centro de educación continua
facultad de ingeniería, unam

TRATAMIENTO DE AGUAS RESIDUALES

NEUTRALIZACION

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UNIVERSIDAD NACIONAL AUTONOMA DE MEXICO
Facultad de Ingeniería D.E.S.-C.E.C.

CURSO SOBRE TRATAMIENTO DE AGUAS RESIDUALES INDUSTRIALES
2 al 14 de diciembre 1974, México, D. F.

HORA	LUNES 2	MARTES 3	MIERCOLES 4	JUEVES 5	VIERNES 6	SABADO 7
9:00 10:00	Inscripción e Inauguración	Caracterización de Aguas Residuales Laboratorio (CIECCA)	Sedimentación G. Mendoza G.	Neutralización y Control de pH U. Bonilla	Filtros Biológicos E. Izurieta	Lagunas Facultativas y de Maduración J. Aguirre
10:00 11:00	Fuentes y efectos de Contaminación del agua. Importancia del Tratamiento. E. Izurieta				Filtros Biológicos. J. Malina (OPS)	
11:00 12:00	Legislación y Programas de Control P. Martínez P.		Flotación J. Malina (OPS)	Filtración Rápida J. Malina (OPS)	Intercambio Iónico J. Malina	Operación y Mantenimiento J. Molina Riquelme
12:00 13:00	Caracterización de Aguas Residuales P. Martínez P.				Adsorción J. Malina (OPS)	
14:00 15:00	Caracterización de Aguas Residuales. P. Martínez P.	Laboratorio J. Aguirre F. Romero P. Martínez	Homogenización J. Malina (OPS)	Disposición de Lodos J. Malina (OPS)	Lagunas de Oxidación. J. Aguirre	
15:00 16:00					Lagunas Anaerobias J. Aguirre	
16:00 17:00	Procesos de Tratamiento de Aguas Residuales. J. Irivijo			Filtros Biológicos E. Izurieta (OPS)	Lagunas Aerobias J. Aguirre	

UNIVERSIDAD NACIONAL AUTONOMA DE MEXICO
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2a Semana

CURSO SOBRE TRATAMIENTO DE AGUAS RESIDUALES INDUSTRIALES
2 al 14 de diciembre 1974, México, D. F.

HORA	LUNES 9	MARTES 10	MIERCOLES 11	JUEVES 12	VIERNES 13	SABADO 14
9:00 10:00	Aireación Mecánica F. Yánez (OPS)	Industria del Petroleo E. F. Gloyna (OPS)	Industria de la Pulpa y el Papel F. Yánez (OPS)	Industria de la Curtiduría F. Yánez (OPS)	Industria Farmacéutica D. Ford (OPS)	Costos del Tratamiento F. Yánez D. Ford (OPS)
10:00 11:00	Lagunas Aireadas F. Yánez (OPS)					
11:00 12:00	Lodos Activados F. Yánez (OPS)			Industria Textil E. F. Gloyna (OPS)		Plantas Piloto D. Ford (OPS)
12:00 13:00			Industria del Acero E.F. Gloyna (OPS)			
14:00 15:00	Aireación Extendida y	Industria Azucarera F. Yánez (OPS)	Industria del Acero E.F. Gloyna (OPS)	Industria de Enlatados y Alimentos E. F. Gloyna (OPS)	Industria Cervecera D. Ford (OPS)	CLAUSURA
15:00 16:00	Zanjas de Oxidación					
16:00 17:00	F. Yánez (OPS)		Industria del Cromado. U. Bonilla		Costos del Tratamiento. F. Yánez	

1.- Introducción

Se denomina "acidez" de una solución acuosa a su capacidad para ceder iones de hidrógeno; al concepto inverso, es decir a la capacidad de una solución para aceptar iones de hidrógeno se le denomina "alcalinidad o basicidad".

Por otro lado, la intensidad de la acidez o basicidad de una solución se mide convenientemente en función de la concentración de los iones de hidrógeno en el seno del líquido, Así, el "potencial hidrógeno" se define como el logaritmo de base 10 de la inversa de la concentración de iones de hidrógeno

$$pH = - \log [H^+] \qquad (1)$$

Se consideran neutras las soluciones con pH 7, alcalinas las que muestran $pH > 7$, y ácidas las tienen $pH < 7$.

