as carbonates which increase sludge production.

The basic test configuration (two upflow rock-filled fixed-film biological reactors) was in operation for nearly two years. Detention time averaged 1.5 - 2.5 hours each; optimum hydraulic loading rate per cubic meter of reactor volume was 250 L/hr for both nitrate and selenium removal. Under optimum conditions, nitrate removals were 700 g/d-m^3 in the first stage, and 180 g/d-m^3 in the second. Similarly, the selenium removal rate was 0.8 g/d-m^3 in the first reactor and 0.41 g/d-m^3 in the second.

Calcium carbonate scaling fouled the fixed-film reactors and reduced the bed's porosity. The time interval between cleaning depended on the carbon source used: three months for Steffens waste, six months for methanol. Effective removal of the carbonate scale required an acid wash of the rock-filled bed, followed by extensive flushing (24 hours) and reseeding with active biomass. Due to the cleaning procedure required, and the large volume of cleaning effluent generated, it was concluded that fixed-film reactors would not be a practical design for

full-scale facilities.

Experimentation with other test trains and reactor designs began with the addition of up to four fluidized sand bed reactors operated in series and dosed with both methanol and concentrated Steffens waste. The rates for nitrate and selenium removal in the first bed receiving raw drainage water were 2.8 kg/d-m^3 and 3.6 g/d-m^3, respectively. The second bed removed an additional 2.4 kg nitrate/d-m^3 and 4 g Se/d-m^3. Further selenium reduction was reportedly not evident beyond two reactors in series.

As in the fixed-film reactors, calcium carbonate scaling occurred in the fluidized bed column reactors, especially in the first one receiving the raw drainage water. Scaling caused the sand grains to grow from an initial 0.5 mm to between 5 and 8 mm, too large for the grains to fluidize.

To investigate selenate removal rates in concentrated drain water, reverse osmosis brine was processed through the fluidized bed reactors. The drain water was clarified by crossflow microfiltration prior to desalting. The electrical conductivity of the brine measured 65,300 uS/cm. The first reactor denitrified at a rate of 5.8 kg/d-m^3 and removed 29.7 g Se/d-m^3. Far lower removal rates for both contaminants were observed in subsequent reactors.

The problems caused by calcium carbonate scaling in fixed-film and fluidized bed reactors led to the testing of a sludge-blanket reactor. Previous laboratory studies indicated successful selenium and nitrate removals with this reactor type.

In addition, the precipitation of carbonates within the sludge blanket would increase its density, thereby increasing the reactor's upflow velocity capacity.

The rates recorded for the sludge blanket reactor for nitrate and selenium removal were found to be six and ten times greater, respectively, than those observed for the fixed-film reactors. The daily removal rates ranged from 2.3 to 4.0 kg/m^3 for nitrate and 3.5 to 8 g/m^3 for selenium. The optimum upflow velocity was determined to be 3 m/h. The use of Steffens waste as the carbon source increased the inorganic fraction of the sludge to almost 70%. Although no value was reported for the inorganic percentage using methanol, this increase was interpreted to be detrimental to biomass growth.

After the drain water was denitrified and partially softened in the sludge blanket reactor, it was fed to a fluidized bed for additional selenium removal. Depending on what carbon source was used, the average selenium removal rate from this second reactor was 4 $g/d\text{-}m^3$ (Steffens waste) and 7 $g/d\text{-}m^3$ (methanol). These rates combined with those observed in the sludge blanket reactor amount to a maximum selenium removal of 15 $g/d\text{-}m^3$ for these two reactors.

THE MECHANISM BEHIND THE BINNIE PROCESS

Laboratory experiments preceding the field testing of the Binnie Process attempted to reveal the mechanism by which selenium is transformed from selenate to insoluble/particulate

forms removable by crossflow microfiltration. Because the mechanism involves changes in selenium speciation, its detection relies on the method of selenium determination used.

Analysis by atomic absorption spectroscopy (AAS) utilizes different sample digestion techniques to identify the species present. Selenate must be reduced to selenite before hydride generation. Elemental selenium and organic selenium compounds must first be oxidized to selenate, then reduced to selenite for their detection.

It had been recognized early on in these laboratory experiments that measurements of total selenium concentration in "after" samples (i.e., effluent, supernatent after a contact period) did not equal that in the "before" samples (i.e. actual and simulated drainage water). The discrepancy was initially interpreted to signify the presence of compounds comprising an "organic selenium complex" (OSC). It was theorized that under anaerobic conditions, selenate converts to soluble OSC which is assimilated, thus captured, by microorganisms. Selenium accumulation in the biomass and its effect on removal rates studied in bench-scale continuously-stirred reactors revealed that the removal rate drops dramatically as the biomass selenium concentration increases. The maximum concentration was estimated to be 400 mg Se/kg sludge measured on a dry weight basis.

An analysis of sludge from the pilot plant reactors indicated that the majority of the selenium present was in its elemental state. This suggests that attributing all selenium

present in oxidation states lower than selenite to OSC was an inadequate explanation of the mechanism behind the Binnie Process. In any event, the process does demonstrate the transformation of selenate to reduced forms which do seem to be assimilated into microbial or inorganic colloidal particles.

It appears to be necessary to waste biological reactor sludge when accumulated selenium approaches a certain threshold level. The factors affecting the rate at which elemental selenium accumulates in the reactor biomass is a parameter requiring additional study. Another aspect worth investigating is the feasibility of treating the sludge to remove elemental selenium and other accumulated heavy metals, thereby reducing its toxicity and allowing the treated bio-sludge to be disposed of as a non-hazardous waste.

EVALUATING PILOT PLANT PERFORMANCE--A CRITIQUE

The research team involved in developing and testing the Binnie Process explored a wide variety of methods to remove selenium from subsurface drain water. Several reactor types and configurations were tested to derive one efficient treatment train: sludge blanket to fluidized bed to crossflow microfiltration. The final polishing with ion exchange for boron removal proved to be a relatively expensive process due to the resin cost and its periodic replacement. Plus, the acid used to regenerate the resin bed would constitute a significant hazardous waste stream. However, trials which involved coating the crossflow microfilter with powdered resin capable of being regenerated by

sodium chloride (in laboratory tests) extended the time between regeneration and reportedly increased the resin's capacity significantly.

At the suggestion of Westlands Water District, a soil percolating column was tested as a final polishing step. Further reductions in effluent selenium levels, observed as the drain water passed through the soil column, are believed to be caused by a combination of biological and adsorptive mechanisms (Binnie California 1988).

Additional selenium removal of up to 15% was obtained by air stripping the biological reactor effluent to volatilize low molecular weight organic selenium species, dimethylselenide and dimethyldiselenide. Experimentation with ferric salts to assist in the coagulation of particulate selenium removed over 50% of the soluble selenium in reactor effluents. When used as a precoat for the crossflow microfilter, ferric salts reportedly removed up to 45% of the effluent's particulate selenium.

While the research team can be credited with arriving at one optimum process train configuration, valid interpretations of the data generated are complicated by the ever changing nature of the pilot plant's operation.

Under ideal conditions with constant influent quality, any change in process performance due to plant modifications would be readily discernible. However, the pilot plant operated under field conditions characterized by significant and oftentimes

violent changes in drainage quality, as well as diurnal and seasonal temperature variation. Assigning a particular performance result to a set of deliberate modifications in plant operation must first rule out the effects of a matrix of uncontrollable parameters.

One attempt to interpret plant performance made by EPOC AG involved a detailed comparison of the data generated by the fixed-film reactor operation during two periods: mid-October to mid-November 1985 and May 1986. Parameters compared include redox potential, nitrate levels, and concentrations of total, soluble, inorganic and organic selenium. In comparing the reactor performance, particular attention was given to the relative percentages of selenium species present in each reactor effluent.

The feedwater quality varied significantly during these two periods. Compared to May, fall nitrate levels were lower and selenium levels fluctuated more radically. Added to this natural variation were several major changes in reactor operation. During the fall period, the feedwater flow and carbon dosage were reduced by over 60% and 50%, respectively. In May, in addition to substantially fluctuating methanol dosages, the carbon source was switched to Steffens waste during the last week. The reactors were cleaned and reseeded in the second week of May, resulting in a lag time for the biomass to acclimate to resume nitrate and selenate reduction.

In the context of the variability inherent in the feedwater supply **plus** that caused by operational changes, interpretations of reactor performance based on data generated under such conditions are liable to be inaccurate and inappropriate.

BINNIE PROCESS SLUDGE AND WASTESTREAM PRODUCTION

The Binnie Process generates at least four distinct waste streams: two biological sludges, spent acid regenerant from ion exchange operations, and gaseous emissions from biological reactors. Of the two biological sludges, one consists of the necessary "wasting" of biomass to control selenium accumulation, the other is the reject stream of the crossflow microfilter. The former may have up to 400 mg/kg Se (dry weight), which is apparently the upper limit for optimum biological reactor performance.

The report and supporting documentation submitted to DWR contains sporadic references to the quantity of biomass produced in the various reactors. Most of the biomass is apparently generated in the first stage denitrification reactor. However, no information was provided on the amount of sludge which would be regularly wasted for optimum reactor performance, except that it would likely occur on a daily basis.

Because the Binnie Process focuses on selenium and boron removal, little data were reported on the elimination of other "substances of concern" from subsurface drainage. The potential of the process for heavy metal removal is indicated by the accumulation of some metals in biological sludge. Two samples of

sludge, one each from the second-stage fixed-film and fluidized bed reactors, were analyzed for 18 elements. Calcium was the most abundant element in both samples.

The fixed-film reactor had been in operation for over five months before the sludge sample was taken. In contrast, the media from the fluidized bed was sampled when the reactor went on-line; its analysis revealed little accumulation of heavy metals. Subsequent fluidized bed media samples were analyzed only for selenium concentration. Thus, the claimed potential for heavy metal removal by the Binnie Process is based on the analysis of only one sample, that from the fixed-film reactor.

The biomass sample from the fixed-film reactor receiving denitrified feedwater contained high concentrations of selenium (575 mg/kg) and molybdenum (125 mg/kg), measured on a dry weight basis. Almost 12% of the sample was calcium (by weight), while an additional 4% consisted of aluminum, magnesium, and iron. Elements of "probable concern" which accumulated in the sludge were, expressed as mg/kg: chromium (175), copper (60), manganese (295), nickel (42), and zinc (156). Although these substances comprise only a minute fraction of the dried biomass, they may be concentrated enough to classify the waste as hazardous. If the sludge (treated or untreated) is determined to be hazardous, then sludge drying beds will require fail-safe leachate collection and treatment systems, in addition to nearby monitoring wells. A mechanical dewatering device may be more cost effective in this situation. The final deposition of untreated dewatered sludge

will most likely be a certified hazardous waste landfill.

The second biological sludge generated by the Binnie Process is the reject stream from the crossflow microfiltration unit. Since the pressure filters are designed to operate at 98% water recovery or higher, the amount of sludge produced will equal as much as two percent of the treatment flow. No chemical analyses were reported for this waste sludge. If ferric salts are used to form the membrane precoat layer, then it can be expected to contain high levels of iron. From the selenium removal rates obtained by the filtration unit, selenium in the reject stream could range from 0.5 to 7 mg/L. As such, it will constitute a hazardous waste requiring special handling and treatment similar to the reactor biomass waste sludge.

The third waste stream is the gas produced by the anaerobic/anoxic reactors. Gaseous emissions from biological reactors were apparently never analyzed during pilot plant operations. Because of the negative redox potentials maintained in the reactors, the potential exists for the generation of hydrogen sulfide, methane and volatile selenium species.

The fourth wastestream is generated from the ion exchange operation. Initially, when the unit was designed for boron removal, a strong acid was used as the regenerant. This wastestream can be reused after being filtered to remove boric acid crystals. Some acid will be wasted to maintain regenerant quality. Due its corrosivity, the waste acid will constitute a

hazardous waste which must be neutralized prior to disposal.

ESTIMATED TREATMENT COSTS

Cost estimates for the construction and operation of a prototype facility (1 MGD) were developed for five different treatment schemes, three of which differ only with respect to final drainage disposal to be discussed later. Common to all five schemes is the use of crossflow microfiltration and mechanical sludge dewatering (sludge press).

The first scheme is a scaled-up version of the successfully tested pilot plant process: sludge-blanket reactor to fluidized bed reactor to microfiltration to ion exchange for boron removal and selenium polishing. The second scheme uses an experimental ion exchange process for selenium polishing which employs concentrated brine as a regenerant. The third scheme, and its other two variations, is presented as the "target" process in which denitrification and selenium removal are combined in a single-stage reactor. None of the reactors tested achieved the necessary selenium removals to function in isolation as a single-stage reactor. As such, the feasibility of this target process has yet to be evaluated.

To simplify the evaluation of cost estimates developed by EPOC AG, only two treatment schemes will be considered: the full treatment for selenium and boron removal and the target process which utilizes a single-stage reactor with no ion exchange.

It is assumed that the reactors and appurtenances will be sized to operate at full capacity year round, although at one point it is suggested that the treatment plant operate only half the year when evaporation rates are high. This relates primarily to the salt works operation and not to biological treatment. Based on values presented by EPOC AG, it appears that the yearly volume treated will be approaching 1,100 af, which is the capacity of a 1 MGD plant operating year round. To compensate for the lack of evaporation during the winter months, it may be necessary to construct holding reservoirs to retain the treatment flow until it can be processed in the salt works when evaporation rates are high. The costs of these reservoirs have not been determined.

EPOC AG's capital cost estimate parameters include: present worth values representing engineering subtotal, with no contingency; amortization over a 20-year design period; and an interest rate of 4%. Annual operation and maintenance (O&M) costs assumed the following: a total yearly labor cost of $30,000; maintenance costs for general upkeep and ion exchange resin replacement; carbon dosing costing $30/af; electrical demand of 100 kW/af treated; and electrical cost of $0.045/kWhr. There is no provision for disposal of dewatered hazardous and non-hazardous waste sludge.

Table 2-1 presents the cost estimates derived by EPOC AG for two treatment schemes in a 1 MGD or 1,100 af/yr prototype facility.

1: BINNIE PROCESS COST ESTIMATE FOR 1 MGD PROTOTYPE FACILITY BASED ON 20-YEAR DESIGN PERIOD.

it	Capital Costs Total ($)	Capital Costs Annual ($/yr)	O & M Annual ($/yr)	Total Annual Costs ($/yr)	Total Annual Costs ($/af)
	1,131,440	83,274	162,800	246,074	224
	648,800	47,752	145,200	192,952	175

ole 2-2 presents revised cost estimates reflecting the g changes: (1) replacement costs for pumps, painting and after 10 years; (2) capital costs increased by 10% for items, 25% for contingencies; (3) 27% of adjusted total overhead and profit; (4) interest rate of 9-3/8%; (5) labor requirement of at least three persons at an average f $40,000/person, including benefits and overtime wages;) electrical rate of $0.08/kWhr. Operating capacity is sumed to be approximately 1,100 af/yr.

-2: REVISED BINNIE PROCESS COST ESTIMATE FOR 1 MGD RE FACILITY BASED ON 20-YEAR DESIGN PERIOD.

it	Capital Costs Total ($)	Capital Costs Annual ($/yr)	O & M Annual ($/yr)	Total Annual Costs ($/yr)	Total Annual Costs ($/af)
	1,950,350	219,414	282,700	502,114	456
	1,121,492	126,168	260,700	386,868	352

ger capacity facilities will undoubtedly reduce treatment nsiderably, as economies of scale will occur for most omponents. Estimated capital costs for larger facilities

were calculated by EPOC AG using the capacity-ratio exponent method (Perry and Green 1984): if the cost of a facility of capacity Q1 is C1, then the cost of a similar facility of capacity Q2 can be calculated as

$$C2 = C1(Q2/Q1)^n$$

where the value of the exponent n depends on the type of plant. EPOC AG compares its selenium removal plant to a chemical engineering process plant characterized by an exponent value ranging from 0.7 to 0.8. Using the revised capital cost estimates and a value of 0.8 for n, the capital costs for full and target treatment processes of a 10 MGD and 100 MGD facilities are presented in Table 2-3. Annualized costs reflect amortization over a 20-year period using an interest rate of 9-3/8 percent. Estimated annual O&M costs employ the same cost/af presented in EPOC AG (1987: Appendix 9), with the exception of labor, estimated earlier as $40,000/person-yr. Staff requirements for a 10 MGD and 100 MGD plant are assumed to be 7 and 19 individuals, respectively.

Two means of disposing the treated drainage were considered: evaporation for salt recovery and dilution for discharge. The dilution disposal scheme cited a study by CH2M Hill (1985) to estimate the volume of fresh water needed to mix with treated drainage to meet San Joaquin River discharge requirements. However, the dilution factors are not equivalent to those calculated by CH2M Hill. For treated drainage, the governing parameter for dilution will be TDS. The ratio of new water to drainage to dilute TDS to a discharge requirement of 500 mg/L is

TABLE 2-3: ESTIMATED CAPITAL COSTS FOR 10 AND 100 MGD FACILITIES USING THE CAPACITY-RATIO METHOD BASED ON REVISED COST ESTIMATES FOR 1 MGD PROTOTYPE FACILITY, AND ESTIMATED ANNUAL OPERATION AND MAINTENANCE COSTS.

FACILITY CAPACITY	COST PARAMETER	FULL TREATMENT	TARGET TREATMENT
1 MGD	Installation	$1,950,350	$1,121,492
	Annualized	$219,414	$126,168
	O & M	$282,700	$260,700
	Total Annual	$502,114	$386,868
	Treatment	$456/af	$352/af
10 MGD	Installation	$12,305,880	$7,076,140
	Annualized	$1,384,410	$796,970
	O & M	$1,930,000	$1,710,000
	Total Annual	$3,314,410	$2,506,970
	Treatment	$301/af	$228/af
100 MGD	Installation	$77,644,830	$44,647,400
	Annualized	$8,735,040	$15,022,830
	O & M	$17,260,000	$15,060,000
	Treatment	$236/af	$182/af

about 32:1 provided the TDS of drain and dilution water is 10,000 and 200 mg/L, respectively. In EPOC AG's report, this dilution factor is incorrectly given as 7.7:1; it is further assumed that discharge requirements to wetlands can be met by a ratio of 3:1, which yields a discharge TDS of 2,650 mg/L. The feasibility of this wetlands disposal approach requires site-specific evaluation, since the governing factor is the impact of brackish surface water on ground water quality.

A cost estimate for a solar salt works was developed and added to the treatment costs for three of the five schemes. One disposal scheme consisted of processing the treated drainage through a reverse osmosis (RO) unit operating at 50% recovery; the brine stream comprising the other half of the treatment flow would be diverted to a salt works sized at half-capacity. The cost of RO treatment was obtained from a study using a water recovery in excess of 85% (CH2M Hill 1986), much higher than EPOC AG's design recovery of 50%. Due to differences in water recovery, the use of CH2M Hill's cost estimate is inappropriate.

The salts produced by the salt works are mainly sodium sulfate and sodium chloride. EPOC AG claimed that its pilot salt works was capable of producing sodium sulfate of the "required purity," although no data substantiating this claim was submitted to DWR.

The proposed prototype salt works consists of five strategically situated evaporation ponds through which the treated drainage would pass, becoming increasingly concentrated, on its way to a salt crystallizer. Waste brine from that unit would be contained in an on-site solar pond. The capital cost for the 1 MGD salt works, calculated by EPOC AG to be $800,000, was amortized over a 20-year period at 4% interest to yield a cost of $54/af. This cost is revised to $140/af to reflect the following changes: (1) 10% total added for unlisted items; (2) 25% total added for contingencies; (3) 27% of adjusted total added as overhead and profit; and (4) amortization interest rate

of 9-3/8%. A value of $44/af was assigned by EPOC AG for O&M costs, although no justification for its selection was presented. In lieu of the low O&M costs assigned by EPOC AG to other treatment facilities, it may be assumed that the salt works O&M estimate is also low. Combined with capital costs, the cost of the entire salt works facility treatment will probably exceed $200/af, not including costs for disposal of undesirable salts.

Based on treatment cost estimates and expected salt production, EPOC AG calculated the value of sodium sulfate which would have to be obtained in order to defray the total costs of treatment and disposal. The drainage has the potential of producing 18 tons/af glaubers salt (8 tons/af anhydrous sodium sulfate). It was postulated that a value of $36/ton for glaubers salt would offset treatment costs by $268/af. Additional offsets would derive from boric acid recovery from the ion exchange units. The savings projected by EPOC AG may be unrealistically high. However, their approach, in which drainage and its treatment by-products are conceived as exploitable resources, may prove to be practical in the long-run due to high disposal costs.

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SELENIUM REDUCTION BY FACULTATIVE BACTERIA

Selenate reduction to elemental selenium by facultative bacteria was studied by the research team headed by Altringer at the U. S. Department of the Interior, Bureau of Mines, Salt Lake City Research Center. The research began by isolating and identifying several bacteria species indigenous to ponded westside agricultural drain water believed to be responsible for precipitating selenium at Kesterson Reservoir. The most active selenium reducers were found to be: Pseudomonas alcaligenes, (2) Ps. fluorescens, (3) Ps. aeruginosa, (4) Citrobacter freundii, (5) Enterobacter aerogenes, (6) Enterobacter agglomerans, (7) Enterobacter cloacae, and (8) Klebsiella oxytoca (Larsen et al. 1989). These were used either as isolates or mixed cultures in subsequent experiments.