El término "alcalinidad total" se refiere a la cantidad total de ácido que debe agregarse a una muestra de solución para bajar su pH hasta 4.5, y el "término "acidez total", a la cantidad de base requerida para elevar el pH de la muestra hasta 8.3. Ambos son términos de capacidad, y pueden expresarse convenientemente en mg/l como $CaCO_3$.

Las aguas residuales procedentes de un gran número de industrias son alcalinas o ácidas. Entre estas industrias destacan las de productos químicos, las de pulpa y papel, las metalúrgicas, las de galvanoplastia, las textiles, la hulera , las de carbón mineral, las de películas fotográficas, las embotelladoras de refrescos, artículos de cuero, y enlatadoras.

Los desechos ácidos o alcalinos ocasionan daños a los cuerpos de agua receptores, produciendo, según su concentración reducción o muerte de la vida acuática. Se considera que el rango de pH para que exista actividad vital efectiva en las aguas es 6.5 a 8.5, por tanto, se recomienda que los desechos fuera de estos límites se sujeten a neutralización antes de ser descargados(1), lo cual debe estar de acuerdo obviamente con las características de la corriente receptora y los reglamentos en vigor.

2.- Métodos de neutralización

Al presente existen diversos métodos aceptables desde el punto de vista económico para efectuar la neutralización de las aguas residuales que lo requieran. Los más usuales son:

a) - mezclado de aguas residuales ácidas y alcalinas.- Los desechos pueden proceder de la misma o diversas industrias, mezclándose para obtener un pH lo más cercano posible a 7.

Este método requiere de capacidad suficiente de almacenamiento y homogeización para absorber las variaciones en las concentraciones de los desechos.

Si este método es aplicado debe tenerse cuidado en el control de la producción de compuestos tóxicos.

Aguas ácidas:

b) - Paso de las aguas residuales por mantos de piedra caliza.- En este procedimiento, se usa generalmente flujo ascendente, lográndose con ello arrastrar a la mayor parte de los productos de la reacción antes de que se precipiten sobre la caliza. La carga recomendada máxima es de 35 $l/min-m^2$, para obtener tiempos de contacto suficientes para que se efectúe la reacción. Se recomienda limitar la concentración de ácido en el agua residual al 5% para evitar la obstrucción de la superficie caliza debido a precipitados. Para evitar la formación de capas no reactivas de sulfato de calcio sobre la caliza, la concentración de ácido sulfúrico debe ser menor a 0.6%. Debe considerarse que los metales disueltos tienden a precipitarse como hidróxidos obstruyendo la superficie de la piedra caliza.

c) - Adición de lechada de cal a desechos ácidos.- Este método resulta más efectivo que el anterior en el tratamiento de desechos ácidos. Se usa normalmente en tratamiento continuo, de mo-

do que los productos de la reacción, que quedan en solución, son arrastrados con el efluente.

No obstante las dificultades de dosificación de la cal hidratada, su empleo es muy conveniente cuando se trata de volúmenes relativamente pequeños de desechos. Como el contenido magnésico de la cal es más reactivo en aguas fuertemente ácidas, el tipo de cal que se use influirá en el grado de neutralización obtenido. Los resultados son generalmente eficientes cuando el pH del agua por tratar es menor de 4.2.

d) - Adición de NaOH o $Na_2 CO_3$:-

Estos compuestos son agentes neutralizadores más potentes que la cal o la piedra caliza, sin embargo su alto costo influye generalmente en forma negativa en la selección de este proceso. Su aplicación tiene como ventaja el que los productos de la reacción son solubles y no incrementan la dureza de las aguas receptoras. Por tanto, este método se usa para tratar pequeños volúmenes de desechos.

Aguas alcalinas:

e) - Adición de CO_2 :-

La adición de CO_2 a aguas residuales alcalinas puede ser de diversas formas, a saber

- difusión de gases provenientes de chimeneas de calderas
- inyección de CO_2 comprimido
- combustión sumergida

En el primer caso se aprovecha el contenido de CO_2 de los exhaustos de las calderas (aproximadamente 14%). Para ello, los gases se filtran para remover azufre y partículas, aplicándose posteriormente al agua mediante difusores. Si las aguas residuales tienen altos contenidos de azufre, puede formarse ácido sulfídrico, que debe controlarse para evitar condiciones desagradables.

El CO_2 comprimido comercial tiene ventajas sobre el CO_2 procedente de procesos de combustión en calderas, sobre todo en lo que se refiere a su pureza y sencillez para su aplicación. Por otro lado, su costo resulta alto, sobre todo cuando se trata de grandes volúmenes por tratar.

El método de combustión sumergida ha sido usado en forma experimental, siendo necesario realizar investigaciones amplias para determinar si puede o no ser usado como proceso normal de neutralización.[4]

f) - Adición de ácido sulfúrico.-

Este método se usa para neutralizar pequeños volúmenes de aguas

residuales, debido al alto costo de este reactivo. Como desventaja se señala además, la dificultad y peligro en su manejo. Las reacciones típicas de neutralización de la acidez, que se efectúan en los procesos descritos en el capítulo anterior, son las siguientes:

$$Ca\,CO_3 + H_2\,SO_4 \longrightarrow Ca\,SO_4 + H_2O + CO_2 \qquad (2)$$

$$Ca(OH)_2 + H_2\,SO_4 \longrightarrow Ca\,SO_4 + 2H_2O \qquad (3)$$

$$Na(OH) + H_2\,SO_4 \longrightarrow Na_2\,SO_4 + 2H_2O \qquad (4)$$

$$Na_2\,CO_3 + H_2\,SO_4 \longrightarrow Na_2\,SO_4 + H_2O + CO_2\uparrow \qquad (5)$$

Las reacciones típicas de neutralización de la alcalinidad son:

$$CO_2 + H_2\,O \longrightarrow H_2\,CO_3 \qquad (6)$$

$$H_2\,CO_3 + 2\,Na\,OH \longrightarrow 2\,Na_2\,CO_3 \qquad (7)$$

$$H_2\,CO_3 + 2\,Na_2\,CO_3 \xrightarrow{H_2O} 2\,Na\,H\,CO_3 \qquad (8)$$

3.- Diseño de lechos de caliza

Al proceder al diseño de una instalación de neutralización mediante el uso de piedra caliza, se debe determinar experimentalmente la profundidad del lecho, en función de las características del influente y del reactante. Los experimentos se

efectúan en columnas de filtración de 4 a 6 in. de diámetro, dispuestas como se muestra en la figura 1.

a - La caliza triturada (1 a 2 in de diámetro), previamente lavada, se coloca en sendas columnas para tener profundidades de lecho de 1, 2 y 3 ft.

b - Se alimenta agua residual a las columnas en la forma ascendente o descendente, según se piense hacer en la realidad. El gasto por unidad de sección recta (carga superficial), se varía entre 50 y 1000 gal/hora/ft^2 (0.030 a 0.60 l/min/m^2.)

c - Se mide el pH del efluente de cada columna hasta que este se estabilice.

d - Después de cada prueba se remueve la caliza de cada columna, y se registra el peso utilizado.

Los resultados del experimento permiten dibujar una gráfica que representa el valor del pH efluente en función de la carga superficial y la profundidad del lecho. Esta gráfica (figura 2), constituye el principal elemento de diseño, el cual puede realizarse como sigue:

a - Para el pH deseado en el efluente, se determina, usando la gráfica de diseño, las cargas superficiales que corresponden a cada profundidad de lecho.

b - Se calcula el área necesaria de lecho de neutralización, en función del gasto real, para cada carga superficial determinada en el paso anterior (area igual a gasto entre carga superficial)

c - Se calcula el volumen requerido de caliza para cada - profundidad de lecho.

d - Se determina el gasto por unidad de volumen de caliza, para cada una de las profundidades consideradas.

e - La profundidad óptima se determina graficando los gastos por unidad de volumen de caliza, contra las profundidades correspondientes; el máximo gasto unitario corresponde a la profundidad óptima (figura 3)

f - Se grafica el volumen o peso de caliza requerido por cada 1000 gal. de agua residual contra el pH del -- efluente, para la profundidad óptima. Esta gráfica - (figura 4) puede usarse para determinar las cantidades de calcita requeridas para obtener diversos valores de pH en el efluente, diferentes al originalmente deseado.