Initial batch tests used water from Kesterson Reservoir which had been supplemented by nutrients, sterilized, then inoculated with six different bacterial cultures. After 20 days, the mixture of water and bacteria was filtered and the filtrate analyzed for selenium content. Two of the bacteria cultures (Pseudomonas sp. and Pseudomonas alcaligenes) associated with the highest removal rates of total soluble selenium (over 80%) were selected for further testing in both batch and continuous static-bed columns.

The static-bed columns were designed to operate in a recirculating, downflow mode. In the batch column tests, a nutrient solution was recirculated through two columns which had

been inoculated with one of the two cultures identified above. After two weeks, the nutrient solution was replaced by mixture consisting of Kesterson water containing 280 ug/L Se and nutrients. In both columns, removals of total soluble selenium exceeded 85% after three days. Similar results were obtained for Kesterson water containing 3,800 ug/L. Thus selenium removal appears to be independent of initial concentration, and apparently reflects equilibrium conditions (Altringer et al. 1990). Additional tests which included selenium speciation analyses revealed that selenite was formed as an intermediate product, the final form of selenium appears to be elemental selenium.

In the continuous column tests, untreated drainage water was added to the top of the column while a fraction of the effluent was bled from the system. Substantial selenium removals (around 90%) were obtained for retention times of approximately an hour for the test columns (flowrate 40 ml/min). The columns eventually became plugged with a red-brown precipitate, believed to be elemental selenium.

Bacterial reduction of selenium was further investigated through the long-term operation of a laboratory-scale rotating biological contactor. The inoculated unit processed a mixture of simulated drain water containing 620 ug/l Se and nutrients. Varied parameters include retention time, disk rotation rate, effluent recycle, nutrient addition, and air intake.

After steady-state conditions were reached, a selenium removal of 85% was observed for a detention time of 30 hours (0.3 ml/min). Reducing the retention time to 3 hours decreased the amount of selenium removed to 44%. Although selenium removal was reduced when the system operated on a recycle mode, a slight increase (5%) occurred when the air supply to the system was restricted. A gas scrubber was installed on the unit to determine if selenium was being volatilized; test results confirmed that approximately 15% of the available selenium was transformed into gaseous compounds.

A plug-flow reactor was continuously operated over a 60-day period. Sampling ports were situated along the reactor's 45-ft length to provide data for correlating retention time to reactor performance. The reactor was packed with a sterile media (small ceramic saddles), then inoculated with a mixed Pseudomonas sp. culture. The feedwater to the plug-flow reactor, simulated drain water supplemented with nutrients, was sparged with air prior to entering the reactor. The researchers contend that this ensured aerobic conditions in the reactor (Larsen et al. 1989). Yet, with a retention time approaching 5 days in a nutrient-rich environment, it is more likely that anoxic conditions prevailed. This could have been easily confirmed had the effluent's dissolved oxygen content been measured, something which was apparently not done. In any event, the reactor removed about 80% of the total soluble selenium at a 1-day retention time, and greater than 90% at a 4-day retention time.

Batch kinetic tests conducted over a 168-day period demonstrated that the mechanism of selenium removal is influenced by nutrient addition, oxygen supply, and temperature. Although aerobic conditions encouraged bacterial growth, selenate reduction was enhanced when air supply was restricted. The results of one batch test conducted under anaerobic conditions showed increased selenate concentrations after 72 days. The mechanism responsible for this result is unclear, yet may signify that minute amounts of oxygen may be required by these bacteria for optimal selenate reduction. A similar finding was reported for the selenate reducing bacteria in the Algal-Bacterial Selenium Removal System (ABSRS) (Gerhardt and Oswald 1990).

The researchers propose that with the properly designed reactor, selenium removals of 100% can be obtained. However, the values obtained for selenium removal were based on **filtered** samples; no experiments were reportedly conducted on the combined performance of bacterial reduction **and** solids separation techniques.

In many respects, the mechanism of selenium removal investigated by Altringer and other appears to be similar to that which occurs in anoxic bacteriological selenate reduction reactors utilized in other treatment schemes (e.g., the Binnie Process and ABSRS). The selenium removal mechanism in these schemes involves reducing selenate to selenite to elemental selenium, which accumulates in the reactor's biological sludge.

One important similarity between this research and that conducted by EPOC AG was the bacteria identified as active selenate reducers. The bacteria population contained in one sample of anoxic fixed-film reactor sludge at the Binnie Process pilot plant was dominated by Pseudomonas sp. (Jones 1986), the same bacteria which were shown to reduce selenate at a fast rate and adapt well under conditions of high selenium concentrations (Larsen et al. 1989). The research conducted by Altringer verified that optimal selenate reduction by facultative bacteria occurs under anoxic conditions.

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ALGAL-BACTERIAL SELENIUM REMOVAL SYSTEM

The Algal-Bacterial Selenium Removal System (ABSRS) was developed by the University of California, Berkeley (UCB) Applied Algae Research Group research team headed by Dr. William Oswald. In all, six reports have been issued on ABSRS pilot plant and laboratory work: a final report to DWR (Oswald et al. 1987) and five reports to the San Joaquin Valley Drainage Program (Oswald et al. 1988a, 1988b, 1988c, 1990; Gerhardt and Oswald 1990).

THE USE OF MICROALGAE IN WASTEWATER TREATMENT

The potential of using microalgae wastewater treatment technology to remove selenium from subsurface agricultural drainage water was initially addressed in a feasibility study by Oswald (1985). In his report, Oswald referred to earlier attempts of treating agricultural drainage water with algae to remove nitrate, but noted that positive results were not attained largely due to inefficient mixing methods. Since that time, the need for continuous mixing has been recognized to keep algae cells in suspension and to prevent thermal stratification.

Experimentation with algae cultivation in conjunction with wastewater treatment has led to the concept of High Rate Ponds (HRP). Efficient continuous mixing in these shallow, channelized ponds is accomplished by paddle wheels. Along with optimizing the process by which inorganic nutrients in wastewater are converted into organic matter, the fermentation of the biomass generated by such ponds produces methane which can be readily converted to electrical energy. Furthermore, because algae

absorb light and convert it to heat, the rate of evaporation is increased, thereby decreasing the volume of water to be treated.

SELENIUM REMOVAL IN THE ABSRS

Algae cultivated in HRP fed by subsurface drainage water take up inorganic nutrients such as nitrate. A supplemental pretreatment denitrification step is included if feedwater nitrate levels exceed 30 mg/L as N. The actual removal of selenium from drain water is accomplished by the reduction of selenate to more insoluble forms as denitrified HRP water passes through an anaerobic sludge-blanket reactor fed with concentrated algae as a carbon source. The reactor effluent is coagulated with iron salts prior to its passage through a dissolved air flotation (DAF) unit to remove suspended floc containing selenite and organic colloids, while elemental selenium accumulates in the reactor sludge. A flow diagram of the ABSRS is presented in Figure 4-1.

DEVELOPMENT OF THE ABSRS

The impetus for investigating the potential of algae for selenium removal was due to the successful results of early experiments which contacted agricultural drainage water with effluent from digesters fermenting sewage-grown algae. The supernatent from these tests revealed that a substantial decrease in soluble selenium had occurred. The black liquor was considered to be a strong reducing agent which transformed selenate into less soluble forms.

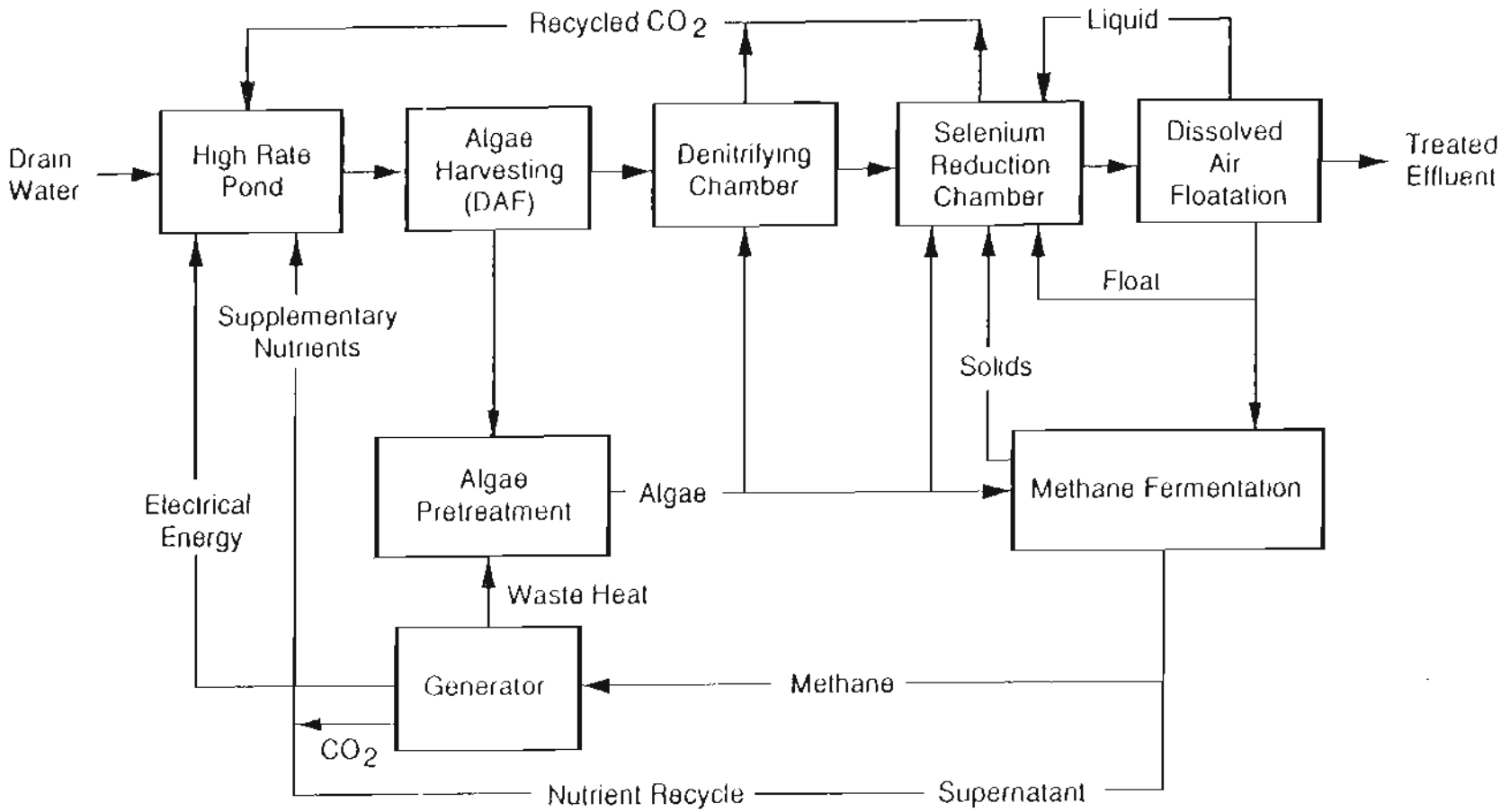

FIGURE 4-1: ALGAL-BACTERIAL SELENIUM REMOVAL SYSTEM PROCESS FLOW SHEET.
From Oswald et al. 1990:2.

The potential of an algae-derived organic reductant for selenium removal led to eight research questions which guided laboratory experimentation and pilot plant operations:

1. What is the composition of the drainage water?
2. Can algae be grown on the drainage water?
3. Can such algae be harvested and concentrated?
4. Can the harvested algae be purified sufficiently for anaerobic digestion?
5. Can the purified algae be fermented in an anaerobic digester to produce methane gas?
6. Under what conditions will the digester effluent reduce selenium and remove it from solution?
7. Can the reduction chamber effluent be clarified to produce clear water?
8. How should the selenium-rich sludge be disposed of?

The pilot plant was located south of Mendota on Murrieta Farms adjacent to EPOC AG's field facility. The site plan of the pilot plant is reproduced as Figure 4-2. The feedwater for both plants was typical of westside subsurface drainage water (See Table 1-1) with the exception of high average nitrate levels, over 100 mg/L as N. Feedwater selenium concentration averaged 340 ug/L; average sulfate concentration was 3400 mg/L.

The first HRP operated on batch mode from August 1986 until continuous flow was initiated in May 1987. As daytime pH increases due to photosynthesis, carbon precipitates as calcium carbonate and interferes with light transmission. Because of this, and the inherently low carbon content of drainage, carbon dioxide was diffused into the pond whenever pH rose above 8.3.

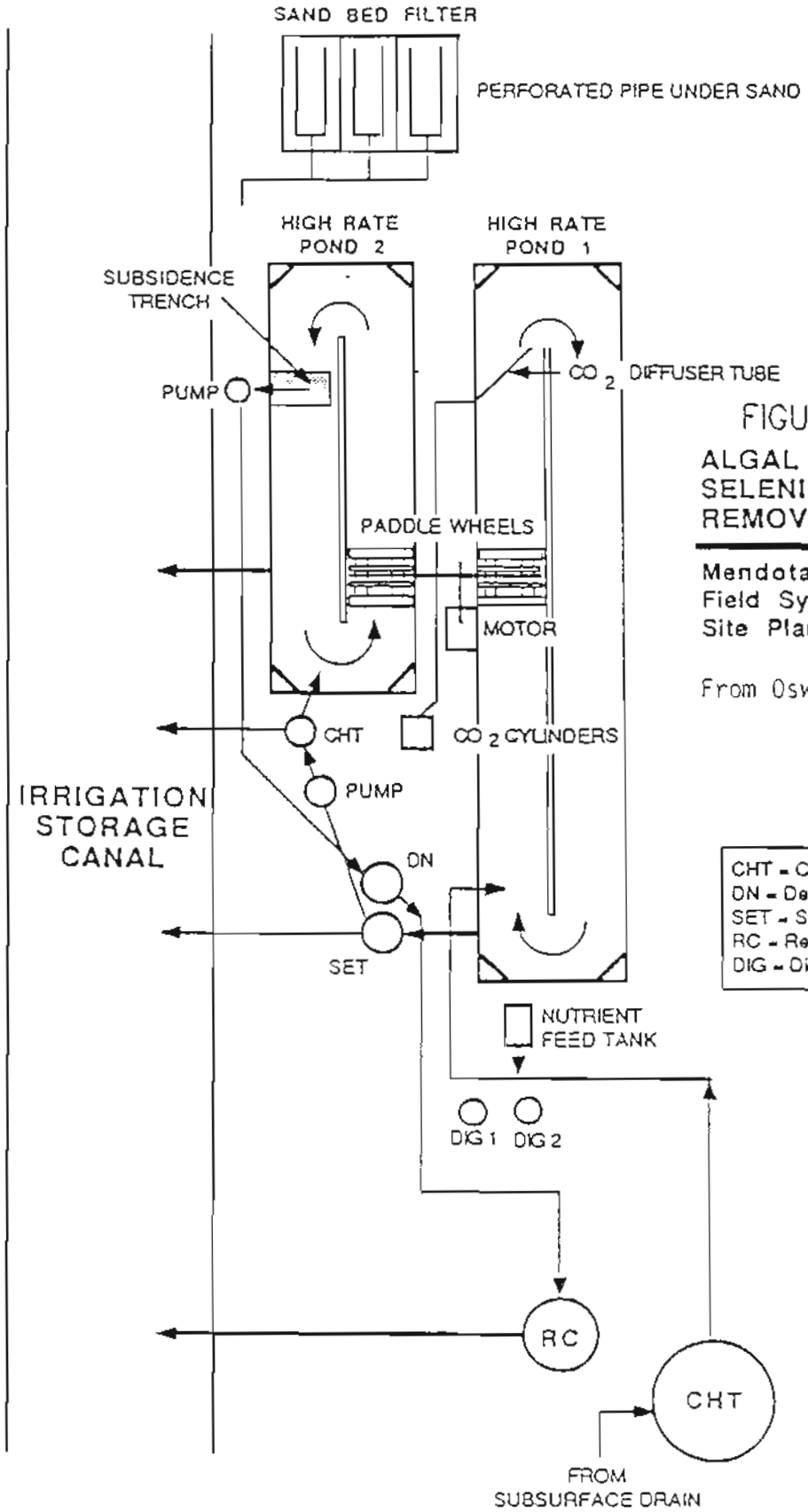

FIGURE 4-2

ALGAL BACTERIAL SELENIUM REMOVAL SYSTEM

Mendota Field System Site Plan

From Oswald et al. 1990:2.

CHT = Constant Head Tank
DN = Denitrifier
SET = Settling Chamber
RC = Reduction Chamber
DIG = Digester

Other supplements added to the HRP for optimal algae growth included phosphorus and trace nutrients. Algae concentration, measured as volatile suspended solids (VSS), varied seasonally from an average high of 209 mg/L in summer to 121 mg/L in winter. The average VSS was 178 mg/L (Gerhardt and Oswald 1990).

Although actual algae productivity is a function of solar input, optimal algae productivity can be estimated by the following rational formula (Oswald 1985:22):

$$P = [k\ d\ Cc]/\theta$$

where P = productivity, g/m^2-d
k = constant, 0.01 for algae
d = pond depth, cm
Cc = cell concentration (VSS), mg/L
θ = cell residence time, days

Given an average pond depth of 9 inches at the Murrieta Farms pilot HRP, a summer residence time and average VSS of 3 days and 209 mg/L, respectively, yields a productivity of 16 g/m^2-d. During the winter the residence time increased to 5 days, and productivity dropped to 5.5 g/m^2-d. The overall average productivity based on seasonal averages was 13 g/m^2-d, which translates to an annual yield of 47.5 metric tons/hectare (21 tons/acre) (Gerhardt and Oswald 1990).

Algal sludge was initially thickened by gravity settling to about 3% solids. Prior to installing the carbonation system, the settled algae solids were only 20% volatile, indicating that a substantial amount of inorganic precipitates settled along with the algae. Maintaining the pH below 8.3 with carbon dioxide increased the volatile component of the sludge to 50%. However,

the water which comprised 97% of the sludge was rich in sulfate and nitrate, two compounds which inhibited methane fermentation in laboratory studies. To improve methane production, the settled algae was centrifuged to about 15% solids, then diluted with digester supernatent or tap water to a consistency adequate for digester injection.

Because of high selenium removals observed in early experiments which contacted effluent from digesters fermenting sewage-grown algae with drainage water, it was theorized that selenium removal depended on optimizing methane production. Thus, research focused on improving methane fermentation and increasing digester Methane Specific Gas Production (MSGP). This parameter is expressed as liters of methane generated per gram of volatile solids digested. While sewage-grown algae MSGP ranges from 0.3 to 0.5 L/g volatile solids, the highest MSGP obtained from digesting concentrated drainage-grown algae under controlled laboratory conditions was 0.25 L/g (Oswald et al. 1988a). Heating the algae feed to 60°C yielded only a slight increase in MSGP. Nevertheless, the UCB researchers incorporated this heating pretreatment step in subsequent experiments and pilot plant work.

Another major research objective was to discover the conditions under which algae digester effluent reduces selenate and removes selenium from solution. Laboratory tests using sewage-grown algae digester effluent revealed that soluble selenium levels could be reduced by 99% within 12 hours of

contacting two parts digester effluent to one part drainage water (Oswald et al. 1987). Subsequent tests using 1:1 volumes of effluent from laboratory digesters fed with drainage-grown algae and HRP water contacted for 12 hours with ferrous chloride removed 95% of the soluble selenium (Oswald et al. 1988a).

Fermentation of drainage-grown algae at Murrieta Farms was initially hampered by poorly designed digesters. The primary reasons for poor performance include air intrusion, insufficient mixing, and diurnal and seasonal temperature variations. In any event, field digester effluent had been regularly transferred to the reduction chamber for well over a year before its effluent was sampled and analyzed for selenium. Single selenium determinations (no duplicates) of HRP influent and reduction chamber effluent sampled on three days in the summer of 1988 suggest field removal efficiencies ranging from 50% to 80%.

The dilution factor in the field reduction chamber, although not specifically calculated, can be roughly estimated at 1 part digester effluent to over 5,000 parts HRP water. This is substantially different than the operationally impractical 2:1 and 1:1 volumes employed in laboratory experiments. Yet, over 50% of the selenium was reportedly removed by the pilot plant.

Subsequent laboratory experiments verified the necessity of nitrate removal for successful selenate reduction. One consisted of a continuous column system to simulate the field reactors: one column denitrified the feedwater (field HRP water)

prior to its passage through the second column which functioned as a selenate reduction chamber. The hydraulic residence time varied from 36 to 48 hours. The reactors were fed a preheated algae sludge of 3% solids. The dilution ratios were 32:1000 and 30:1000 for the first and second columns, respectively. The system lowered nitrates from 100 to 8 mg/L as N, and reduced the soluble selenium concentration from 365 to 46 ug/L.

The feasibility of using anoxic algal sludge as a reducing agent/carbon source in lieu of digester effluent is indicated in the values reported for the redox potentials measured in the field digester system (Oswald et al. 1988a: Table A-3). The thickened algae had a slightly lower potential than the digester effluent, a finding which had been attributed to air intrusion.

The theoretical "window of opportunity" for optimal selenate and selenite reduction at a pH of 8 exists between a redox potential of -280 mV and +380 mV (Oswald et al. 1988c). Lower values result in the undesirable reduction of sulfates. To reach the optimal range, both nitrate and dissolved oxygen must be removed from the reduction chamber influent. The optimal range within the reactor can be controlled by adjusting the rate of reductant loading.