Ejemplo:

Los desechos líquidos de cierta industria tienen una concentración 0.10 N de $H_2 SO_4$. Si el gasto por tratar es de -- 50 gal/min, y el pH final debe ser de 6.0, determinar a) la profundidad más económica del filtro, b) los volúmenes de caliza que debe de tener el lecho, si el pH final es 6.0.

a - La figura 2 corresponde a las condiciones del problema y a lechos de calcita magnésica calcinada. Entrando en -- las ordenadas con pH 6, en las abscisas se leen las cargas - superficiales correspondientes a 0.5 ft, 1 ft, 3 ft, etc. de

profundidad de lecho. Estos resultados aparecen en la columna 2 de la tabla 1. El área de lecho respectiva, columna 3, se obtiene dividiendo el gasto (0.50 gal/min = 3000 gal/hr), entre la carga superficial (3000/65 = 46; 3000/3000/250 = 12, etc).

El volumen de caliza, columna 4, se obtiene multiplicando el área de lecho por la profundidad (46 x 0.5 = 23, 12 x 1 = 12, etc).

El gasto por volumen unitario, columna 5, es el gasto (3000 gal/hr) entre el volumen de caliza (3000/23 = 130, etc).

Graficando las profundidades contra los gastos por volumen - unitario, se obtiene la curva de la figura 3, donde se observa que la profundidad óptima es 3 ft.

b - Considerando un lecho de 3 ft de profundidad, en la figura 2 se leen los valores carga superficial correspondientes a pH 5, 6, 7, etc. Tales valores aparecen en la columna 2 de la tabla 2.

Las cargas superficiales divididas por la profundidad del lecho (3 ft), resultan en los gastos por volumen unitario de ca-

liza, columna 3, (3000/3 = 1000, etc).

Los volúmenes de lecho de caliza, por cada 1000 galones por hora de desechos tratados, columna 4, se obtiene multiplicando los inversos de la columna 3, por 1000.

c) Como la concentración ácida de los desechos es 0.1 N y el gasto es 3000 gal/hr., el peso de ácido neutralizado será:

$$3000 \frac{gal}{hr} \times 0.1\ N \times \frac{49\ g}{N\ 1} \times \frac{1b}{453\ g} \times 3.785 \frac{1}{gal} \times \frac{24\ hr}{día}$$

$$= 2950 \frac{lb}{día}$$

Si se supone que la caliza usada tiene una reactividad del 60% el consumo de caliza será

$$2950 \times \frac{49}{50} \times \frac{1}{0.60} = 5000 \frac{lb}{día}$$

4 - Diseño de sistemas de neutralización a base de lechada de cal.

Para determinar las propiedades neutralizantes de la cal que se vaya a usar en un proceso, se realizan pruebas de laboratorio que consisten en:

TABLA 1

Cálculo del gasto por volumen unitario de reactante em lechos de caliza

Profundidad ft	carga superficial gal/hr-ft^2	área, ft^2	Volumen de caliza ft^3	Gasto por volumen unitario gal/hr-ft^3
(1)	(2)	(3)	(4)	(5)
0.5	65	46	23	130
1	250	12	12	250
2	1040	2.9	5.8	520
3	1800	1.67	5.0	600
4	2100	1.42	5.7	525

TABLA 2

Cálculo del volumen necesario de caliza por 1000 galones de agua residual tratada

pH	carga superficial gal/hr-ft^2	gasto por volumen unitario gal/hr-ft^3	Volumen de caliza por 1000 gal/hr. de desechos ft^3
(1)	(2)	(3)	(4)
5	3000	1000	1.00
6	1850	617	1.63
7	1500	500	2.00
8	1220	407	2.46
9	860	287	3.50

a - Tomar una muestra de la cal que se vaya a usar en el proceso, y preparar una suspensión con concentración tal que permita ser manejada convenientemente por el equipo de que pueda disponerse en la instalación real.

b - Agregar pequeños incrementos medidos de suspensión a 500 ml de muestra de agua residual, agitar, y medir el pH después de cada dosificación, hasta que el pH se estabilice. Registrar el pH de estabilización, y proseguir agregando suspensión de cal hasta que se alcance pH 10

Con los resultados del experimento se puede dibujar una curva similar a la que aparece en la figura 5, graficando los miligramos de cal por litro de muestra, gastados para obtener un cierto pH, contra los valores de pH respectivos.