A basic premise held during much of the research period was that successful selenate reduction occurred when digester effluent was contacted with HRP water and as such, was a function of optimal methane fermentation. However, calculations of reductant strength of digested algae suggest that as methane

production decreases, the amount of reducing equivalents per gram of algae increases (Oswald et al. 1988c). In the latest phase of field research, when it was realized that selenate reduction is mainly a biological process, the denitrification and reduction reactors were fed thickened algae sludge instead of digester effluent. The algae became the carbon source for bacteriological reduction of selenate in a anaerobic sludge blanket reactor. This revised field process yielded unfiltered reduction chamber effluent selenium levels of 70 to 80 ug/L (Oswald et al. 1990).

Clarification of reduction chamber effluent was never attempted in the field. However, laboratory experiments using iron salts and dissolved air flotation simulation produced a clear effluent in a matter of minutes; the amount of ferric chloride required was less than 100 mg/L.

An analysis of the field reduction chamber effluent in September 1989, when selenium levels were 70 to 80 ug/L, revealed a total reduction of selenate, much of it having been transformed into elemental selenium. Further reductions in the field reduction chamber effluent were achieved in laboratory coagulation tests using 30 mg/L ferric chloride to reduce selenium levels from 89 to 7 ug/L (Oswald et al. 1990).

ABSRS SLUDGE AND WASTESTREAM PRODUCTION

Although the primary objective of the ABSRS is to generate a carbon source from harvested HRP algae for biological denitrification and selenate reduction reactors, excess algae can be

fermented to produce methane (used for power generation) and carbon dioxide (recycled to HRP for pH control). Once digested, the sludge can be diverted to the biological reactors to supplement the algal feed. Supernatent from the digesters, high in biological oxygen demand, can be used to deoxygenate the feedwater to the selenate reduction reactor.

One crucial parameter which needs refinement is the minimum amount of algae required for total treatment. In the ABSRS, significant selenate reduction occurs only after nitrate is reduced to 2 - 8 mg/L as N. The net nitrate uptake by algae in the field HRP was about 14 mg/L as N. The nitrate concentration in typical drainage waters was cited to average 47 mg/L as N (Gerhardt and Oswald 1990). If the net uptake of nitrate by algae in HRP is 14 mg/L, then the 33 mg/L remaining will require denitrification. The average dissolved oxygen content and selenate in drainage water were assumed to be 8 mg/L and 400 ug/L, respectively. The reduction of these constituents at these concentrations will require 12.82 oxidizing milliequivalents per liter (meq/L). Each milligram of algae generates 0.194 meq upon total decomposition into its base constituents (carbon dioxide, ammonium and phosphate ions). The minimum concentration of algae required to reduce 12.82 meq/L is theoretically 66 mg/L (Gerhardt and Oswald 1990).

Laboratory batch studies revealed that not all the algae are oxidized, because more than 66 mg/L are required in the reactions. The crucial parameter for design purposes, then, is

the amount or fraction of algae available for reduction reactions. The value of this fraction was extrapolated from batch denitrification experiments which indicated that 1,000 mg/L of algae reductant were required denitrify drainage water with high nitrate concentrations (over 100 mg/L as N). The slope of reductant required versus nitrate removed generated from the batch experiments was interpolated to yield a range of 184 mg/L to 229 mg/L for the amount of reductant required to remove 33 mg/L nitrate as N. This extrapolation signifies that only 29% - 36% of the algae is available for reduction reactions. The minimum algae concentration required to treat typical drainage water was interpreted to range from 174 - 200 mg/L (Gerhardt and Oswald 1990).

The approach taken by the UCB researchers in estimating the minimum amount of algae required for total treatment focuses solely on the productivity of algae in HRP. The fraction of algae available for reducing reactions is estimated via an extrapolation of batch experiments conducted under controlled laboratory conditions. Yet, the ABSRS is a continuous system which removes selenium by contacting drainage water with a sludge comprised of harvested algae. An algae concentration of 200 mg/L may be the required minimum for treating typical drainage water. However, this assumes that all of the algae is captured as sludge, an achievement not realized during the field operations.

The acreage requirement selected in developing cost estimates for full-scale ABSRS facilities is about 10 acres/MGD

(Oswald et al. 1988c). The maximum amount of sludge produced per 10 acre HRP system, assuming total capture, is calculated by assuming the following: (1) algal sludge is 3% solids; (2) inert solids constitute 50% of the algal sludge; (3) specific gravity of algal sludge is 1.06; (4) HRP design depth is 9 inches; and (5) overall HRP production is 13 g/m^2-d. These parameters indicate that a 10 acre HRP system will produce about 8,750 gallons of sludge per day, less than 1% of the treatment flow. In contrast, results of a continuous column experiment designed to simulate the field process indicated that the required sludge volume will approximate 6% of a feedwater flow containing high nitrate concentrations.

Improved efficiencies can be obtained if the overall algae productivity is increased and the inert fraction of the algal sludge is reduced. Furthermore, the fraction of algae available for reduction reactions may be increased by some form of pretreatment which would improve algae biodegradability.

The production of an algal feed with a low inert solids content requires a process step in which carbonates are precipitated and separated from the HRP flow prior to the algae harvesting unit. This was the rationale behind the installation of the Phase II HRP at the pilot plant during the summer of 1988. In the absence of any pH control (i.e. carbonation system), high daytime pH levels favored the formation of precipitates which were to be trapped in a subsidence chamber within the pond.

The precipitation of heavy metals in HRP may contaminate the carbonate sludge. Heavy metal concentration in pond solids is demonstrated by an analysis of accumulated solids in Phase I HRP (Oswald et al. 1988b). Periodic failures in the pond's carbonation system caused intensive precipitation of solids. Before the installation of the second pond, algae were collected from the first pond at mid-depth, a practice which allowed heavier inorganic precipitates to accumulate. The composition of these solids reveal some concentration of boron, and major concentrations of manganese, chromium, copper, nickel, and lead.

The Phase II HRP subsidence chamber trapped inorganic solids and a considerable amount of algae. Because of the high organic content of the subsidence chamber sludge, the researchers stated their intention to use it as a carbon source for the denitrification reactor (Oswald et al. 1988b). Despite the demonstrated potential of heavy metal contamination, they do not anticipate this sludge to be hazardous (Oswald et al. 1988c). Unfortunately, the accumulated solids in the Phase II HRP were not analyzed for heavy metals. As such, their assumption that the sludge will be non-hazardous remains to be confirmed.

Quality concerns aside, the potential quantity of inorganic solids produced by the ABSRS will be prodigious. The process has the potential of generating 5 - 10 tons of calcium and magnesium carbonates (dry weight) per million gallons treated. Reclaiming the carbon for use in biological reactors will reduce this volume significantly, but will require heavy metal monitoring.

Another wastestream is the sludge from the DAF unit. An estimated 1,000 pounds of DAF sludge (dry weight) will be produced per million gallons of water treated (Oswald et al. 1988c). If the effluent from the reduction chamber is coagulated with ferric chloride prior to its passage through the DAF unit, the resulting sludge will be rich in iron and selenite. Because of its hazardous nature, the use of sand beds for drying DAF sludge requires a fail-safe leach system and possibly several groundwater monitoring wells. Alternatively, the sludge could be dewatered by a self-contained mechanical system such as a rotary vacuum filter or belt press filter. Unless a use can be found for selenium-rich DAF cake (e.g., a livestock feed supplement), it will require disposal in a certified hazardous waste facility.

Assuming that the ABSRS generates enough algae to serve as a carbon source for biological reactors, the amount of sludge which will have to be wasted from the reactors for optimum performance has yet to be determined. Also unknown at present is the chemical composition of "spent" algal sludge. The waste biomass from the selenate reduction reactor is expected to contain high levels of elemental selenium and, like the DAF float, will require similar treatment and disposal.

One wastestream considered in the first feasibility study (Oswald 1985) but not in subsequent reports is the "scrubber" water used to remove hydrogen sulfide and hydrogen selenide from digester gas. This wastestream is anticipated to be very toxic and will minimally require lined evaporation pits.

ESTIMATED TREATMENT COSTS

Cost estimates for the design, construction, operation, and maintenance of 1, 10 and 100 MGD facilities were developed (Oswald et al. 1988c). A brief discussion of estimated treatment cost is presented within the report's text, while detailed breakdowns of equipment costs for each facility are contained in an appendix.

The selected design period was 40 years, representing the life expectancy of ponds and earthen structures. The service lives of high maintenance items (pumps, generators, motors) and low maintenance items (electrical equipment) were assumed to be 10 and 20 years, respectively. The facilities were designed to operate year round at an efficiency of 98% or above.

Capital cost estimate parameters included: present worth values representing engineering subtotal and 25% extra for contingencies; amortization over a weighted average of 27.5 years based on predicted life expectancy of key elements; and an interest rate of 9-3/8 percent. Annual operation and maintenance (O&M) costs assumed the following: an average labor cost of $31,000/person-yr; maintenance costs based on equipment life expectancy and degree of maintenance required; and no cost or electrical power, since the system is designed to operate on its own generating capacity. While some unspecified chemical costs are included in O&M costs, there is no provision for disposal of hazardous and non-hazardous waste sludge and treated drainage.

Table 4-1 presents the cost estimates calculated for 1, 10, and 100 MGD selenium removal treatment plants.

TABLE 4-1: ABSRS COST ESTIMATES FOR 1, 10, AND 100 MGD SYSTEMS BASED ON 40-YEAR DESIGN PERIOD.

Plant Size (MGD)	Capital Costs Total ($)	Capital Costs Annual ($/yr)	O & M Annual ($/yr)	Total Annual Costs ($/yr)	Total Annual Costs ($/af)
1	1,469,000	150,268	149,420	299,688	268
10	6,731,000	688,514	439,000	1,127,514	101
100	51,388,000	5,256,480	2,230,640	7,487,120	67

The selenium removal process design upon which the above cost estimates were based was revised to eliminate the methane production component. Therefore, the costs for digester, digester gas collection and scrubbing facilities, generator, and centrifuge can all be eliminated.

The cost of electrical power must be added because methane production is eliminated in the revised treatment process. The electrical demand for HRP mixing per acre pond area was estimated by Oswald (1987) to be approximately 50 kWhr/day, but varies according to pond design and operating conditions. If 10 acres of HRP are required per 1 MGD treated, then the annual HRP electrical demand for each MGD processed will be 182,500 kWhr. Other electrical costs associated primarily with pumping demands can be estimated to be 400kWhr/AF processed (1,230 kWhr/MG), representing an annual demand of 448,950 kWhr per MGD processed. Annual electrical demand per MGD treated will be 631,450 kWhr. At an average estimated cost of $0.08/kWhr, this represents an

annual electrical cost of $50,516/MGD.

Table 4-2 presents a revised cost estimate reflecting the elimination of methane production and the addition of electrical power costs to annualized capital and O&M costs, respectively. The following changes were made: (1) 20-year design period; (2) installation costs increased by an additional 10% for unlisted items; (3) installation subtotal increased by 27% for overhead and profit; and (4) labor cost of $40,000/person-yr, including benefits and overtime expenses.

TABLE 4-2: REVISED ABSRS COST ESTIMATES FOR 1, 10, AND 100 MGD SYSTEMS BASED ON 20-YEAR DESIGN PERIOD.

Plant Size (MGD)	Capital Costs* Total ($)	Capital Costs* Annual ($/yr)	O & M Annual ($/yr)	Total Annual Costs ($/yr)	Total Annual Costs ($/af)
1	1,861,678	209,439	262,852	472,291	422
10	8,229,574	925,827	1,366,320	2,292,147	205
100	65,865,648	7,409,885	10,284,840	17,694,725	156

* includes costs for replacing pumps after 10 years.

These costs do not include the price of land required by the HRP, sand filters, sludge drying beds, reactors, and facility building. The costs of non-hazardous sludge disposal and of hazardous sludge treatment and disposal are also not included. Furthermore, no consideration is given to the ultimate fate of the treated drain water which will be rendered non-hazardous but more saline due to evaporation as it passes through the system.

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ANOXIC SELENIUM REDUCTION STUDIES

The mechanisms of bacterial removal of selenium from agricultural drainage were investigated by Schroeder and co-workers at the University of California, Davis. The research was a follow-up to the bacterial processes investigated by Binnie California, Inc. In the first report issued (Elkholy et al. 1988), two objectives were considered; (1) the microbial transformations of selenate in the presence of nitrate, and (2) the sorption of selenium onto $CaCO_3$ precipitate (calcite). Both phases of this work were inconclusive. Apparently, a considerable portion of the research time was devoted to establishing analytical procedures for the measurement of selenium. Analysis by hydride generation/atomic absorption spectrometry (AAS) was found to give poor results on undigested samples. This means that the measurement of selenate and selenite species was in error by AAS measurement. Digested samples gave good results for total selenium. The other selenium analysis investigated was fluorometry. Results indicated good results in the range of 0 to 10 ug/L with an error of approximately 10 percent.

In the microbial transformation phase of the study, bacterial strains were isolated by plating on solid media containing selenate. The isolates that showed selenate reduction on the solid media were selected for further studies in liquid culture under aerobic, anaerobic, and anoxic conditions. The response of the selected isolates under these conditions did not

correlate well with their behavior on solid media (i.e., they no longer reduced selenate). The authors offer several experiments that should have been run to give meaningful results.

In the selenium sorption phase of the study, a change in the experimental methodology caused this phase to give inconclusive results. Initially, a slurry of elemental selenium was to be added to a slurry of calcite precipitates ($CaCO_3$) and the amount of selenium retained on a filter would be a measure of the amount of Se^0 adsorbed onto the calcite. This procedure in itself would not appear to adequately measure adsorption since some of the colloidal elemental selenium would be retained on the filter whether adsorbed on calcite or not. However, due to difficulties in producing the Se^0 slurry, the student performing the experiment substituted Na_2SeO_3 (sodium selenite), and no adsorption of selenium occurred. This would be expected.

An additional study objective was to determine whether bacterial selenate reduction occurs primarily by respiration or detoxification mechanisms (Schroeder et al. 1989). This objective was addressed by attempting to determine if the reduction of nitrate and selenate was a sequential or simultaneous process. Results from studies using laboratory-scale (4.5 L) sequencing batch reactors and fluidized bed reactors showed that selenate reduction occurred simultaneously with nitrate reduction. This was taken as an indication that the selenate reduction was primarily a detoxification mechanism rather than respiration. In respiration, electron acceptors are

normally used in the order of their redox potential and nitrate would be used before selenate. Thus, the researchers postulated that the bacteria were detoxifying their environment of high concentrations of selenate while simultaneously respiring on nitrate. The investigators did not address the issue of whether this would be strictly true in a mixed bacterial culture, as would have been found in the reactors. Perhaps one or more species of bacteria preferentially use nitrate, while others use selenate.

Work with the fluidized bed reactors indicated that selenate concentrations in the feed could be reduced by 70 to 99 percent (Schroeder et al. 1989). However, a serious drawback in this study was the composition of the feed solution. It consisted of molasses, $NaNO_3$, KH_2PO_4, Na_2SeO_4, and tap water. Sulfate, the major anion in a typical agricultural drainage water, was not added to this synthetic feed. Apparently, this was done to avoid interfering with the measurement of selenate by the chosen analytical method, ion chromatography. It should also be noted that only selenate reduction was measured in these experiments and not total selenium removal as indicated in the tabulated results. Additional information on reactor operation was provided in a recent report (Ergas et al. 1990). Results of selenium analysis for the fluidized bed reactors (FBR1 and FBR2) are presented in Table 5-1. While good reduction of selenate occurred, total selenium and total soluble selenium remained quite high in the reactor effluent.

TABLE 5-1: SELENIUM REMOVALS IN THE FLUIDIZED BED REACTORS.
Average values for 28 days of operation in ug/L.

	FBR1	FBR2
Selenate-Se		
Feed	526	547
Effluent	47	74
Total Effluent Se		
Unfiltered (total)	324	281
Filtered (soluble)	142	189

(From Ergas et al. 1990)

COST ESTIMATES FOR SEQUENCING BATCH REACTOR SYSTEM

Preliminary cost estimates for a sequencing batch reactor system for selenium removal were presented (Ergas et al. 1990). Costs are presented in Table 5-2 for three design flow rates. The capital cost of the treatment plant was based on the cost of an activated sludge plant. This would seem to overestimate the capital cost since the air supply system would not be required for an anoxic system. The annualized capital cost is based on a 10% interest rate over a useful life of 25 years.

TABLE 5-2: COST ESTIMATE OF A SEQUENCING BATCH REACTOR FOR SELENIUM REMOVAL.

	Design Flow Rate, MGD		
	1.44	14.4	144
Capital Cost			
1989 cost ($million)	0.571	4.235	31.392
Annual cost ($million)	0.063	0.467	3.458
Unit cost ($/af)	71	53	39
Organic Feed (Sucrose) solids retention time of 40 days ($/af)	2.2	2.2	2.2
Miscellaneous Costs ($/af)			
Power (2.7 kW/af at $0.12/kW-hr)	7.75	7.75	7.75
Operators	3.00	3.00	3.00
Monitoring	6.50	6.50	6.50
Maintenance	0.50	0.50	0.50
General Overhead	0.25	0.25	0.25
Sludge Disposal (Estimated minimum)	10.00	10.00	10.00
TOTAL ($/af)	91.20	73.20	59.20

(From Ergas et al. 1990)

The costs presented appear to be quite low since the treatment process would be very similar to the Binnie Process discussed in Chapter 2. In that chapter, revised cost estimates for 1, 10, and 100 MGD plants for "target treatment" were $352/af, $228/af, and $182/af, respectively. This is approximately three times the costs estimated by Ergas (Ergas et al. 1990).

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MICROBIAL VOLATILIZATION OF SELENIUM IN EVAPORATION PONDS

The biomethylation of selenium in evaporation pond water was investigated by Frankenberger and Thompson-Eagle (1989). This research evaluated the microbial transformation of aqueous selenium into gaseous dimethylselenide (DMSe), which is subsequently volatilized into the atmosphere. In earlier studies conducted at U.C. Davis and reported by Frankenberger and Karlson, (1988), inhaled DMSe at concentrations as high as 8,034 ppm were found to be nontoxic to rats. However, this was based on a 1-hour acute toxicity exposure and neglects chronic effects of long-term low-level exposure. Research concerning selenium volatilization from soils has been reported elsewhere (Frankenberger 1990), but this study was directed at volatilization from evaporation pond waters.

Earlier studies demonstrated that methylation and volatilization of selenium did occur in agricultural drainage evaporation pond waters (Frankenberger and Thompson-Eagle 1988). Selenium-methylating microorganisms were isolated by diluting and plating evaporation pond water samples which had produced DMSe. The microorganism capable of methylating selenium at the greatest rate was a fungus, Alternaria alternata. However, later studies indicated that the fungi were the most active methylators only in artificial media and bacteria were predominant in actual pond water.

Initial studies of the effects of adding various organic carbon sources indicated the addition of proteins could increase volatilization greatly over unamended controls. The addition of gluten, albumen, and casein caused 10, 23, and 41 percent loss of the total aqueous selenium after 43 days incubation, respectively. Other carbon sources, such as sugars, fats, alcohols, and amino acids, increased volatilization slightly or not at all. With casein showing the greatest promise as an amendment, further experiments were conducted using various components and treatments of casein. These experiments indicated that the active ingredient is probably a peptide (a protein sub-unit) or a mixture of peptides with molecular weights of less than 6,000 to 8,000. Unincorporated amino acids, the individual building blocks of peptides and proteins, did not increase volatilization significantly over unamended samples.

Because casein is a milk protein, dairy by-products were investigated as an economical amendment to increase volatilization in evaporation pond water. These products were effective in stimulating selenium volatilization above the unamended control in the following order: 75% whey protein (327-fold increase) > 25% liquid whey protein (188-fold) > yeast (111-fold) ≥ animal feed (98-fold) > cheese whey (74-fold) ≥ evaporator concentrate (70-fold) ≥ desalted whey (70-fold) > whey butter (4-fold) > unamended pond water. These compare to an approximate 204-fold increase using crude casein as the amendment. Vegetative protein sources including cottonseed meal, soybean meal, safflower meal, and straw caused only a 29-fold,

18-fold, 13-fold, and 2-fold increase in selenium volatilization, respectively. It appears that dairy by-products would provide ecomomical amendments, since many of these are waste products requiring treatment and disposal.

In shake flask experiments, it was established that a well-mixed aerobic environment was optimal for stimulating volatilization. Additional attachment sites for biofilm growth were not necessary when the pond water was amended (in this experiment with peptone). The addition of supplemental nitrate and nitrite to a pond water sample inhibited volatilization, but the concentrations used in the experiment, 0.1 and 1.0 M (1.4 g/L as nitrogen), were substantially above those normally found in evaporation ponds. The addition of supplemental sulfate to the sample caused a slight increase (10%) in methlyation in a peptone-amended water. As the concentration of selenium increased, the amount of DMSe released also increased, but the efficiency of removal, expressed as removal rate, decreased.