Para determinar el tiempo en que se completa la reacción:

a - Se usa la gráfica obtenida anteriormente, para determinar la cantidad de cal que debe agregarse a una muestra de 500 ml para obtener el pH deseado.

b - La cantidad de cal así determinada se agrega a la muestra, se agita continuamente, y se mide el tiempo en que se estabiliza el pH. Este dato representa el tiempo de mezclado necesario.

La potencia requerida en el mezclador se calcula con la siguiente fórmula:

$$P = \frac{k}{g} \; p \; n^3 \; D^5 \qquad (9)$$

donde:

P - potencia, ft-lb/sec.

k - coeficiente de mezclado

p - peso unitario de la mezcla

n - velocidad angular, r.p.s.

D - diámetro del impelente, ft.

Ejemplo:

El gasto de desechos líquidos de una cierta instalación industrial es de 6 l/sec. Mediante pruebas de laboratorio - se encontraron los resultados mostrados en la figura 6. Se desea neutralizar los desechos hasta alcanzar pH 7; determinar: a) la cantidad de cal consumida, b) el volumen - del tanque de reacción, si el tiempo de contacto es de 5 min, y c) la potencia necesaria en el impelente del mezclador.

($K = 0.4$; $D = 2.5$ ft; $\rho = 69.5 \frac{lb}{ft^3}$; $n = 4$ rps.

a) En la figura 6 se lee que para pH 7 se requieren 2250 mg de cal para tratar un l de agua residual, por tanto, para tratar 6 l/sec. se requerirán:

$$6 \frac{l}{sec} \times 2250 \frac{mg}{l.} \times \frac{Kg}{10^{+6}\ mg} \times \frac{86\ 400\ sec}{día} = 1166 \frac{Kg}{día}$$

b) El volumen del tanque de mezclado se obtiene multiplicando el gasto por el tiempo de mezclado:

$$6 \frac{lt}{sec} \times 5\ min \times \frac{60\ sec}{min} = 1800\ lt.$$

c) La potencia en el impelente del mezclador se obtiene - aplicando la fórmula 9.

$$P = \frac{0.4}{32.2} (69.5)(4)^3(2.5)^3 \frac{sec^2}{ft} \frac{lb}{ft^3} \frac{1}{sec^3} \frac{ft^5}{550\ ft\text{-}lb} \frac{sec}{HP}$$

$$P = 9.75\ H.\ P.$$

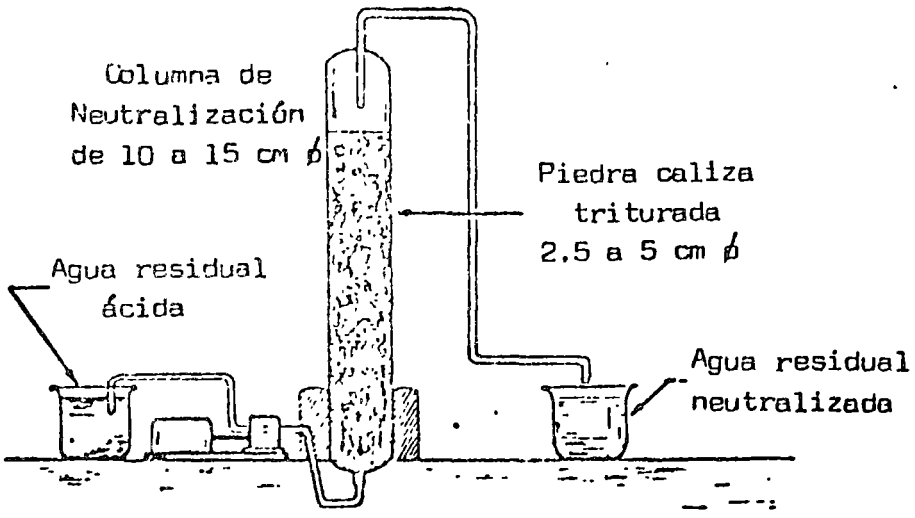


FIG. 1. Columnas de neutralización con piedra caliza.