Field measurements were made using glass tubes submerged and pushed into the sediment of an evaporation pond at the Sumner Peck Ranch. DMSe was trapped on activated carbon. The water in the tubes was left unamended (controls) or was amended with casein at 0.2 g/L. A second set of columns containing sediment and water from the pond were transported back to the laboratory for controlled incubation. The field and laboratory columns were incubated for 142 days. DMSe produced in the laboratory columns was measured by headspace analysis with gas chromatography (GC)

and by activated carbon traps, elution, and atomic adsorption spectrophotometry (AAS). Similar results were obtained by both methods. The casein-amended pond water produced 22 and 28 times the amount of DMSe released by the unamended controls in the field and laboratory, respectively. A considerably greater amount of DMSe was produced (measured) in the field (Figure 6-1). This discrepancy between the field and laboratory studies may be due to the activated carbon tubes in the field adsorbing volatile selenium from the atmosphere outside the column. One serious gap in the data presented is the lack of measurement of the selenium inventory in the pond water during or at the completion of the incubation period. This would give an indication of the possible percentage removals that could be achieved *in situ*.

Although the addition of nutrients to evaporation pond water was shown to increase selenium volatilization significantly, particularly with the addition of a dairy by-product with a high protein content (casein), the benefits of selenium removal through such a system may well be offset both by the creation of eutrophic ponds and the added potential for attracting water birds.

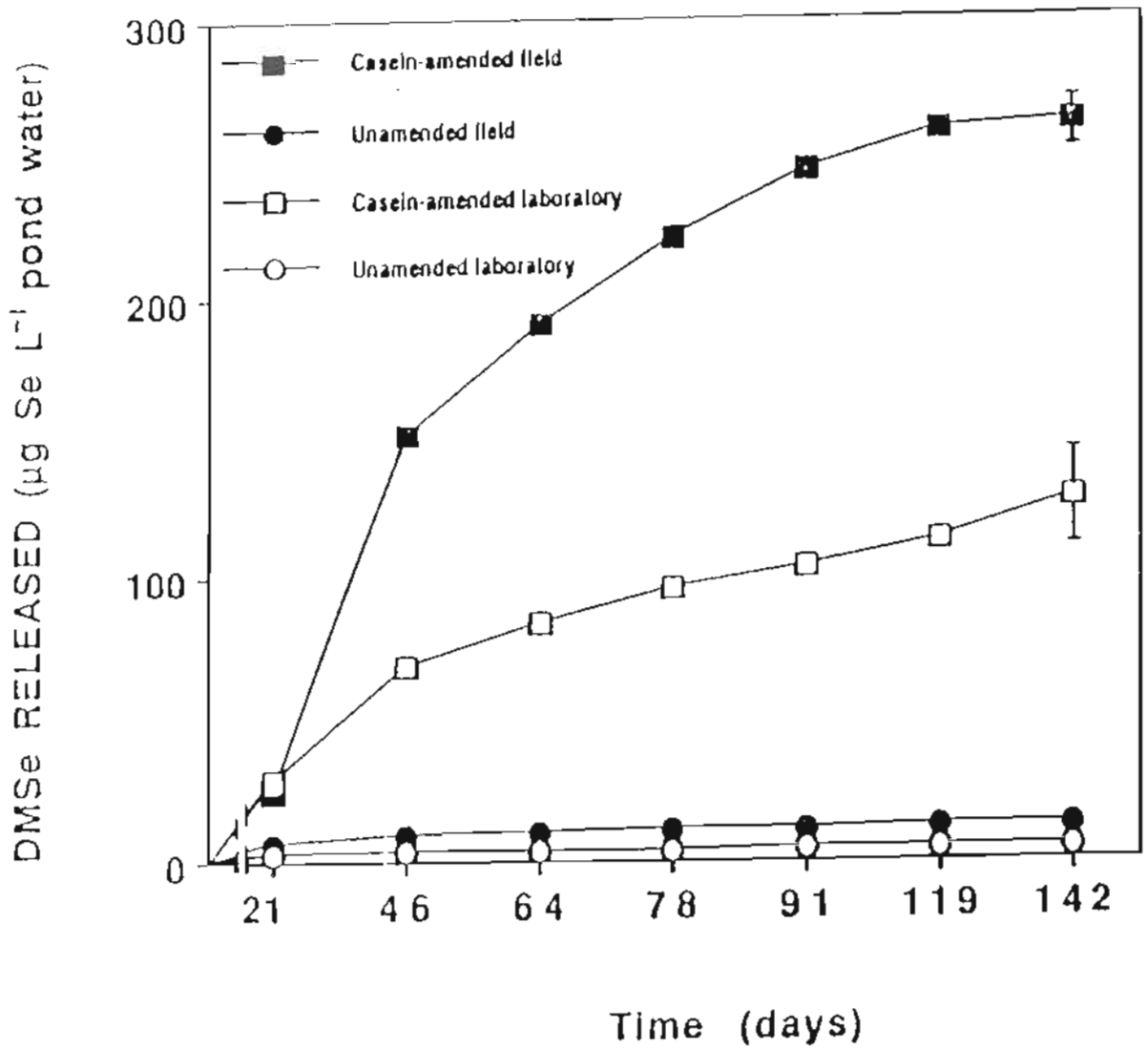

Fig. 6-1. Stimulation of Se biomethylation as a result of a single casein amendment (0.2 g C L^{-1}) in water columns incubated in the laboratory and the field.

(From Frankenberger 1990)

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DISSIPATION OF SOIL SELENIUM BY MICROBIAL VOLATILIZATION AT KESTERSON RESERVOIR

KESTERSON RESERVOIR STUDY

Microbial volatilization of selenium as a remediation technique for the soils at Kesterson Reservoir was investigated by W. T. Frankenberger. This was a continuation of work initiated in 1987. The main objective was to determine the most effective management practices for increasing the selenium volatilization from the soil. The final report (Frankenberger 1989) is comprehensive, covering the results of all field experiments conducted from 1987-1989. It is believed that indigenous soil fungi are the primary microorganisms responsible for the volatilization of the selenium. Dimethylselenide (DMSe) is the primary gaseous end product produced. The DMSe is released into the atmosphere from the soil and is dispersed. Studies concerning toxicity of DMSe were addressed in the previous chapter. Three different soils were studied: (1) cattail-enriched sediments (Pond 4), (2) upland habitat (Pond 11), and (3) San Luis Drain sediments.

Pond 4 Sediments

Pond 4 sediments had a high selenium concentration varying from 10 to 209 mg/kg (ppm) with a median of 39 mg/kg. This work was begun in July 1987. Sixteen 12ft x 12ft subplots (13.4 m^2) were amended with various combinations of organic matter and nutrients. Soil samples were taken from 0 to 6 inch depth and the gaseous selenium was sampled by placing an inverted box in the center of the subplot and trapping volatilized selenium in an

alkaline peroxide trap. Recovery of DMSe standards injected into the tubing leading to the alkaline peroxide trap was approximately 85%. Recovery of DMSe injected into the inverted sampling box was 18.4% (Frankenberger and Karlson 1988, page 8-56). The researchers speculated that DMSe was adsorbing to the interior surface of the sampling chamber or to the soil. The result of applying Teflon spray to the interior surface of the chambers was not reported. Due to low field recoveries of DMSe, it would appear that the volatilization data is qualitative at best. A more quantitative indication of selenium removal is provided by the soil analyses.

A summary of the results for the Pond 4 sediments is shown in Table 7-1. Selenium volatilization was highly temperature dependent with the highest rates occurring in the late spring and summer months. Emissions during the summer of 1988 were higher than those of the summer of 1989, presumably because of a lower selenium inventory in the soil and thus lower volatilization rates in 1989. All treatments enhanced the volatilization of selenium over background levels. The treatment of citrus peel + ammonium nitrate + zinc sulfate (Citrus peel + N + Zn) increased selenium emission more than any other treatment. The average emission rate was 42 times greater than background levels.

A minor criticism of the results given is the use of emission units of ug Se/h/subplot rather than ug Se/h/m^2 (or ft^2) as was used in the 1988 report. The use of subplot as a unit of measure makes the results specific to this study, whereas using

m^2 or ft^2 would be more general and more readily useful for extrapolation.

TABLE 7-1: SUMMARY OF RESULTS FOR POND 4 EXPERIMENTS. FOR SELENIUM GAS EMISSIONS AND SOIL SELENIUM CONCENTATIONS

Treatment	Se Emissions (ug/h/subplot) Average	Highest	% Se removed in top 6" 23 months	Rate Constant (1/month)	$t_{1/2}$* (years)
Background	35	107	N/A	N/A	N/A
Moist only	216	1867	48.7	0.0355	1.74
Cattail straw + N	144	523	44.1	0.0274	2.27
Cattle manure	150	1554	29.9	0.0119	5.46
Citrus peel	425	3980	40.1	0.0205	3.09
Citrus peel + N + Zn	1486	10827	62.1	0.0368	1.71
Casein	667	10036	68.5	0.0428	1.45
Gluten	599	5239	35.4	0.0284	2.22

* $t_{1/2}$ = the time required to convert half of the residual soil Se into DMSe

Note: All treatments received moisture and rototilling. (From Frankenberger 1989).

Samples of the upper 6 inches of the soil profile documented the decline in residual selenium content. Percentage removals in each subplot are listed in Table 7-1. The possibility of factors other than volatilization in the reduction of soil selenium were addressed. These possible factors are: (1) leaching of the soluble selenium below 6 inch depth, (2) dilution effect caused by rototilling, and (3) dilution effect caused by adding bulk

materials. The first two possibilities were addressed by conducting tests in closed systems (PVC containers). Volatilization was the only route of selenium removal in these systems and similar results were obtained. Also, work at Lawrence Berkeley Laboratory (LBL) has shown that there was no movement of soluble selenium below the 6 inch depth. To address the third factor of adding bulk materials, for the case of manure addition to a closed PVC container with soil from the Sumner Peck Ranch, bulk dilution would account for 12.7% of the decrease in the selenium inventory, while the remaining 86.3% can be attributed to volatilization.

Using first-order reaction kinetics and the soil selenium data, the rate constant and half-life times for volatilization of selenium from Pond 4 sediments were calculated (Table 7-1). Again, casein and citrus peel + N + Zn show the greatest promise to enhance the volatilization of selenium. The moist-only treatment also shows a low $t_{1/2}$ (1.74 years), essentially the same as the citrus peel + N + Zn (1.71 years). This is somewhat inconsistent with the volatilization data as emission rates for moist-only treatment were about 20% of the citrus peel + N + Zn rates. Using the $t_{1/2}$ of the moist-only treatment, the calculated time to achieve the cleanup goal of 4 mg/kg from an initial concentration of 39 mg/kg would be about 7 years.

Pond 11 Sediments

Pond 11 represented an upland habitat with lower soil selenium levels. Concentrations ranged from 1.17 to 8.63 mg/kg

with a mean value of 3.98 mg/kg. Table 7-2 is a summary of Pond 11 results. Emission rates were temperature dependent for both Pond 4 and Pond 11 sediments, with the highest rates of emission occurring in the summer of 1988. The addition of citrus peel and casein increased the rate of selenium volatilization over that provided by irrigation and tillage (moist-only treatment), but the addition of other carbon sources to these sediments was not as effective as the moist-only treatment in increasing volatilization. In terms of residual soil selenium, a lower percentage of selenium was removed by volatilization in Pond 11 than in Pond 4, but that was due to the low existing concentrations in Pond 11 soils. The concentrations in the subplots were all near or below the treatment goal of 4 mg/kg. The moist-only treatment was as effective as any other in reducing the soil selenium inventory.

San Luis Drain Sediment

Sediments were removed from the San Luis Drain, air dried, mixed, and placed in PVC boxes to 6 inch depth. Various organic amendments were used as treatments along with a background control. Summary data are given in Table 7-3.

Seasonal variation of methylation activity was also observed in these plots, with the highest rates of volatilization occurring in the summer months. Diurnal variation was also observed in this experiment with maximum volatilization occurring from 1 to 6 p.m., which correlates with high soil and air temperatures. The addition of albumin to the sediments was

most effective in stimulating volatilization (Table 7-3).

TABLE 7-2: SUMMARY OF RESULTS FOR POND 11 EXPERIMENTS

Treatment	Se Emissions (ug/h/subplot) Average	Se Emissions (ug/h/subplot) Highest	% Se removed in top 6" 23 months	Rate Constant (1/month)	$t_{1/2}$* (years)
Background	5.3	10.7	N/A	N/A	N/A
Moist only	31.2	158	17.6	0.0172	3.13
Barley straw	17.9	84	14.9	0.0095	6.08
Barley straw (C/N=5)	25.6	141	12.1	0.0174	3.32
Barley straw (C/N=20)	21.9	88	2.3	0.0046	12.55
Cattle manure	32.7	140	27.8	0.0097	5.97
Citrus peel	49.7	260	26.1	0.0130	4.43
Casein	153.5	1295	-	-	-

* $t_{1/2}$ = the time required to convert half of the residual soil Se into DMSe

Note: All treatments received moisture and rototilling.
(From Frankenberger 1989)

Soil samples showed a rapid decrease in the selenium inventory with 17.5 to 25.2 percent of the selenium being removed in 10 months (Table 7-3). A first-order equation was used to fit the soil selenium data, and rate constants and half-life times were calculated (Table 7-3). Based on these results, the moist-only treatment would be as effective as any other of the treatments and a cleanup time of about 8.5 years would be

estimated. Percentages of selenium removed based on volatilization analysis and on soil analysis were in good agreement.

TABLE 7-3: SUMMARY OF RESULTS FOR SAN LUIS DRAIN SEDIMENTS.

Treatment	Se Emissions (ug/h/subplot) Average	Highest	% Se removed in top 6" 10 months	Rate Constant (1/month)	$t_{1/2}$* (years)
Background	26	107	-	-	-
Moist only	284	1433	23.1	0.0224	2.58
Gluten	370	1960	20.6	0.0189	3.05
Casein	324	1397	25.2	0.0233	2.48
Albumin	410	3163	23.6	0.0219	2.64
Citrus peel	380	1601	24.0	0.0212	2.73
Citrus peel + Co	392	2928	21.8	0.0198	2.91
Barley straw + N	201	1048	19.4	0.0130	4.45
Cottonseed meal	300	1533	17.5	0.0148	3.90

* $t_{1/2}$ = the time required to convert half of the residual soil Se into DMSe

Note: All treatments received moisture and rototilling.
(From Frankenberger 1989)

Costs for Kesterson Soils Remediation

The costs associated with using microbial volatilization to remove selenium from the soils at Kesterson Reservoir were not addressed in the 1989 Final Report (Frankenberger 1989). Based on preliminary data, some cost estimates were provided in the 1988 Final Report (Frankenberger and Karlson 1988). Estimates

and price quotes for some of the carbon amendments are given in Table 7-4.

TABLE 7.4: COSTS AND SOURCES OF VARIOUS SOIL AMENDMENTS.

Material	Source	Costs
Citrus Peel	CCPi and Sunkist	$10/wet ton + $11/ton freight
Cattle manure	Coast Grain	$20/ton incl. freight $3/ton for spreading
Cottonseed meal	Harris Ranch	$250/ton
Soybean meal	Harris Ranch	$280/ton
Safflower meal	Harris Ranch	$180/ton

(Frankenberger and Karlson 1988)

A price quote for irrigation equipment for 1200 acres was given as $425,000 (Water-Ways). For a treatment of irrigation and tillage (moist-only treatment), bioremediation of the Kesterson soils would cost approximately $1.0 - $1.5 million per year ($833 - $1,250/acre-year). With the application of citrus at 50 tons wet weight per acre, the cost would increase to about $2.8 million per year ($2,333/acre-year).

PECK POND STUDIES

In a separate study funded by the California State Water Resources Control Board using Section 205(j) grant funds made available by the U.S. Environmental Protection Agency, Frankenberger performed similar soil selenium volatilization studies in a dried-up evaporation pond at the Sumner Peck Ranch

(Frankenberger et al. 1990). Plot treatments consisted of the addition of moisture only, citrus peel, cattle manure, barley straw, and grape pomace. Some of the plots also received ammonium sulfate (for nitrogen) and zinc sulfate. All plots were rototilled. In contrast to the Kesterson sediment studies, the addition of cattle manure provided the greatest increase in volatilization over background levels.

Soil Volatilization as a Drainage Water Treatment

The Frankenberger-Karlson selenium volatilization process was proposed as a method of drainage water treatment (Frankenberger et al., 1990). In the process, evaporation ponds are used either in series or singly to evaporate agricultural drainage water to dryness. The evaporation cycle is repeated until the peak soil selenium concentration in the treatment pond approaches 100 mg/kg (hazardous waste level). The treatment pond sediments are then subjected to the selenium volatilization process to reduce the selenium concentration back to an acceptable value (not specified). The entire process of filling, evaporation, and volatilization would then be repeated. Calculated land requirements are presented in Table 7-5 for series operation of the evaporation ponds, at an average selenium volatilization rate of 1.94 g Se/acre-day, and three drainage water production rates (0.25, 0.50, and 0.75 af/acre-year). Assumptions for Table 7-5 include 4.7 feet of evaporation per year, a 180-day effective volatilization period per year, and an additional land requirement of 20% of the combined surface area for evaporation and volatilization.

TABLE 7-5: LAND REQUIREMENTS FOR THE FRANKENBERGER-KARLSON PROCESS.

Drainage Production af/acre-year	Se conc. in Drainage ug/L	% of total acreage required for evaporation and volatilization %
0.25	10	7
	30	9
	50	11
	70	12
	100	15
	300	29
	500	40
0.50	10	13
	30	17
	50	20
	70	22
	100	27
	300	47
	500	60
0.75	10	19
	30	23
	50	27
	70	31
	100	36
	300	59
	500	72

(Frankenberger et al. 1990)

The long-term effect of salt build-up on microbial volatilization has not been determined. However, there is preliminary evidence to indicate that extremely high salt concentrations can be tolerated without diminishing volatilization efficiency.

Estimated Costs of Frankenberger-Karlson Process

Estimated costs of the Frankenberger-Karlson process are

presented in Table 7-6. For this table, the following assumptions were used:

1. Manure costs $8/ton and is applied at 15 tons/acre-year.
2. Irrigation water costs $17.50/af and is applied to the treatment area at 0.5 af/acre-year.
3. Labor and equipment (tractor) costs are $27.65/acre-year for each acre treated.
4. Pond construction is $1,500 per acre of pond.
5. Discount rate is 10% over a 40-year useful life.

TABLE 7-6: COSTS OF THE FRANKENBERGER-KARLSON SELENIUM VOLATILIZATION PROCESS. ($/af of drainage water)

Se conc. in drainage water	Income loss from nonproductive land used for evaporation and volatilization	
ug/L	$50/acre	$100/acre
50	184	209
70	216	245
100	267	302

(Frankenberger et al. 1990)

This analysis neglects the costs for monitoring, even though monitoring is said to be an important part of the process. The costs for wildlife management at the ponds are also neglected. Further, the cost of final disposal of accumulating salts is not addressed.

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SOIL COLUMN TESTS FOR SELENIUM REMOVAL

A study on the effectiveness of soil columns for the removal of selenium from drainwater was conducted in 1989 by Dr. Oleh Weres, Sonoma Research Company (Weres 1989). The research was conducted at Lawrence-Berkeley Laboratory with support from USBR. The study objectives were to: (1) model selenium removal by submerged soil columns at laboratory and pilot plant levels; (2) describe the mechanisms involved and identify influencing factors; (3) project from this data the applicability of the process on a prototype plant scale; and (4) develop preliminary cost estimates.

The aquatic ecosystem in the Kesterson Reservoir has been shown to be highly productive of organic matter due to the concentration of nitrate and other nutrients in the drainwater. (Horne and Roth 1989). Algae growth in the pond water tends to maintain aerobic conditions, while the sediment accumulation at the pond bottom becomes anoxic. The resulting ecosystem with a reducing environment favors denitrification. The organic matter in the pond sediment is identified as the reducing agent, while the nitrate is the major oxidizing agent.

LABORATORY AND PILOT PLANT TESTS

Based on the observations at Kesterson Reservoir that very little selenium passed through the underlying soils to the shallow aquifer beneath the ponds, and that most of the selenium removed from the water was captured and retained in the upper few inches of soil, the removal process was laboratory tested, and

then pilot tested for 100 days in a 31-inch diameter column with a volume of 150 gallons. Weres reported an apparent blocking effect of nitrate on selenium removal. The data showed a strong correlation of Se removal to feedwater nitrate concentration. Laboratory experiments demonstrated over 95% removal of selenate from the soil column drainwater effluent in the absence of nitrate. When nitrate was added to the soil column, selenium removal was reportedly blocked, an effect which was found to be reversible. A wet sterilization of the soil completely halted the selenate removal from water. This was interpreted to indicate that the process is microbiological. Conversely, the sterilization had no effect on selenite removal, implying that this process is inorganic in nature.

Laboratory experiments were also conducted to determine the ratio of organic matter to nitrate that would result in effective selenium removal, and a mathematical expression was derived to express this relationship. The organic matter/nitrate relation was extended to describe the maximum average rate of water percolation through the soil conforming to good selenium removal.

LARGE-SCALE PLANT PROJECTIONS

Weres proposed this selenium treatment system as applicable both to design of water treatment ponds, and to Kesterson Reservoir. In order to start up an engineered treatment pond, it was suggested that some organic matter might have to be added; however, the process should be sustained by organic matter produced by pond algae and vegetation.

The average standing vegetation in the permanently flooded area of Kesterson Pond 5 was measured at 1.8 kg/m^2 on a dry weight basis (Horne and Roth 1989), and the excess nitrate and sufficient phosphate in the drainwater were identified as contributing to high biological productivity. While the pilot plant contained only about 6 inches of organic sediment to affect the removal of nitrate and Se from the water, Weres postulated that a well-designed treatment pond would contain some three feet of mineral soil beneath the black sediment which would remove additional selenium from the water.

A projected treatment system was sized for evaporating about 8,000 af/yr of drain water based on an average percolation rate of 100 ft/yr, and an average evaporation rate of 5 ft/yr. On this basis, it was predicted that the treatment pond would be about 80 acres, followed by five evaporation cells in series with a total area of 1,500 acres. The first and largest evaporation cell would support sufficient vegetation, when harvested, to provide the organic feed to the water treatment pond. This process would depend upon the development of sufficient biomass in the first evaporation pond to provide the carbon source and other nutrients required to fuel the water treatment pond. It would also require that this material be chopped up or macerated sufficiently to aid in its easy assimilation into cell mass. Both of these qualifications are somewhat problematical at this stage of process development. Further, in order for this process to be viable, the selenium treatment phase would have to be sufficiently reliable to prevent selenium accumulations above 5

ug/L (established as the exposure limit for wildlife) in the evaporation pond cells.

TREATMENT COSTS

The preliminary construction cost for the treatment pond only was estimated at $50,000 per acre, and the annual amortized capital cost plus operating and maintenance costs were estimated at $10,000 per acre per year. Thus for an 80-acre treatment pond treating 8,000 af/yr, the cost was indicated at about $100/af. Weres stated that this cost should be used to compare with estimates for other treatment processes, since other costs would be the same. This reasoning appears to be speculative, and at best would apply only to processes with similar facilities such as the evaporation ponds for final water treatment and disposal. A value of $100/af to $150/af was also quoted as the cost for selenium removal from the sediment. No backup information including interest rate used was provided for calculating the treatment pond costs or the costs of selenium removal from the sediment. Operation and maintenance costs, including the proposed growing and harvesting of organic feed for the treatment process, also need to be evaluated further.

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ATTENUATION OF SELENIUM IN IRRIGATED SOILS

Most schemes for treating agricultural drainage consist of designing a process to remove selenium and other substances of concern from a single influent generated by the drainage of extensive networks of buried perforated pipe. In contrast, the research conducted by Neal and Sposito (1988a, 1988b) on selenium attenuation in irrigated soils was an attempt at source reduction, (i.e., immobilizing selenium within the soil profile thereby decreasing its concentration in subsurface drainage).

The research on selenium attenuation identified several variables within the irrigated soil profile which apparently influence the transport of selenium. Ancillary objectives were the investigation of the transformation and speciation of selenium, and how the different forms interact with surfaces within the soil profile. Identifying the conditions under which attenuation is enhanced is a prerequisite to formulating farm managerial practices which may reduce the amount of selenium leached into the subsurface drainage flow.

EXPERIMENTAL DESIGN AND RESULTS

Preliminary laboratory experiments confirmed that selenate is the predominant inorganic species in the alkaline soils of the western San Joaquin Valley. Investigating the behavior of selenite and selenate in soil sorption studies revealed selenate was the least reactive towards soil surfaces and consequently more mobile. In contrast, selenite predominates in acidic soils, and tends to adsorb to soil surfaces.

Soil column experiments were conducted under "glass-house" conditions to monitor the movement of selenium within the soil profile. The two soil types investigated, Panhill and Panoche series, were sampled to a depth of 2 m in four uniform increments of 0.5 m each. Soil from each increment was homogenized by mechanical mixing, and then inserted into the test columns. A particle size analysis revealed that the Panhill soil profile had equal distributions of sand, silt, and clay. The Panoche soil had higher percentages of sand, especially in the 0.5 to 1.0 m level. While electrical conductivity of both soils increased with depth, the Panoche soil contained much greater values throughout the profile. In addition, the Panoche soil also contained a higher inherent selenium concentration.

Each experiment required four columns for each soil type, representing the four arbitrary strata sampled. The input variable was influent water composition, consisting of variations of simulated agricultural drain water.

In the first set of experiments, three columns were regularly "irrigated" with a fixed quantity of simulated drain water over the course of two weeks. The first column served as a control, the second was fed nitrate-free influent, while the input water of the third was supplemented by a soluble carbon source, glucose. Leachate from the top column was measured, then allowed to flow into the second column and so on. Samples of leachate from each increment were analyzed for selenium

concentration and speciation, redox potential, and soluble manganese (indicative of redox conditions which favor the reduction of selenate to selenite).

After the two-week test period, the soil from each column was analyzed for soluble selenium and nitrate. Total selenium was measured by Inductively Coupled Plasma spectroscopy. Selenite and selenate were measured by Hydride Generated Atomic Absorption Spectrophotometry. Like other investigators working in agricultural drainage treatment research, Neal and Sposito assume that the quantitative difference between total selenium and selenate/selenite represents unidentified organic selenium species (-2 oxidation state), which neglects the possibility of elemental selenium.

The results of the short-term irrigation column study were: (1) the chemical composition of the input water influenced the selenium speciation of the leachate; (2) the absence of nitrate in the input water resulted in negligible transformation of selenium in the soil profile, in contrast to the results of the soil column study; (3) selenium in the leachate from the glucose-fed column was predominately of the "organic" form; (4) the concentration of soluble manganese increased 100-200 times in the leachate of the glucose-fed column, indicating a drop in redox potential relative to the other two columns. [Redox potential was measured on saturation extracts, not soil, and exhibited only slight variation during the two week period]; and, (5) the addition of glucose resulted in significant reductions in nitrate within

the soil column, perhaps by microbial activity.

In a follow-up study, long-term irrigation conditions were tested in similar column experiments again using Panoche and Panhill soil. Seven equal dosages of simulated drain water were applied over a 9 week period. Again, the input variable was input water composition. Of the four columns tested, the first served as a control, the second was supplemented with glucose, the third was supplemented by ferrous sulfate, and the fourth was nitrate-free.

The justification for adding ferrous sulfate to the input water of one column stems from the research by USBR on ferrous hydroxide as a reagent capable of reducing selenate to elemental selenium (see Chapter 11). Although the reaction requires a hydroxide source, none was provided in the soil column experiments. It is doubtful, therefore, that the reaction could have occurred within the soil profile.

The results of the long-term irrigation column study were as follows: (1) enhanced selenium mobility was observed in the ferrous sulfate amended column and in the nitrate-free column; (2) in the Panhill soil column, the addition of glucose resulted in the depletion of selenium throughout the column; and (3) in the Panoche soil (high inherent selenium concentration), the glucose amended column revealed higher soil selenium concentrations than the control.

Under control conditions, selenium was leached no further than half the column distance in both soil types. The proposed mechanism(s) responsible for the observed attenuation include: reduction processes (chemical or microbial mediated) which transform selenate into more reactive, less mobile forms; soil adsorption processes (selenite-specific); and/or aerobic microbial transformation into volatile and non-volatile species.

Addition of a carbon source resulted in the transformation of selenate to "organically associated" selenium species. Like the control column, the glucose-fed column contained elevated concentrations of soluble mangnanese and a depletion of nitrates within the profile indicating relatively low redox potentials.

The selenium mobility observed in the iron-supplemented and nitrate-free columns was interpreted to indicate conditions of higher redox potentials. The absence of soluble manganese in these columns reinforces this interpretation.

Adding a carbon source to influent water reportedly reduced soil nitrate concentrations to trace levels by flushing out relatively large quantities in the initial leachate. This has serious implications for those treatment processes in which nitrate is an inhibiting substance. An estimate of the mass balance of selenium in the long-term irrigation column experiments revealed that the greatest loss occurred under control - and glucose-amended conditions in which selenate and organic selenium were the predominant soluble species. Microbial volatilization was cited as the probable major cause for

selenium loss, although the experiment was not designed to collect and analyze gaseous products. However it is suggested that the major loss would be due to soluble selenium species escaping in the column effluent. Sorption processes were also cited to account for the loss observed in other columns.

The research on selenium attenuation in irrigated soils requires additional laboratory experimentation and field testing. Because simulated agricultural drainage water was used in the column experiments, the research does not address how attenuation might occur under standard irrigation conditions (using either ground or imported water with low levels of selenium). This must first be determined before effective field management strategies for selenium attenuation can be developed.

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SELENIUM REMOVAL BY ADSORPTION ON IRON FILINGS (THE HARZA PROCESS)

In 1985, Harza Engineering Company began investigating the effectiveness of Harza's patented heavy metals adsorption process for removing selenium from agricultural drainage water. Compared to other proposed strategies for agricultural drainage treatment, the Harza Process is relatively simple: as drainage flows slowly through a bed of "activated" iron filings, heavy and toxic metals are adsorbed on iron filing surfaces and removed from solution.

The patent for the process contains data confirming its effectiveness for removing nickel, copper, lead, hexavalent chromium, cadmium, selenium, and arsenic (Mayenkar 1986). No sludge is produced because the process is based on adsorption. Before the bed becomes exhausted, the iron filings are replaced, activated, and returned on-line. The spent bed material is claimed to be non-toxic and can be disposed by recycling back to the metal manufacture industry or by landfilling (Mayenkar 1986).

The selenium removal research conducted by Harza Engineering was funded by Panoche Drainage District and the San Joaquin Valley Drainage Program. Reports prepared include a brief initial selenium removal study (Harza 1986), a discussion of experiments designed to investigate the chemistry of selenate removal by the Harza Process (Zeltner and Patlak 1988), and a summary of laboratory and pilot plant research submitted to the San Joaquin Valley Drainage Program (Harza 1989).

IRON FILINGS: CHARACTERISTICS AND PRETREATMENT

As described in the Harza patent, degreased iron filings from the metal working industry are the material of choice for the adsorbent bed. Particle size is an important design criterion: the majority of filings should range from 0.48 to 0.70 mm for optimum performance. The filings should be over 50% iron; higher percentages of iron improve bed performance.

The activation step is described as the formation of an oxyhydroxide adsorptive surface coating on the filings resulting from aeration and hydration. It is accomplished by slowly filling the bed with water in the presence of air. The contact period for activation can be measured by the vertical velocity of water through the bed. For the filing sizes mentioned earlier, a rate of about 1 inch per hour to 2 feet per hour is recommended. Once the iron surfaces are activated, the bed remains submerged to inhibit the formation of ferric oxide (hematite). Data on batch adsorption studies presented in the process patent indicate that adsorption occurs slower and at greatly reduced efficiencies if the iron filings are not activated (Mayenkar 1986).

Bench-scale studies on activated filings indicated that optimum activation conditions occur when the initial water entering the bed has a pH between 6 and 10, and a temperature between 15°C and 20°C. Apparently, the wastewater to be treated can also be used in the activation step, provided its temperature and pH are within the stated ranges. Adsorption performance is enhanced if the temperature and pH of the wastewater remain

similar to those specified for the activation step.

The adsorbent iron species formed during activation is believed to be ferric hydroxide oxide (also known as iron oxyhydroxide or ferric hydroxide), a hydrated form of ferric oxide. Its color ranges from red to brown to brownish black. It is used as an adsorbent in chemical processing (Windholz 1983). The feasibility of using iron-bearing waste liquids as source materials for the precipitation of amorphous iron oxyhydroxide in trace element removal processes was assessed in a study prepared by Stanford University (Leckie et al. 1980).

FIELD AND BENCH SCALE STUDIES

Field testing of the Harza Process took place at a small pilot plant located in the Panoche Drainage District. The feed-water was typical of westside subsurface drainage (i.e., the dominant form of selenium is selenate; its concentration, along with other drainage constituents, varies with respect to time).

The plant, which operated around the clock for 4 months, consisted of three 55-gallon drum reactors, a 4-inch reactor column, and continuous sampling equipment. Contact times ranging from 1/2 to 6 hours were tested. Samples of influent and effluent were analyzed for total selenium and pH. Periodic analyses were conducted for selenate and selenite speciation, suspended solids, total iron, and boron (Harza 1986).

While the pilot plant was in operation, bench-scale column exhaustion tests were performed to assess the selenium adsorptive

capacity of the iron filings used in the field. To accelerate conditions leading to breakthrough, the drainage water was spiked with either 25 mg/L selenite or 35 mg/L selenate. Influent and effluent selenium concentration was measured by the Inductively Coupled Plasma (ICP) method (Harza 1986).

Long contact periods resulted in higher selenium removals: over 85% for a six-hour contact time. A direct relationship reportedly exists between influent selenium concentration and the resulting percentage of removal. Although breakthrough was not observed in the bench-scale tests, the data were interpreted to predict that the iron filings will be effective for about 40 years, provided the quality of the drainage water remains relatively constant. It is claimed that 1000 lb of filings could remove 1.1 lb of selenium.

One unforeseen development occurred during the field testing of the Harza Process: the filings eventually solidified in the bottom of the bed where the feedwater enters the column. This caused large headlosses, diminished flows, and possible channeling through the bed. In addition, the effluent generated by the field and lab reactors contained between 5 and 50 mg/l of iron, indicating that some dissolution of filings was occurring (Harza 1986).

THE MECHANISM BEHIND THE HARZA PROCESS

Additional laboratory studies were conducted in the attempt to reveal: (1) what species are formed on the iron surfaces, (2) what mechanism is responsible for removing selenium from water,

and (3) what causes the iron filings to agglomerate after prolonged use. The first objective was unsuccessful despite repeated attempts at detecting surface species with several analytical techniques. The second objective was addressed by column studies using either selenate-spiked deionized water or agricultural drain water. The columns, made from transparent plastic tubes to allow for visual inspection of the filing bed, were initially operated in an upflow mode. The water entering the column is in equilibrium with air; as it passes through the column, its dissolved oxygen content was observed to decrease.

Shortly after start-up, a thin rust-colored layer was observed at the bottom of each filing bed, indicating the presence of Fe (III) species. Above this layer, the iron filings changed color slightly from a very dark brown to dull black. In columns treating agricultural drain water, a bluish-green precipitate was observed above the top of the filing bed and in the column's effluent jar. The effluent from all columns was observed to have a rusty tint. The effluent from columns treating agricultural drainage also contained various precipitates which were not identified.

One experiment to determine whether oxidizing or reducing conditions were responsible for selenate removal involved purging selenate-spiked deionized water with either nitrogen or oxygen prior to passing through the test columns. High selenate removals (over 90%) were observed for both conditions.

Another experiment was a batch-adsorption study which contacted either aerated or nitrogen-purged iron filings with a selenate-spiked solution. Two types of iron filings were used (non-activated and activated). The solids produced from the nitrogen-purged batch tests were dark black; those from the aerated tests were orange-red. The selenate removal for all filings tested exceeded 95%. This finding contradicts the experimental results discussed in the Harza Process patent which correlate significant heavy metal adsorption removal with a pretreatment activation step (Harza 1986).

Samples of iron filings taken at various levels within a test column were digested for selenium analysis. Two columns were compared with respect to their vertical selenium distribution: one had "aged" sufficiently to possess the rust-colored layer, the other had not. In the aged column, selenium was found to concentrate in the rust-colored layer, the zone of initial contact between iron filings and influent. Above this layer the selenium concentrations were reportedly below the detection limit of the ICP method. In the other column, selenium concentrations throughout the column were also below the detection limit. These findings were interpreted as follows: the rust-colored layer indicates the formation of ferric hydroxide oxide, the compound believed to adsorb heavy metals thereby removing them from solution. Low selenium levels elsewhere in the column are reportedly evidence of weak physical adsorption; the rust-colored layer represents a zone of strong chemical adsorption. The hypothesis that this layer is an

exclusive zone of iron oxyhydroxide formation contradicts the information contained in the Harza Process patent, which states that the activation step creates iron oxyhydroxide surfaces throughout the bed.

Attributing the selenate concentrating layer exclusively to the formation of iron oxyhydroxide in the absence of surface speciation evidence is speculative, especially since nitrogen-purged batch adsorption tests demonstrated high selenate removals without the production of rust-colored solids. An alternative explanation is that the column was sampled at a time when the rust-colored layer coincided with the initial presence of the adsorption zone within the column.

FILING BED SOLIDIFICATION

The problem of bed agglomeration was experienced in both pilot plant reactors and laboratory columns, even those which processed selenate-spiked distilled water. The filing beds in the pilot plant reactors eventually solidified in the zone where influent contacts the bed. In the laboratory column studies, particle agglomeration apparently occurred throughout the bench-scale filing beds.

Particle agglomeration is not dependent on the source of influent used because it occurred in columns receiving spiked distilled water. Consequently, it cannot be attributable to precipitate formation such as carbonate scaling.

Based on reactor pH and redox potential, the predominant iron species throughout the filing bed is magnetite, a ferro-magnetic solid (Harza 1989). The activation step was initially believed to generate ferric hydroxide oxide surfaces on the iron filings as water first passed through the bed in the presence of air (Harza 1986). The latest report by Harza (1989) suggests that the ferric hydroxide oxide is formed exclusively within the zone of initial contact of influent and filing bed. In the field reactors, it was this zone which eventually solidified, although additional particle agglomeration could have occurred elsewhere.

Bed hardening was postulated to result from the formation of ferromagnetic species (e.g., magnetite) within the bed which bonds the filings together in a strong magnetic field (Harza 1989). This is speculative, and more research is needed to determine what causes bed solidification. Options for mitigating its effects are few if it is proven to result from magnetism.

APPLYING THE HARZA PROCESS IN THE BINNIE PROCESS

An attempt to detoxify agricultural drainage using the Harza Process was made by EPOC AG at their pilot plant on Murrieta Farms (EPOC AG 1987). A reactor packed with steel wool which had been degreased with trichloroethane was activated with oxygenated drain water during a three-hour contact period. No significant removal of trace metals was observed in subsequent operation. Because the bed was packed with steel wool and not iron filings of specified size range, it is doubtful that selenium removal could have been obtained under these conditions.

Another attempt was made using iron filings supplied by Harza Engineering Company. A test column was operated according to instructions provided by Harza for processing effluent from a third-stage fixed film biological reactor packed with iron filings. A second experiment was conducted to process raw drain water. Determinations of soluble and total selenium entering and exiting the column were made to assess the performance of the test column. In processing biological reactor effluent, the column removed particulate selenium but allowed soluble selenium to pass. In effect, it operated as a filter.

In contrast with the results observed at Harza's pilot plant, no selenium removal was reportedly obtained when the test column processed "raw" drain water. The Harza pilot plant feedwater contained relatively low concentrations of nitrate and sulfate, unlike the Binnie pilot plant feedwater. In EPOC AG's report on its pilot plant operation (1987), it was suggested that high levels of nitrate and/or sulfate inhibit selenium adsorption onto activated iron filing surfaces. Additional evidence of inhibitory substances is contained in the Stanford study, in which sulfate, chromate and arsenate were determined to compete for the same adsorption sites as selenate (Leckie et al. 1980).

ESTIMATED TREATMENT COSTS

A treatment facility using the Harza Process requires: embankments to form the beds, sand for supporting the filings, and flow collection and distribution systems. Iron filing bed life, estimated to range between 2 to 15 years, is a function of

solidification and exhaustion reactions. At a cost of $100/ton, filings constitute 80% to 95% of total treatment costs. For a removal efficiency of 75% and a bed life of 5 years, Harza (1986) estimates that the treatment cost will be $120/af, excluding the cost of land. Continued research on the phenomenon of iron filing bed solidification and its effect on bed life expectancy is essential to confirm this treatment cost estimate.

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SELENIUM REMOVAL BY CHEMICAL REDUCTION (THE FERROUS HYDROXIDE/SELENATE REACTION)

The reaction in which freshly made ferrous hydroxide reduces selenate to elemental selenium was discovered by chemists in the Chemistry, Petrography, and Chemical Engineering Section of the U. S. Bureau of Reclamation (USBR) Denver Office. The chemistry of the reaction is discussed in a technical article by Murphy (1988). Aspects of its applicability in agricultural drainage treatment are discussed in five reports submitted to the San Joaquin Valley Drainage Program by USBR scientists (Moody et al. 1988; Price and Eisenhauer 1988; Moody, Howard, and Murphy 1988; Rowley 1989; and Rowley, Moody and Murphy 1989).

THE FERROUS HYDROXIDE/SELENATE REACTION

The reaction between sodium selenate and ferrous hydroxide produces elemental selenium, iron oxide, sodium hydroxide and water. The reaction rate is a function of pH; optimum conditions require a pH range of 8 - 10. The resulting oxide species depends on the molar ratio of ferrous hydroxide to sodium selenate used: magnetite (9:1) and hematite (6:1). Red, amorphous elemental selenium is captured within the iron oxide precipitate. Because selenium is insoluble in most acids which dissolve iron oxide, it can be recovered from the iron oxide sludge (Murphy 1988).

Laboratory experiments conducted in the summer of 1987 by USBR chemists generated information on reactor sizing and operation (e.g., ferrous hydroxide concentration and pH) for

selenate removal under different environmental conditions (e.g., temperature and feedwater composition) (Moody et al. 1988).

Over 50 different experimental conditions were tested using either selenate-spiked deionized water or agricultural drainage water. Samples were deoxygenated with argon gas before and during the reaction. In selenate-spiked deionized water, fresh ferrous hydroxide removes 99% of the selenate from solution within minutes. Increasing the temperature by 10°C doubles the reaction rate. The reaction rates were observed to be much slower in experiments using drainage water and/or aged ferrous hydroxide (made over 24 hours before use) (Moody et al. 1988).

In the fall of 1987, USBR chemists tested the reaction in the field, to verify the results obtained in the laboratory. The reaction between ferrous hydroxide and selenate ions occurred in a temperature-controlled (30°C) reactor tank. After reacting for three to six hours, the suspension was pumped to either a gravity settler or a magnetic separator. Settling velocity measurements were obtained in the former; the magnetic separation capabilities of the precipitate were observed in the latter. Samples of supernatant and sludge were taken the next day for chemical analyses for selenium and selected trace metals.

FIELD TESTING OF THE FERROUS HYDROXIDE/SELENATE REACTION

In field verification experiments, reactor pH and temperature varied from 8.4 to 9.6 and 10°C to 30°C, respectively; ferrous hydroxide dosage ranged from 3.25 to 11.25 millimol per liter (mmol/L). Nitrogen gas was used to lower

dissolved oxygen to a constant 6.4 mg/l before all experimental runs. Since each mg/l of dissolved oxygen consumes 0.20 mmol/l ferrous hydroxide, approximately 1.25 mmol/l were unavailable for selenate reduction during the field tests.

Analysis of the chemical sludges produced during the field tests revealed accumulations, and hence removal from water, of selenium, chromium, and nickel. The rate of selenium removal was much slower than anticipated, even in tests operating at high ferrous hydroxide dosages (11.25 mmol/l) and temperature (30°C). Samples of reactor water in these tests were filtered through a 0.45 micron filter to remove residual suspended iron oxides prior to selenium determination. Under these conditions, about 90% of the selenate was removed in one hour; over 95% in 3 hours. The slower rate was attributed to substances in the drain water which inhibited the reaction.

THE EFFECT OF INHIBITING SUBSTANCES

Laboratory bench-scale experiments conducted in Denver during the spring of 1988 identified several substances which inhibit the chemical reduction reaction. In addition to verifying that dissolved oxygen consumes ferrous hydroxide, these experiments identified nitrate and bicarbonate as major inhibitors. While the former oxidizes ferrous hydroxide, bicarbonates temporarily combine with it to form a precipitate which eventually dissolves. Other substances which were discovered to slow the reaction to a lesser degree are silica, hardness, and trace metals.

During the inhibitor identification experiments, seven constituents found in agricultural drain water were varied in spiked deionized water: dissolved oxygen, nitrate, silicate, bicarbonate, hardness, trace metals, and phosphates. Based on the resulting data, an empirical equation for the rate of selenium removal was developed and manipulated to generate a relationship between optimum ferrous hydroxide dosage, reactor detention time and product water selenium concentration. As expected, both dosage and reactor time increase as product selenium concentration decreases.

The derivation of the empirical equation contained in the draft report (Moody, Howard, and Murphy 1988) was corrected and revised by Moody (1990). Crucial to this expression is an empirically derived variable (labeled "a") defined as a natural logarithmic function of the seven inhibiting substances evaluated. Fluctuations in the concentration of these substances can change the value of "a" dramatically, thereby increasing or decreasing the ferrous hydroxide dosage required. In the absence of dissolved oxygen, nitrate, and bicarbonate and in the presence of hardness, silicates, and trace metals, a baseline value of "a" was determined for design purposes. With nitrate and bicarbonate concentrations of 32 mg/l as N and 183 mg/l, respectively, "a" decreases by a factor of 170, and the amount of ferrous hydroxide required increases by a factor of 13. Because of its importance in design calculations, experiments similar to those which calculated the value of "a" using spiked deionized water should be

replicated using actual drain water.

The ferrous hydroxide used in the reaction is generated by the rapid reaction following the addition of a hydroxide source to ferrous sulfate. Lime and caustic soda were evaluated as possible hydroxide sources; lime costs about half as much as caustic soda. The cost effectiveness of the process is largely a function of feedwater composition. Without pretreatment to remove nitrate, dissolved oxygen, and bicarbonate, the chemical cost alone makes the process prohibitively expensive.

PRETREATMENT OPTIONS

Experiments focusing on chemical pretreatment processes were discussed in a draft report (Rowley 1989). Bicarbonate removal was accomplished with either acidification with aeration or lime precipitation, while dissolved oxygen was removed with sulfur dioxide. Denitrification experiments using a proprietary nitrate-specific ion exchange resin on simulated agricultural drain water revealed low nitrate capacities and frequent regeneration cycles.

Bench-scale biological denitrification was judged to be very difficult to test and was not attempted even though other scientists and engineers engaged in selenium removal research have reported success with such bench-scale units (e.g., EPOC AG 1987, Oswald et al. 1990). It is unfortunate that no attempt was made by USBR researchers to experiment with biological denitrification. The effluent from these units contain at most trace levels of nitrate and dissolved oxygen. As such, biological

denitrification would appear to be an excellent choice of pre-treatment. The ferrous hydroxide reaction can also be tested as a polishing step to further reduce selenium levels in the effluent from anaerobic biological selenium reduction reactors.

FERROUS HYDROXIDE SLUDGE AND WASTESTREAM PRODUCTION

The application of the ferrous hydroxide chemical reduction reaction requires pretreating the drain water to remove, at a minimum: dissolved oxygen, bicarbonates, and nitrates. Possible chemical pretreatment processes include the use of sulfur dioxide for dissolved oxygen removal, and two forms of bicarbonate removal: acidification and lime precipitation. Dissolved oxygen can also be removed by vacuum deaeration or by adding other deoxygenating reagents (e.g., sodium sulfite or hydrazine) (Rowley 1989).

The downward pH shift caused by the formation of sulfuric acid in the reaction between dissolved oxygen and sulfur dioxide produces a side benefit of adjusting carbon equilibrium conditions to favor the conversion of bicarbonates to carbon dioxide gas. In this dual removal step, the major design challenge is to cost effectively remove the carbon dioxide gas without reintroducing dissolved oxygen. Under these conditions, the only "wastestream" is carbon dioxide gas. Bicarbonate removal via lime precipitation, in contrast, generates a non-hazardous sludge which can be easily dewatered on sand drying beds.

The volume of iron oxide sludge produced by the ferrous hydroxide/selenate reaction is estimated to equal two percent of the treatment flow (Moody, Howard and Murphy 1988). In the verification experiments, sludge volume amounted to almost 20% of the reactor's contents (Moody et al. 1988). Although information was gathered on iron oxide floc settling velocities, no tests were performed on sludge dewatering (Moody 1990). As such, the proposed design sludge flow amounting to 2% of the treatment flow is more of a goal than an accurate estimate.

Because the iron oxide sludge will be rich in selenium, chromium, and nickel, it will be a hazardous wastestream requiring special treatment, handling, and disposal. The concentrated sludge can be acidified to dissolve the iron oxides, leaving behind particles of elemental selenium. The remaining acid soluble metals can be selectively precipitated and removed by solids separation processes. Comparison of the cost of this treatment with the expense of hazardous waste disposal of concentrated untreated sludge will decide its feasibility.

ESTIMATED TREATMENT COSTS

The cost estimate equations developed in the preliminary process design draft report (Moody, Howard and Murphy 1988) were derived from cost analyses of treatment facilities of various capacity using dosages and reaction times ranging from 2.5 to 10.0 mmol/l and 10 minutes to 4 hours, respectively. The treatment costs calculated for processing various flowrates using different dosages and reaction times assumed a 50-year plant life

and used an interest rate of 9-3/8 percent. The treatment costs are a function of chemical dosage and reaction time. The final cost estimate equations, which have optimum chemical dosage and reaction time as input variables, were based on the resulting linear relationship between treatment flowrate and the two major cost variables.

The proposed treatment cost estimates generated in the draft report, and later revised by Moody (1990), are for conditions of low ferrous hydroxide dosages (0.8 mmol/L) and long reaction times (19 hours) in the absence of dissolved oxygen, nitrate, and bicarbonate. The feasibility of these untested conditions rely upon an extrapolation from 2-hour experiments with a dosage of 10 mmol/L ferrous hydroxide. Verifying this assumed feasibility should have high priority in future research on this chemical reduction process.

The low optimum dose of 0.8 mmol/L, while untested, is only slightly below the range utilized to develop the chemical cost equation. As such, chemical costs estimated by this equation should be valid. However, applying the equipment cost equation based on short reaction times to the design value of 19 hours will almost certainly underestimate actual equipment costs, especially since the reactor requires an impermeable roof to minimize the diffusion of atmospheric oxygen into the feedwater while inside the tank.

The required dosage of ferrous hydroxide strongly influences total treatment costs. Using lime as the hydroxide source, a

dosage of 0.8 mmol/l costs approximately $30/af for chemicals alone. If the feedwater is not pretreated to remove oxygen, nitrates, and bicarbonates, then the dosage increases to around 10.5 mmol/L and chemical costs soar to above $400/af, and over $700/af using caustic soda. In the absence of dissolved oxygen, nitrate, and bicarbonate, the combined chemical and equipment cost of reducing selenium to 4 ug/l using lime as the hydroxide source is estimated to be $70/af, not including the cost of sludge treatment and disposal.

Based on the experimental results, pretreatment costs for oxygen and bicarbonate removal were estimated to range from $44/af to $54/af, not including sludge treatment and disposal (Rowley 1989). Evidently, denitrification was not considered a prerequisite for reducing selenium to target levels due to the reported success in lowering product levels to 10 ug/L in less than 4 hours despite the presence of nitrate (32 mg/L as N). However, the ferrous hydroxide dosage used in obtaining this result, 10 mmol/L, is substantially higher than the proposed optimum of 0.8 mmol/L upon which cost estimates were made. The expense involved in adjusting the pH to optimum levels prior to the ferrous hydroxide reaction was not considered in either the pretreatment or treatment cost estimates.

Verifying the feasibility of low ferrous hydroxide dosages and lengthy reactor detention times is essential to confirm these costs estimates. Additional research is required on iron oxide sludge characteristics (e.g., settling behavior, dewatering

efficiency, and chemical composition) for estimating sludge treatment and disposal costs.

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ION EXCHANGE FOR SELENIUM REMOVAL

LITERATURE REVIEW AND PROCESS ANALYSIS

The use of selective resins for selenium removal from water by ion exchange has been evaluated by several investigators. Maneval reported effective selenium removal from drinking water by ion exchange (maneval et al. 1985). He further reported that in ion exchange, the behavior of selenate and sulfate was identical, and selenite behaved similar to nitrate. Boyle and Clifford (1986) reported on removal by ion exchange of trace amounts of selenium from groundwaters. Process efficiency was found to depend on the selenium oxidation state, with selenate showing the greatest affinity for the anion exchange resin. Herrmann (1985) presented a review of recent literature relating to selenium species separations through ion exchange, and its applicability for quality improvement of agricultural drainage water. Cited references in the Herrmann report include the work of Clifford and Weber (1983), and Klein (1985). The former provided guidelines for monovalent-divalent selectivity which could be extrapolated to selenate-sulfate selectivity, inasmuch as ion size is involved. It has not been determined whether the difference in size between the sulfate and selenate ions (selenate about 10 percent larger) is sufficient to make the process feasible. Klein evaluated exchanger costs, considering an unselective strong-base exchanger with calcium chloride as regenerant. On this basis he estimated the Kesterson cleanup to cost about $30 million, with the resulting water free of both

selenate and sulfate, and suitable for feed to reverse osmosis desalination.

The Herrmann report also presented a brief analysis of the process, and identified large concentrations of sulfate as a major problem for selenate removal. Recommendations for future study included:

1. An overall assessment of the role of ion-exchange in selenium removal;
2. Development of ion-exchange resins having a significant preference for selenate over sulfate, and cost effective and environmentally acceptable methods of regeneration;
3. Reduction of selenate to selenite or selenium;
4. A precipitation process study to determine the extent of selenate co-precipitation with sulfate in a calcium chloride regeneration step.

ION EXCHANGE STUDIES

A study to explore the application of the ion exchange process for treatment of agricultural drainage water was conducted by Boyle Engineering Corporation (1988). The study objective was to determine if selenium selective ion-exchange resins could be developed. Initial isotherm tests on strong base ion resins indicated that those with larger alkyl groups (e.g. tributyl compared to tripropyl and trimethyl) demonstrated increasing selectivity for selenate over sulfate with increasing size of the alkyl group. This reinforced the earlier work of Clifford and Weber cited in the report by Herrmann (1985).

Laboratory column tests were run to determine breakthrough on a simulated drainwater containing 10 meq/L each of sodium sulfate and sodium selenate. Selenate breakthrough occurred at nearly twice the bed volumes as the sulfate, showing a preferred selectivity for selenate ion over sulfate ion. Following breakthrough for the sulfate ion, sulfate recovery values at first exceeded the sulfate input concentration, indicating a displacement of sulfate ion in favor of the selenate as more solution passed through the resin bed. The second column test on a sample of Kesterson drainage water was reported inconclusive due to selenium contamination of the apparatus.

Concentration values of sulfate and selenate in the resin, and in aqueous solution as predicted by computer simulation, agreed reasonably well with experimental tests. The Boyle study confirmed that selenate can be removed by selective resin ion exchange under laboratory conditions, and that in the presence of sulfate the resin with larger alkyl groups demonstrates more selective affinity for the selenate. Studies were not conducted to demonstrate field-scale reliability, and the effectiveness of the process on a large scale remains unknown.

As an additional note, Binnie Process researchers experimented with boron removal by ion exchange, and found that the process also provided a polishing effect in removal of trace selenium amounts (see Chapter 2).

FURTHER STUDIES

Further studies should be directed toward developing new resins with a better selective affinity for selenium. For example, the nitrate ion effects, though referred to briefly in the work, were not sufficiently addressed. In general, use of the process by itself for selenium removal from agricultural drainage water containing high concentrations of sulfate is considered to be relatively ineffective. Further, the cost data presented based on various assumptions and the laboratory tests performed, are at best partial estimates relying on high process efficiencies, and included no data for capital costs or costs of brine disposal. Any further assessment of this process for drainwater treatment should include a complete cost analysis of the application with particular emphasis on the regeneration step and the disposal of the spent regenerant.

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REVERSE OSMOSIS

The technical aspects of reverse osmosis (RO) desalination of westside agricultural waste water were investigated by DWR. Initial feasibility studies were conducted in the 1970s at DWR's Waste Water Treatment Evaluation Facility near Firebaugh.

After the pilot RO operations were completed and evaluated, DWR initiated an ambitious research program focusing on the design, construction, and operation of the Los Banos Demonstration Desalting Facility (LBDDF), a prototype plant with an nominal capacity of 0.5 MGD (PRC Engineering 1981 and 1983).

Critical to the success of any RO system is proper pretreatment to avoid scaling and/or fouling of membranes. Pretreatment of westside agricultural drain water involves removing silica, calcium sulfate, and suspended solids to required levels; disinfection is also required to prevent biological membrane fouling.

Two different pretreatment systems were tested at the LBDDF: biological (DWR 1987) and chemical coagulation/gravity filtration (DWR 1986). The reports covering the operation and performance evaluation of the ion exchange (IX) and RO systems at the LBDDF (DWR 1988 and 1987, respectively) are still in draft form. A conceptual level study of desalting of San Luis Drain water in a 10 MGD RO plant was conducted by CH2M-Hill (1986) for the SJVDP.

EARLY STUDIES AT FIREBAUGH

Three RO systems (tubular, spiral-wound, and hollow fiber) operated continuously for about 18 months using feedwater from a subsurface tile drainage system (DWR 1976). All three systems demonstrated adequate desalting capability with respect to membrane and plant performance.

Several conditions which governed the desalination process in these early pilot studies include: (1) seasonal variations in the level of feedwater total dissolved solids (TDS), (2) high calcium sulfate concentration and the limitations caused by the low solubility of this salt, and (3) presence of bacteria capable of membrane fouling. Successful RO performance was contingent upon adequate feedwater pretreatment and module maintenance; the productivity was limited by the scaling characteristics of the feedwater.

Investigations continued at Firebaugh in the late 1970s on improving equipment design, RO productivity, and feedwater treatment methods (DWR 1983). One RO system tested consisted of 500 tubes arranged in a two-stage parallel-series configuration; nominal capacity was 25,000 gallons per day (gpd). Maximum recovery was limited by calcium sulfate scaling on the RO membranes. A recovery rate of 90% was achieved by use of an ion exchange softening unit as part of the pretreatment.

Ancillary to the RO unit testing was an investigation of ion exchange (IX) pretreatment using RO brine for regenerating IX resins. Bench-scale IX tests which indicated the technical

feasibility of regeneration with RO process brine represented a significant innovation in desalting technology.

LOS BANOS DEMONSTRATION DESALTING FACILITY

In the early 1980s, DWR expanded its investigation into the technical feasibility of desalting agricultural drainage water at the LBDDF. The plant's feedwater source was the adjacent San Luis Drain, a canal which conveyed the subsurface drainage water from approximately 42,000 acres in Westlands Water District towards its terminus at Kesterson Reservoir.

Initial operations focused on optimizing RO pretreatment schemes: biological and physical/chemical. The goal of the pretreatment systems was to improve the feedwater quality for the downstream IX and RO units by reducing: (1) silica content to at least 15 mg/L, (2) turbidity to 0.5 nephelometric turbidity units (NTU); and (3) silt density index (SDI) to 3.0 or less (DWR 1986).

The biological pretreatment system consisted of marshponds planted with alkali bulrush followed by gravity filtration. Although the system removed silica to the desired levels, the turbidity requirement was generally not met, even with the assistance of gravity filtration. Operation of the marshpond system resulted in the accumulation of selenium in the roots of the marsh plants. Upon discovery of this development, DWR immediately terminated the biological pretreatment study and discontinued use of the marshpond system.

The physical/chemical pretreatment system consisted of a solids reactor, clarifier, gravity filters, and chemical feed systems. During the system's operation, influent silica levels routinely fell below the 15 mg/L limit; turbidity ranged from 0.1 to 20.0 NTU, but generally varied between 1 and 5 NTU. The performance of the physical/chemical pretreatment system was mixed with respect to suspended solids removal. The turbidity of gravity filter effluent almost exclusively measured below the 0.5 NTU limit. However, the SDI of filter effluent was highly variable and often exceeded the required limit of 3 (DWR 1986).

The hardness constituents comprised of calcium and magnesium salts (principally sulfates) were reduced to specified levels by IX. Following the resolution of mechanical problems, the IX system, which used RO brine for regeneration, met all treatment objectives and allowed high desalting recoveries.

The RO system at the LBDDF consisted of three self-contained skids arranged in a three-stage series configuration. The system was designed to process pretreated feedwater characterized by a total dissolved solids (TDS) content of 6,000 to 9,000 mg/L. When operating at optimal efficiency (90% water recovery), the RO system generated 230,000 gpd of low-salinity product water, in addition to RO brine, clarifier sludge, and spent IX regenerant.

Operation of the LBDDF RO system began in January 1986, after a delay of two years from its scheduled start-up date. An extended shut-down occurred from February to May because of

difficulties experienced in the IX system. After being on-line for a short period, the system was again inoperative for a month beginning in mid-June due to problems with the clarifier unit. In July, the feedwater TDS was lowered substantially due to the introduction of fresh irrigation water into the San Luis Drain. This change required major adjustments in RO operation and resulted in significant changes in membrane performance characteristics. The RO system was designed to process a feedwater containing 6,000 to 9,000 mg/L TDS. Prior to July, the TDS of the San Luis Drain water was above this range and the RO treatment consisted of the second two stages. The first low-pressure stage was placed on-line in August, since the feedwater TDS was then within or below design levels. However, operation of this stage was short-lived due to a malfunctioning high-pressure feed pump.

The second two stages were shut down for the last time in late August due to lack of feedwater. The San Luis Drain was closed by the U. S. Department of the Interior after elevated levels of selenium were reported to pose a serious environmental hazard to migratory birds utilizing Kesterson Reservoir. Total operation time for the second and third stage RO units amounted to 2,000 hours or less (DWR 1987).

Chemical analyses of feedwater, product, and reject were performed at least twice, in January shortly after start-up and in May before the San Luis Drain was diluted with fresh irrigation water. Tables 13-1 and 13-2 contain concentrations of TDS,

selenium, and boron in the various process streams of RO units 2 and 3, respectively.

TABLE 13-1 CHEMICAL ANALYSES OF FEEDWATER, PRODUCT AND REJECT OF SECOND STAGE RO UNIT AT THE DWR LOS BANOS DEMONSTRATION DESALTING FACILITY (1/86 AND 5/86)

DATE: 1/86	TDS (mg/L)	Selenium (ug/L)	Boron (mg/L)
FEED	8,490	224	14
PRODUCT	183 - 452	5 - 6	8.3 - 9.6
REJECT	16,500 - 17,300	422 - 452	19 - 21
DATE: 5/86			
FEED	11,800	388	13
PRODUCT	274 - 418	12 - 14	7.7 - 9.6
REJECT	25,800 - 26,700	758 - 815	18 - 21

TABLE 13-2: CHEMICAL ANALYSES OF FEEDWATER, PRODUCT AND REJECT FOR THIRD STAGE RO UNIT AT THE DWR LOS BANOS DEMONSTRATION DESALTING FACILITY (1/86 AND 5/86).

DATE: 1/86	TDS (mg/L)	Selenium (ug/L)	Boron (mg/L)
FEED	15,800	---	20
REJECT	26,800	---	29
DATE: 5/86			
FEED	19,100	549	17
PRODUCT	219 - 430	7 - 9	3.8 - 12
REJECT	34,900 - 37,700	1,060 - 1,110	22 - 28

As indicated, the selenium removals for the RO system were over 98%; effluent levels were reduced to below 10 ug/L. The brine stream contained selenium levels in excess of 1,000 ug/L, the current hazardous waste limit.

LARGE-SCALE DESALTING: CONCEPTUAL LEVEL STUDY

A conceptual level study for a 10 MGD RO plant to treat agricultural drainage water was performed by CH2M-Hill (1986). It was premised that the treatment process considered would be available technology, with the exception of the brine recycle process which would be thoroughly evaluated as a part of the project.

A review was made of chemical and flow date information furnished by USBR and Westlands Water District; however, the information was limited to the preceding four years when agricultural drain water was delivered to the drain system. Average monthly profiles developed for the main chemicals in the drainwater were found to be relatively consistent over the year.

The conceptual plant would process an annual average flow of about 8 MGD, and would be closed down during the month of October, the low-flow period, for servicing.

Pretreatment is considered to be the most significant part of this study, since it is critical to RO operation. Three pretreatment processes were considered: (A) lime-soda ash softening, (B) ion exchange softening, and (C) Ion exchange softening using RO brine as regenerant. All pretreatment

included multimedia filtration, chlorination, and dechlorination. Pretreatment processes A and B were off-the-shelf technology, and pretreatment process C was in the advanced development stage. It was suggested that each pretreatment process could be operated so that the RO could obtain a maximum recovery of 87.5%.

The proposed RO plant consists of three stages, the first stage operating at 400-450 psi, and the second and third stages operating at 850 to 900 psi. Membranes were polyamide thin film composite (TFC), and were spirally wound. Reduced susceptibility to fouling was the chief reason for selection of the spirally wound over the hollow fine fiber configuration. Product water would have a total dissolved solids (TDS) of 550 to 650 mg/L, and a brine TDS of 55,000 to 67,000 mg/L. Trace metal concentrations in the product water would be below detectable limits conventional analytical methods. Total selenium would be less than 0.01 to 0.02 mg/L. Boron, not easily removed, would approach 7 to 8 mg/L in the product water.

The USBR expressed concern that the 87.5% was not a sustainable recovery figure, and that a lower value of about 75% recovery is more realistic. However, according to the Contractor, based on the osmotic pressure of the third stage RO reject, and the state-of-the-art membrane design, the 87.5% recovery would appear to be sustainable. At the Bureau's request, however, the 75% recovery figure was also evaluated.

Combined wastes from the pretreatment and RO processes would be disposed of in waste ponds. Essentially all of the selenium and trace metals would be contained in the wastes. Further, selenium may reach 25 to 35 mg/L in the pond salt deposits. If the ponds are Class I (hazardous wastes), the desalting cost is 1.5 to 2 times greater than without pond costs. Economics are more reasonable if Class II disposal is acceptable, provided the brine can be treated to remove hazardous constituents.

Conceptual level process flow schematics, process flow diagrams, equipment layouts, and general descriptions, and power summaries were developed for each of the pretreatment processes to develop capital and operating cost estimates. Amortized capital costs (based on 6% interest rate) for the various treatment plants were calculated to exceed $200/af treated. Operation costs were estimated to range from $700/af to $880/af.

Costs of desalting the drainage water are high, excluding waste brine pondage costs. Classification (Class I or Class II) of treatment wastes has a significant effect on the overall desalting economics. Net costs of the treatment plant and Class I ponds range from $1,645/af to $2,250/af. With Class II ponds the cost is reduced somewhat to $1,140/af to $1,120/af. The cost for waste disposal by ponding may be lowered by further concentration of the brine by natural and/or mechanically enhanced evaporation followed by salt recovery.

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DISCUSSION AND RECOMMENDATIONS

Selenium removal treatment schemes utilize pathways and mechanisms that are either biochemical or physicochemical. In several processes, selenium removal occurs as a result of both biological and physicochemical activity. Another distinguishing feature is the medium undergoing treatment. Most schemes are for drainage treatment, while others focus on selenium removal from soil either by volatilization or by attenuation. Soil treatment is one form of source control since it results in less selenium leaching into subsurface drainage.

SELENIUM REMOVAL TREATMENT COMPARISONS

Biological treatment "processes" include the anaerobic-bacterial (Biosel) process patented by Binnie and the Algal-Bacterial Selenium Removal System developed by Oswald and Gerhardt. Aspects of these two processes relating to microbial selenate reduction were investigated independently by Schroeder and Altringer. Biological soil treatment mechanisms include microbial volatilization (Frankenberger), selenium attenuation in irrigated soil (Sposito), and selenium removal from submerged soils under anoxic conditions (Weres).

Physiochemical processes include attenuation of selenite in soil, adsorption of selenium onto iron filings (Harza process), chemical reduction with ferrous hydroxide, ion exchange, and reverse osmosis.

DRAINAGE TREATMENT PROCESS COMPARISONS

Selenium removal processes are defined here as those which have been tested on actual drainage under field conditions, and reflect an effort to reduce influent selenium to residual levels in one treatment scheme. The Binnie Process, for example, begins with denitrification in a carbon-dosed anaerobic/anoxic sludge blanket reactor, followed by selenate reduction in a fluidized-bed reactor. The reactor effluent is coagulated, flocculated, then passed through a proprietary crossflow microfilter. Final polishing by ion exchange for boron removal apparently also reduces selenium to residual levels.

In the Algal-Bacterial Selenium Removal System, algae grown in High Rate Ponds are harvested to provide the carbon source for selenate-reducing bacteria in an anoxic sludge blanket reactor. The effluent from this reactor contains low concentrations of reduced soluble selenium (selenite or colloidal inorganic/organic selenium species) which apparently respond well to coagulation with iron salts. Final clarification is achieved by dissolved air flotation.

The Harza Process involves passing drainage water slowly through a bed of activated iron filings. Heavy and toxic metals are removed from solution by their adsorption on activated iron filing surfaces. Problems with bed solidification appear to develop after prolonged use, causing reduced bed permeability and declining adsorption rates. The viability of this process hinges upon solving the problem of bed solidification. If found

viable, the process would have application on farmsteads rather than regional installations.

Microbial volatilization of selenium in drainage water was studied by Frankenberger. The process consists of applying a low-cost dairy waste, such as whey, to evaporation ponds in order to provide the carbon source necessary to reduce the selenium inventory by biomethylation. However, such an approach would lead to pond eutrophication and provide attractive waterfowl habitat which would be contaminated with selenium and other hazardous drainage constituents. As such, biomethylation in evaporation ponds does not appear to be a feasible drainage treatment scheme.

Selenium removal in submerged soil profiles is associated with the development of an anoxic biomass on the soil surface. In column tests, this biomass removed nitrate and selenate from feedwater as it passed through the column. The proposed treatment system involves a treatment pond (soil column), followed by a large shallow pond rich in organic material to grow the biomass which would be harvested for the nutrient and carbon source utilized in the treatment pond. It was proposed that this would be followed by evaporation ponds.

Several questions need answers. Can the biomass production pond furnish a continuing reliable quantity of nutrient and carbon source material for the treatment pond? How deep does the biological growth and removed substances penetrate into the soil column? How often is it necessary to clean or remove and replace

some of the column to maintain its removal capacity? Does the rate of selenium removal deplete with time, and if so, how much? What are the problems of disposal of the column soil/sludge that is removed? Will the system promote undue eutrophication in the ponds?

Reliability and efficiency of the system under field conditions must be explored. If these problems can be solved, the process may be applicable to provide a water with sufficiently reduced selenium content for reuse in agroforestry, for augmenting wetlands, or for disposal in the San Joaquin River. The proposed biomass production pond followed by evaporation ponds, however is somewhat reminiscent of waterfowl habitat which existed at Kesterson Reservoir and at the marshpond adjacent to DWR's desalting facility. The use of both was discontinued largely because of the threat they posed to migratory waterfowl populations. A monitoring system would be required, and the system feasibility would depend upon assurance that the pond water and/or process effluent water would meet target levels.

A chemical reduction process was developed by the USBR research team headed by Moody and Murphy. In this process, freshly-made ferrous hydroxide reduces selenate to elemental selenium which becomes trapped in iron oxide sludge. Pre-treatment is necesary to remove inhibitory substances, consisting of nitrate, dissolved oxygen, and bicarbonate, otherwise the chemical cost would be prohibitive. Biological denitrification

appears to be a suitable candidate for the nitrate pretreatment. The bicarbonate can be removed either by adding lime and precipitating calcium carbonate at high pH, or by adding acid and releasing carbon dioxide at a low pH. The iron oxide sludge, rich in Se is a hazardous waste, and will require special handling and disposal.

Ion exchange is a standard water treatment technology. However, more research is needed to develop a selenate-specific resin. The removal of selenate in the presence of competing high sulfate concentrations has been identified as a major problem to selenate removal by ion exchange resins. Ion exchange has also been proposed for nitrate removal, and more development is also needed for nitrate specific resins.

Reverse osmosis is a standard water treatment technology for desalting water. Operation of DWR's prototype facility, which processed water from the San Luis Drain, demonstrated selenium removals of over 97%. Reverse osmosis requires pretreatment to remove substances which cause membrane fouling. The process is very expensive to operate due to the large power demands associated with high pressure pumping. However, reverse osmosis does generate a marketable product: water with low TDS which can be re-used to irrigate crops (depending on boron content).

SOIL TREATMENT PROCESS COMPARISONS

Microbial volatilization of selenium in soil involves methylation reactions by indigenous bacteria and/or fungi in

which selenate is transformed into reportedly harmless gases which then dissipate into the atmosphere. Methylation of selenium is a process inherent in the natural cycling of the element. Carbon and other amendments are added to enhance microbial growth and bio-volatilization.

The volatilization process can be employed as a remediation treatment for soil contaminated with selenium as a result of drainage evaporation pond operation. One disadvantage is the relatively long time required to reduce the total selenium to target levels. On the other hand, selenium is completely removed from the system, and there are no high-selenium sludges requiring disposal. Redistribution of selenium through global atmospheric and geochemical cycling would appear to have minimal negative impact and the possibility of a net positive benefit when selenium deficient areas are considered.

Selenium attenuation focuses on developing the optimum conditions under which selenate is reduced to less soluble species that "react" with soil surfaces, thereby decreasing the amount that leaches into drainage. Attenuation may depend upon microbiological action, and also involve bio-volatilization. Studies on natural drainwater are needed to confirm laboratory results before an assessment can be made of the process feasibility.

BIOLOGICAL REACTORS, INPUTS AND SENSITIVITIES

Biological drainage treatment utilizes reactors which operate under anaerobic/anoxic conditions at redox potentials

which favor the bacteriological reduction of selenate. Several biological mechanisms may be involved in the process which results in an accumulation of elemental selenium (and other metals) in reactor biomass. Research on mechanisms of bacteriological reduction of selenate to elemental selenium by Altringer has identified bacteria families which are most effective: Enterobacteriaceae and Pseudomonadaceae. Altringer's research indicates that selenate reduction by these bacteria is independent of initial selenium concentration, and that an equilibrium condition exists between soluble and elemental selenium when conditions reach approximately 85% removal of total soluble selenium.

The research on anoxic selenium reduction by Schroeder focused on the microbial conversion of selenate to less soluble forms in the presence of nitrate. An examination of sorption of selenium onto calcite precipitate was attempted, however the test results were inconclusive. This is a particularly relevant factor in biological reactor design. The conditions under which selenium removal occurs in anoxic biological reactors also apparently favor carbonate precipitation. This causes scale formation on media surfaces in fixed-film and fluidized-bed reactors, shortening their use-life accordingly. On the other hand, carbonate precipitation actually assists in the sludge-blanket reactor operation by weighing down the biomass and allowing for higher upflow velocities.

A major cost item in biological processes is the carbon required, especially for biological denitrification. While methanol may be relatively expensive, the use of alternative "free" carbon sources such as sugarbeet waste may be more costly in the long-run for the following reasons: (1) carbon content may vary from shipment to shipment, requiring expensive chemical monitoring to ensure proper reactor dosage; (2) such carbon sources may contain a fluctuating variety of inhibitory substances; and, (3) much of the waste may be inert, thereby adding undesirable bulk to a selenium-rich biological reactor sludge. Another advantage of using a constant-quality carbon source such as methanol is that the bacterial culture will remain relatively stable. This is because the type of carbon source utilized will select certain groups of bacteria over others.

The distinguishing feature of the ABSRS is the use of algal sludge produced on-site as the carbon source for the biological reactors. It appears that less than a third of the algal mass is actually utilized in the reduction reactions. The sludge also has the potential of trapping large quantities of inert solids, primarily precipitated carbonates. The feasibility of reclaiming the carbon from precipitated carbonate for use in biological reactors has yet to be determined.

The operational performance of the two biological processes tested in pilot plant installations were found to be sensitive to changes in drainwater quality, especially influent nitrate concentrations. This can be controlled somewhat by constant

monitoring and adjusting reactor carbon dosage accordingly. Occasionally, drainage can also contain pesticides and/or herbicides which wipe out a reactor's microbial population, causing major operational delays. On two occasions, the field reactors at EPOC AG's pilot plant were rendered inoperative. The cause of the disruption was believed to be due to excessive pesticide and/or herbicide contamination in the feedwater.

Diurnal and seasonal temperature changes will also impact removal efficiencies. In the two field systems tested, reactor performance was generally enhanced during the summer months.

INHIBITORY SUBSTANCES IN SELENIUM REMOVAL MECHANISMS

Most biological drainage treatment processes involve a reduction of soluble selenate to less soluble forms followed by a solids separation step. Selenium removal by chemical reduction with ferrous hydroxide is essentially accomplished by a similar reduction pathway and solids removal process.

Selenate reduction occurs only under certain redox conditions. The theoretical "window of opportunity" for the selenate to selenite to elemental selenium transformation exists at a lower redox potential than that required for the reduction of oxygen and nitrate, and at a higher potential than which sulfate is reduced to hydrogen sulfide. As such, sulfate does not constitute a significant inhibitory substance in many of the bacteriological selenate reduction mechanisms studied.

The effect of nitrate and dissolved oxygen on selenate reduction, however, is significant. While it appears that biological selenate reduction can occur in the presence of these two inhibitory substances, optimal reduction is generally associated with conditions of low nitrate and dissolved oxygen. There are indications from the work of Altringer and Oswald that certain active selenate reducing bacteria may require small amounts of dissolved oxygen for optimal removals.

Bicarbonates were identified as a problem in chemical reduction with ferrous hydroxide since they combine temporarily with the ferrous hydroxide to form a precipitate. Although this compound eventually dissolves, its effect on the process is a significant lengthening of reaction time.

Sulfate competition with selenate is evident in ion exchange technology. Increasing resin selectivity for selenate over sulfate relates to the size of the alkyl group on the resin. The relative size of the selenate and sulfate ions is considered the major factor affecting the ion selectivity.

Variability of Inhibitory Substances in Westside Drainage

The inhibitory impacts of various drainage constituents can effect the configuration of a treatment process within a given geographical location. The most significant inhibitory substance for most drainage treatment schemes is nitrate, which varies considerably throughout the westside. Typically, nitrate ranges from 30 mg/L to 50 mg/L, as N. In certain areas, however,

drainage nitrate exceeds 150 mg/L, as N. While there is considerable variability in the concentration of naturally occurring nitrate in the soil profile, the extreme values reflect farm managerial practices (excess fertilizer application) and the inherent high solubility and mobility of nitrate salts.

For processes in which nitrate is inhibitory, some form of denitrification will be required prior to selenate reduction. Biological denitrification has proven to be successful in this regard. Nitrate removal using ion exchange requires additional research to develop nitrate-specific resins which can perform effectively within the complex chemical matrix which characterizes agricultural drainage.

WASTESTREAM PRODUCTION, TREATMENT AND DISPOSAL

Waste disposal is a major component of the treatment strategy. It is particularly necessary to identify and quantify those wastestreams which may be deemed hazardous in order to evaluate disposal methods and costs which affect drainage treatment managerial decisions. In general, the wastestreams generated in selenium removal treatment include: sludges and gaseous emissions from biological and/or chemical units and operations, contaminated wastestreams (e.g., spent acid or salt regenerant from ion exchange operation), and treated saline drainage water.

Biomass from biological selenate-reducing reactors must be periodically "wasted" to maintain selenium accumulations below detrimental levels. As such, the spent biomass will be

contaminated by selenium and other metals. In the chemical reduction reaction using ferrous hydroxide, the resulting iron oxide sludge will also contain high concentrations of selenium and other metals. The chemical nature of this sludge is such that these substances can be selectively recovered from the sludge by acid treatment. Depending on the thoroughness of recovery methods, such a treatment would eliminate the need for sludge disposal in a hazardous waste landfill and would instead generate marketable products. The acid used in the separation process, however, would create a hazardous wastestream requiring neutralization as a minimum treatment.

Another distinguishing feature of the ABSRS is the precipitation in high rate ponds of several "substances of concern." One analysis of pond solids indicated major concentrations of manganese, chromium, copper, nickel and lead, and some concentration of boron. Accumulation of these substances in pond solids indicate their removal from drainage.

Another wastestream, the biological reactor gas, may contain hydrogen sulfide, methane, and volatile selenium species. These emissions will constitute an odor nuisance and a potential air quality concern.

Disposal of Treated Drainage

While most agricultural drainage treatment schemes ignore the ultimate problem of treated drainage disposal, EPOC AG investigated salt recovery as the final step in the pilot testing

of the Binnie Process. However, little data were submitted to substantiate their claim of obtaining salts of marketable high purity in their pilot salt works. Salt recovery may be a viable option for finalizing the drainage treatment process. Additional field work is required to optimize salt works operations.

The most marketable resource from the salt works is glaubers salt (sodium sulfate decahydrate) which can be further processed into anhydrous sodium sulfate. The market value for glaubers salt ranges from $10/ton to $40/ton, depending on its purity. Anhydrous sodium sulfate of above 99.5% purity currently sells for $50/ton to $60/ton **delivered** (URS 1987).

In the past, the U.S. wood pulp industry consumed over one million tons of sodium sulfate annually. However, the industry has largely replaced sodium sulfate by an alternative process which uses spent sulfuric acid and caustic soda. Since 1987, the only steady U.S. industrial consumers of sodium sulfate are organic detergent producers and rayon manufacturers (URS 1987). Unless new industrial applications are devised for sodium sulfate, it is doubtful that the sale of recovered salt products will be a profitable option in any treatment scheme.

Process schemes which concentrate drainage salts in a brine stream (e.g., reverse osmosis, salt works) can store some of the brine in salt-gradient solar ponds (DWR 1987). Solar pond heat can be transformed into electricity using specialized generators. However, the efficiency of energy capture is generally low. In addition, these units utilize volatile compounds such as freon

which have been identified as harmful to the earth's ozone layer.

The feasibility of discharging treated drainage is a function of geographical location. In the northern San Joaquin Valley, the final effluent may be discharged to the San Joaquin River provided the drainage is treated to meet applicable discharge requirements. Also, anaerobic processes involving denitrification may find favor in the San Joaquin drainage area due to the resulting lower nitrate levels with less pollution threat to out-of-valley discharges to the Bay/Delta or to the ocean. In the hydrologically land-locked Tulare Lake Basin, however, the only outlet for treated drainage is evaporation ponds. Treatment schemes operating in the South Valley must not only produce an effluent of suitable quality for evaporation disposal, but must maintain that level in pond operation. Selenium removal treatment may not be a viable option in the South Valley if the state and federal wildlife agencies insist that the selenium level in evaporation ponds be maintained at less than 5 ug/L. Effluent selenium levels can be higher for treatment schemes which discharge into the San Joaquin River, provided that the river water quality selenium standard can be maintained.

For the long-term outlook, large reductions in drainage volume can be expected as on-farm managerial practices improve water usage efficiency. Further reductions are possible through agroforestry. The remaining lower volume problem drainage will result in lower relative treatment costs (i.e., a treatment

costing $300/af may be considered affordable if growers can reduce their present-day drainage volume by half).

The feasibility of direct ocean disposal cannot be discounted provided the drainage is treated to meet discharge requirements. The cost effectiveness of ocean disposal will be enhanced for those treatment schemes which concentrate drainage salts (e.g., reverse osmosis, salt works).

TREATMENT COST COMPARISONS

Research on selenium removal has generated several potential drainage treatment schemes which might be applicable to large-scale operation: the Binnie Process, ABSRS, chemical reduction with ferrous hydroxide, the Harza Process, and reverse osmosis. With few exceptions, the only parameters considered were capital and O&M costs for selenium removal treatment; wastestream treatment and disposal costs were seldom evaluated. Another shortcoming for comparative purposes is the selection of incompatible cost parameters in the various schemes evaluated.

The cost estimates for scaled-up applications of the Binnie Process and the ABSRS were revised to equalize the following cost parameters: design period of 20 years, electricity cost of $0.08 kWhr (based on current Pacific Gas and Electric Co. information), interest rate of 9-3/8% (recommended by USBR), and average labor cost of $40,000/person-yr including benefits. Disposal costs for sludges and treated drainage were not included. Revised costs for 10 MGD and 100 MGD facilities using the Binnie Process are

$228/af and $182/af, not including the salt works. Similar revised costs for the ABSRS are $205/af (10 MGD) and $156/af (100 MGD). The difference between the two schemes generally reflects the cost of carbon required by biological reactors. The Binnie Process requires an outside source, such as methanol, while the ABSRS generates its own carbon source in the form of algal sludge.

Costs projected for anoxic selenium reduction and removal using a sequencing-batch reactor system (Ergas et al. 1990), were based on scaled-up activated sludge system cost information. Capital costs were amortized over 25 years, and energy costs were estimated at $0.12/kWhr. However, the report did not provide the rationale for unit costs per acre foot of design flow (Table 5-2) used in the calculations. The overall costs were estimated at $73.20/af and $59.20/af for design flow rates of 14.4 and 144 MGD respectively. If straight-line extrapolation is applied, comparable figures for flow rates of 10 and 100 MGD would be $73.20/af and $64.00/af respectively. In any event, these costs appear exceedingly low compared to Binnie Process figures when considering the similarity of the proposed Schroeder treatment to the Binnie Process.

The cost of large-scale treatment with ferrous hydroxide was estimated by Moody and Murphy based on the use of 0.8 mmol/L ferrous hydroxide and a reactor detention time of 19 hours. These two treatment parameters were never reportedly tested for their feasibility. Nevertheless, the combined chemical and

equipment cost was estimated at $70/af. This value is contingent upon the removal of dissolved oxygen, nitrate, and bicarbonate prior to selenate reduction. The cost of pretreatment schemes was estimated at about $50/af. The necessity of pretreatment in this process is significant since the required dosage of ferrous hydroxide strongly influences total treatment costs. In the absence of pretreatment, the chemical costs alone for this process soar to over $400/af.

The major cost in the Harza Process is for iron filings, estimated at $100/ton. For a removal efficiency of 75% and a bed life of 5 years, Harza estimated the cost of treatment to be $120/af, excluding the cost of land. Solving the problem of bed hardening is essential to confirm this cost estimate.

Reverse osmosis treatment costs were estimated to range from $980 to $1,220/af depending on pretreatment selected, and not including waste evaporation ponds; and from $1,140 to $2,250/af for either Class II or Class I waste evaporation ponds following the process (CH2M Hill 1986). Capital costs were amortized over 20 years with an interest rate of 6%. Energy costs were calculated at $0.075/kWhr. Using the sensitivity analyses diagram developed for ion exchange pretreatment with recycled brine regeneration and an 87.5% salt recovery (CH2M Hill 1986), the RO treatment costs, at interest rate of 9-3/8% and energy cost of $0.08/kWhr, become $1,240/af using Class II evaporation ponds, and $2,120/af if Class I ponds are required.

Costs estimated by Frankenberger for volatilizing selenium from soils as shown in Table 7-6 range from $184/af to $302/af based on an estimated 40-year useful facility life, and interest rate at 10%. Variables considered are: value of income loss from the land used, and the selenium concentration in the drainage water. Costs for pond monitoring, wildlife management, and final disposal of accumulating salts are not included. Insufficient information was available to recalculate the costs for comparative purposes.

Treatment costs projected for large-scale operation of the soil column system proposed by Weres (1989) were estimated at about $100/af to $150/af. Criteria for establishing these values were not given; thus valid cost comparisons with other systems cannot be made.

Table 14-1 below shows costs for selected processes and systems. With the exception of the Binnie, Oswald, and reverse osmosis systems, cost data are too meager to provide comparisons. Except as noted, the values shown are based on 20-year facility life, 9-3/8% interest rate, $0.08/kWhr energy cost, and no sludge or wastestream treatment.

TABLE 14-1: COST COMPARISONS OF VARIOUS DRAINWATER TREATMENT AND SOIL TREATMENT PROCESSES FOR SELENIUM REMOVAL OR REDUCTION

	Cost: $/af	
	10 MGD	100 MGD
Anaerobic-Bacterial (Binnie) Target Treatment	228	182
Full Treatment 301 236		
Algal-Bacterial (Oswald) - - - - - - - - - -	205	156
Anoxic Selenium Reduction in a Sequencing Batch Reactor (Schroeder) -	73 (1)	64 (1)
Chemical Reduction (Ferrous Hydroxide/ Selenate Reduction, including pretreatment	-	120 (2,3,4)
Adsorption on Iron Filings (Harza Process)	- -	120 (2,4,5)
Reverse Osmosis: Including Class II evap. ponds	-	1,248 (2,6)
Including Class I evap. ponds	-	2,120 (2,6)
Selenium Volatilization from Soils (Frankenberger) - - - - - - - - - - - - - -	184 - 302 (2,7)	
Soil Column System (Weres) - - - - - - - - - - -	100 - 150 (2,4)	

NOTES:

1. Costs, based on a 25 year life and 10% interest, appear to be too low when compared to similar Binnie Process.
2. Costs not specific for particular size of plant.
3. Amount of pretreatment significant.
4. Cost criteria not available for uniform comparisons.
5. Plugging of bed will significantly increase costs.
6. Costs include evaporation ponds.
7. 40-yr useful life; interest rate 10%.

A review of the contents in the above table emphasizes the need for developing comparable cost parameters for a program so that decisions on alternative choices can be made with the assurance that common criteria and factors have been addressed in the cost development process. The current cost data leaves much to be desired, and emphasizes the need for a comprehensive and objective economic analysis addressing not only relative treatment costs of various processes, but also what constitutes affordable drainage treatment with respect to the continuation of farming activities in the San Joaquin Valley.

SPECIFIC RECOMMENDATIONS FOR FUTURE WORK

The following recommendations relate to specific process schemes and to overall drainage treatment research. The former contains research suggestions for individual treatment schemes. The latter includes discussions on the need for wastestream characterization, integrating treatment research, enlarging the focus of treatment to include other substances of concern, and standardizing report preparation (e.g., quality control and economic analyses).

Process-specific Recommendations: Drainage Treatment

For schemes employing biological selenate-reduction reactors, additional research is required to determine the amount of biological reactor sludge which must be routinely wasted for optimum performance. Continued testing of reactor design is necessary to effectively deal with the problems associated with carbonate precipitation and concomitant media fouling.

One of the target schemes in scaling-up the Binnie Process relies on a single-stage biological reactor for both selenate reduction and denitrification. Feasibility of this configuration has yet to be determined, although the recent work by Schroeder on selenate reduction in the presence of nitrate will provide information in this regard.

One unresolved problem with the ABSRS is determining how much algae is required for total treatment (denitrification and selenate reduction). While this value may be estimated by algae pond productivity (measured as mg/L VSS), the actual process utilizes algal sludge for reduction reactions. The amount of algal sludge required may be much higher than that estimated by pond productivity alone. This problem requires resolution before reliable estimates of treatment costs can be made.

While the work by Moody and Murphy reveals a possible chemical approach to selenate reduction using ferrous hydroxide, further testing is required to determine whether the dosages and reactor detention times selected for cost estimation purposes are, in fact, feasible.

The Panoche Drainage District is continuing to sponsor field testing of the Harza Process, with an emphasis on discovering a solution to the problem of iron filing bed solidification. While the Harza Process appears to be particularly well-suited for individual farm drainage treatment, its application is contingent upon solving the bed cementation problem.

In regard to selenium removal by ion exchange, research should continue for developing selenate-specific resins. It would seem appropriate, however, that such research be supported by the resin manufacturers who would stand to gain from the sale of the effective products, as opposed to public research support by governmental agencies.

Continuation of treatment research emphasizing field testing of anaerobic processes is planned at the new Adams Avenue Research Facility located south of Mendota. The concept of an integrated research facility was supported by SJVDP, and conceived and realized through cooperation of DWR, Westlands Water District, California State University, Fresno, and University of California, Davis. Initial studies at the Adams Avenue site will consist of continued field testing of aspects of the anaerobic bacterial process, particularly those relating to reactor design. Two reactors will be operated in parallel to determine their relative selenium removal efficiencies: an upflow sludge blanket reactor and a sequencing-batch reactor. The flow rate for both reactors will be about 15 gpm, somewhat higher than that utilized during the field testing of the Binnie Process. Operating the reactors in parallel will ensure comparable parameters (influent quality and environmental conditions) which will assist in evaluating and comparing reactor performance.

Process-specific Recommendations: Soil Treatment

Soil selenium bio-volatilization is a feasible remediation treatment process for detoxifying sediments which have been

contaminated by drainage evaporation pond operation. Additional research on enhancing bio-volatilization appears promising, and will undoubtedly shorten the current time frame required for selenium reduction to permissible soil limits.

Attenuation experiments were conducted with simulated drainage and defined selenium behavior in soil columns with respect to varying amendments. Inasmuch as simulated drain water was utilized in all tests, the results do not reflect attenuation under standard irrigation conditions. The goal of soil selenium attenuation research is to develop farm managerial practices which result in less selenium leaching into drainage collection systems. Further soil attenuation experiments should be conducted using actual farm irrigation water in order to properly assess the potential of this process.

GENERAL RECOMMENDATIONS FOR FUTURE RESEARCH

Quality Control/Quality Assurance Documentation

In order to optimize selenium removal strategies it is necessary first to understand the underlying mechanisms of removal. In many treatment schemes, this involves monitoring the speciation changes of selenium as it passes through the process. Lacking from most research reports is an overall statement of Quality Assurance/Quality Control (QA/QC) procedures. At a minimum, this section should include an explicit description of methodologies used for selenium determination including sample preparation and analysis [e.g., digestion step(s) and reagent(s),

filter size(s), and analytical equipment used].

Cost Estimate Standards

Processes which are advanced enough to project to full-scale treatment should adopt a standardized format for developing cost estimates. This format would delineate the value of certain basic variables: design period, interest rates, electricity costs, average labor, and mark-up percentages for contingencies, unlisted items and overhead and profit.

Characterization of Wastestreams

Although wastestreams may have been identified for most processes, scant attention was given to their chemical composition. Besides selenium, little information was provided on how a process may remove other contaminants. Sludge treatment and disposal will figure prominently in overall treatment costs. Future research which involves sludge production should intensify efforts at sludge characterization. This will include, at a minimum, that the sludges be routinely analyzed for selenium and other hazardous substances. Also important is the study of sludge dewatering characteristics. Unless the sludge is rendered non-hazardous as a result of treatment, then it will require, at a minimum: dewatering, stabilization, and final disposal in a hazardous waste landfill.

Future research should address the possibility of "deselenizing" biological sludges from selenate-reduction reactors by biomethylation. Since the biomass constitutes a carbon source, only irrigation and tillage would be required.

This would help address the issue of biological sludge treatment in which the presence and fate of other metals and trace elements would have to be determined. Biological reactor gas should be monitored for hydrogen sulfide, methane, and volatile selenium species since these emissions may constitute both an odor nuisance and a potential air quality concern.

Boron Removal

Future research on agricultural drainage treatment will pay increasing attention to boron removal if regulatory agencies stipulate that drainage discharge must not be detrimental to downstream agricultural uses. In order to comply with such a regulation, the discharge limit for boron may be reduced to below 1 mg/L. Hence, boron removal will constitute an important component in drainage treatment schemes.

Boron is particularly difficult to remove from drainage due to its high solubility in water. Reverse osmosis removals of boron at DWR's desalting facility were only on the average of 50%, with product water levels ranging from 5 - 9 mg/L.

The only treatment process which to date appears feasible for boron removal is ion exchange using a specific resin with sorbityl functionality (Amberlite IRA-743) manufactured by Rohm and Haas. The field testing of the Binnie Process included a specific ion exchange resin for boron removal. Effluent boron levels of less than 1 mg/L were obtained for flowrates of 0.6-0.8 gpm/ft^3 with a resin capacity of 0.16 lb B/ft^3 using single-

stage regeneration with 10% sulfuric acid (Squires 1986).

The Binnie field test indicated that ion exchange will constitute a significant portion of treatment costs. However, the advantages of this polishing step besides boron removal are: (1) additional selenium removal to trace levels, and (2) recovery from the spent regenerant of boric acid crystals, a marketable product. Research should continue on using powdered ion exchange resin as a precoat for the crossflow filter since this approach appears to increase ion exchange performance significantly.

Molybdenum Removal

At pH values typical for westside drainage, molybdenum will be present as the monomeric tetrahedral oxyanion, molybdate. The only evidence to date regarding the effectiveness of selenium removal treatment technologies on molybdenum removal is derived from the analysis of a single sludge sample from EPOC AG's fixed-film reactor: molybdenum concentration in this sludge sample was 125 mg/kg (dry weight).

Integration of Research Efforts

The exchange of ideas among those participating in drainage treatment research should be encouraged. The tendency among researchers has been to work in relative isolation, while trying to develop the solution to the drainage treatment problem.

Future research should integrate different treatment schemes and other drainage-related processes. Especially

promising is the combination of drainage treatment and agroforestry. By passing the feedwater through agroforestry systems, the volume of drainage will be considerably reduced. This will, in turn, lower overall treatment costs when compared to treating "raw" drainage. Research on adapting treatment schemes to operate effectively at high TDS will be necessary, since the salt concentration in the drainage collected from the final step in the agroforestry system (atriplex) may reach seawater levels.

Another possibility is to investigate the use of ferrous hydroxide reaction as a chemical reductant in lieu of ferric and/or ferrous chloride in clarifying effluent from biological selenate-reduction reactors. Another promising treatment scheme which deserves testing is biological denitrification followed by chemical selenate reduction with ferrous hydroxide.

Treatment schemes which incorporate salt-gradient solar ponds as one form of salt disposal will benefit from the heat generated by such ponds. Examples of the possibilities afforded by on-site solar pond operation include heating two process streams: the carbon feed prior to dosing biological reactors to elevate internal temperature to optimum levels, and reverse osmosis feedwater to increase membrane performance.

One integrated approach for drainage treatment is as follows: drainage volume is first reduced significantly by changes in farm managerial practices (e.g., drip or subsurface irrigation), then further reduced in agroforesty/atriplex systems. The final

leachate from these systems in then subjected to physicochemical and/or biological selenium removal treatment schemes. Chemical reduction of selenate with ferrous hydroxide generates an iron oxide sludge from which selenium and other metals can be harvested. Biological sludges, on the other hand, may be deselenized by bio-volatilization on specially designed sludge treatment beds. It is expected that the biological sludge would itself contain sufficient organics to provide at least a major portion of the carbon required for bio-volatilization, thus reducing the need for carbon amendments.

Treated drainage can either be evaporated for salt recovery, concentrated in salt-gradient solar ponds, or discharged into receiving waters provided adequate dilution of the effluent can occur to meet water quality requirements.

Another option is to create saline wetlands with treated drainage which has been diluted adequately for habitat purposes. The San Joaquin Valley once contained millions of acres of wetland habitat which has been supplanted by extensive irrigated agricultural systems. Enlarging the existing waterfowl habitat with diluted, treated drainage, would restore some of the wetlands, and significantly enhance bird populations.

It is recommended that an "Expert System" approach be developed to assist in decision making regarding the application of specific treatment processes or combinations of processes to meet specific conditions. Such a system would also be helpful in

choosing between individual farm treatment plants or regional treatment facilities. This decision would also have to be addressed in an economic study. An advantage of the regional treatment facility is the leveling out of peak flows and high toxic concentrations that may originate in a localized area due to over-fertilization or pesticide application.

Most of the treatment processes and schemes investigated for selenium removal and/or mitigation have merit under specific conditions as have been noted, and all address the current thrust of solving the problem by in-valley treatment. However, proper attention has not yet been given to the final disposal of waste-streams generated by the various processes. Even less attention has been directed to the prodigious amounts of salt being transported into the valley each year and adding to the already massive accumulation. In the long-run, the only ultimate solution to the entire drainage problem is to consider it in mass-balance terms: establish a level of salt tolerance acceptable to the valley and its activities, and then to develop an economically and politically feasible export system for the excess salt to maintain the selected salt tolerance level in the valley.

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CONCLUSIONS

The following conclusions derived from the assessment are first, specific conclusions, arranged according to specific projects or types of projects and technologies which are addressed in the report; and second, general conclusions which relate to more than one type of process, or to the overall program.

SPECIFIC CONCLUSIONS

Biological Processes and Technologies:

* The anaerobic/anoxic drainwater treatment involving reduction of selenate to selenite and thence to elemental selenium, is a viable technology. Further research should be supported to provide operational information regarding its applications and limitations at the field pilot plant and prototype levels. Reactor design also needs to be perfected. Potential carbon sources should be further evaluated, including growth and harvesting of algae to support the bacterial selenate reduction step. The effect of nitrates, and other potential reaction inhibitors needs to be clarified. The technology would lend itself well to regional plant installations, and this concept should be explored.

* Biological denitrification is a logical pretreatment to selenate reduction where nitrate is inhibitory to the process.

* The feasibility of selenium adsorption on iron filings (Harza Process) is dependent on a solution to the problem of bed solidification, which should be pursued at the existing pilot plant in the Panoche Drainage District. A study of the process mechanism(s) is also necessary to provide a better understanding of the capabilities of and limitations of the system. If found to be technically and economically feasible, this process, because of its compactness, should be a good candidate for individual farmstead installation.

* Microbial volatilization is a viable process for reducing selenium content of drainage pond sediments. Selenium is completely removed from the system, thus eliminating the disposal problem associated with a high-selenium sludge. Future project support should focus on alternative carbon sources, and general process optimization.

* Microbial volatilization appears less attractive when applied to ponded drainage water. The necessary nutrient and carbon source amendments to drive the process create the potential for developing a eutrophic system.

* The concept of selenium removal in submerged soil profiles needs more process development to establish process feasibility. Reliability and efficiency of the system under field conditions must be explored. If the system can consistently produce a low selenium effluent, the resulting product water could be supplied to agroforestry projects, used to augment wetlands, or discharged to the San Joaquin River.

Physicochemical Processes and Technologies

* Soil attenuation studies for selenium removal require field testing with agricultural drainage water in order to determine the process feasibility.

* Chemical reduction of selenium by the ferrous hydroxide/ selenate reaction requires pretreatment for removal of inhibitory substances (oxygen, nitrate, and bicarbonate). Cost effective means of eliminating the inhibition problem will have to be developed for this process to become viable. Biological denitrification is a promising pretreatment technique. Handling and disposal of the selenium-rich iron oxide sludge must also be addressed.

* Ion exchange resin manufacturers should be encouraged to formulate and develop resins specific to both selenate and nitrate removals.

* The reverse osmosis process differs from the others investigated in that it provides a full treatment for brackish or highly saline waters, and produces a high quality product water. The feedwater requires extensive pre-treatment. The overall process is too costly to compete with the other processes noted unless a high quality marketable product water is required.

* Salt gradient ponds, which would be used in conjunction with a system (reverse osmosis) that produces a highly

concentrated brine stream, cannot be justified on the basis of energy production alone. An additional benefit, however, is that of utilization of the brine stream which otherwise would require handling and disposal as a hazardous waste.

GENERAL CONCLUSIONS

* Full cost data including capital costs, operating and maintenance costs, and wastestream(s) treatment and disposal costs should be provided for all projects. Further, standardized cost criteria relating to life of project, interest rate, energy cost, and labor cost should be used for all projects within a program so that meaningful cost comparisons can be made. Data reported for most projects were limited to capital costs, and plant operating and maintenance costs. A comprehensive economic analysis should be made to establish relative process treatment costs. The analysis should also consider what is affordable drainage to the farmer.

* Waste disposal is an integral part of all treatment strategies. Wastestreams must be identified and quantified in order to properly evaluate treating, handling and disposal methods which affect decisions on agricultural drainage management. Sludges should be routinely analyzed for hazardous substances. Organic sludges may be dried and deselenized by application of microbial volatilization. Where an excess of biomass is created (e.g algal-bacterial

process), energy recovery from digester gas may be indicated.

* The potential discharge of treated agricultural drainage water is related to geographical location. In the San Joaquin Basin, discharges to the river may be permitted, providing that the river water quality standard can be maintained. In the Tulare Lake Basin, treated drainage discharged to evaporation ponds, must satisfy wildlife criteria.

* Denitrification should be practiced wherever possible to rid the product water of excess nitrates that promote algal growth and lead to downstream eutrophication.

* Salt works, if considered, should be based on salt product value determined from a comprehensive market survey and analysis.

* Water and drainage districts are uniquely organized to assume the management of regional drainwater treatment facilities, which in many instances would show operational and economic benefits over individual farmstead plants.

* Improvement of farm management practices must be encouraged to optimize irrigation, and pesticide and fertilizer applications. Large reductions in drainage volume can be expected as on-farm managerial practices improve water usage efficiency.

* Agroforestry as a means of agricultural drainage water disposal should be pursued.

* Quality assurance/quality control (QA/QC) procedures should be established for every project undertaken. QA/QC would provide criteria for monitoring, and describe analyses methodologies.

* Exchange of ideas among those participating in drainage research should be encouraged through seminars, symposia, and conferences.

* Integration of different treatment schemes and other drainage-related processes should be considered. Particularly promising is the combination of drainage treatment with agroforestry.

* Where land can be retired, and drainage water quality can be sufficiently improved, augmentation of wetlands should be considered.

* An "Expert system" approach to decision making should be developed to identify optimum treatment processes or combinations thereof to meet specific conditions.

* A mass balance approach to salt accumulation in the valley should be considered, and an economically and politically feasible export system devised to remove the excess salt.