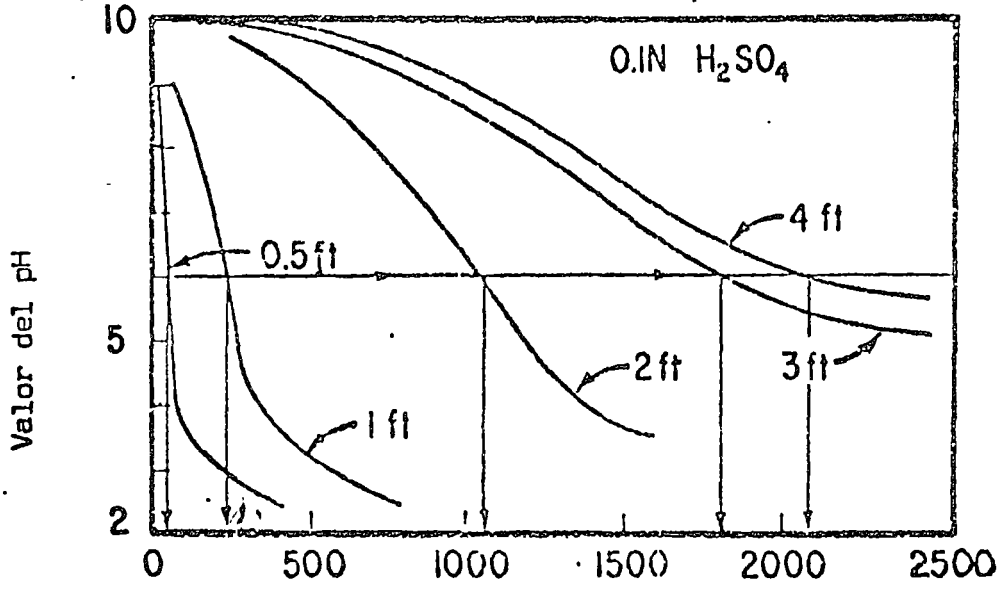


FIG. 2. Relación entre el pH y la carga superficial aplicada.

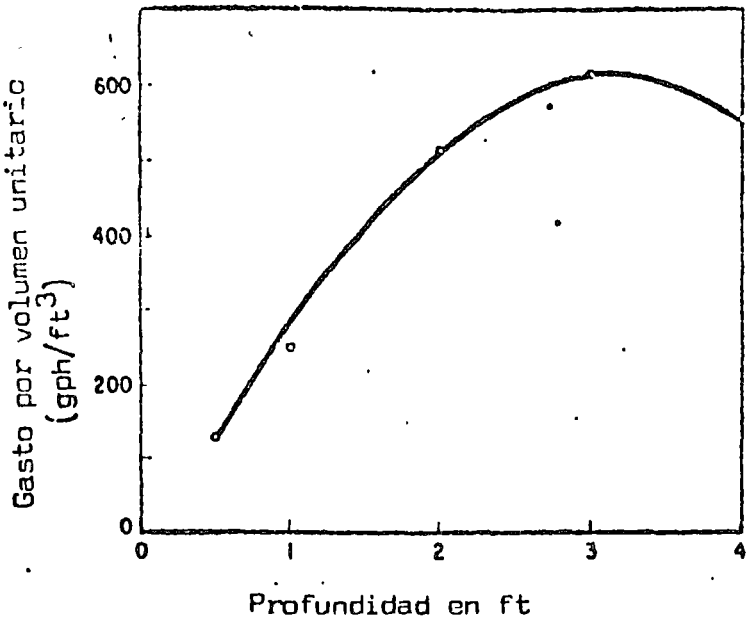


FIG. 3. Determinación de la profundidad óptima del lecho de caliza.

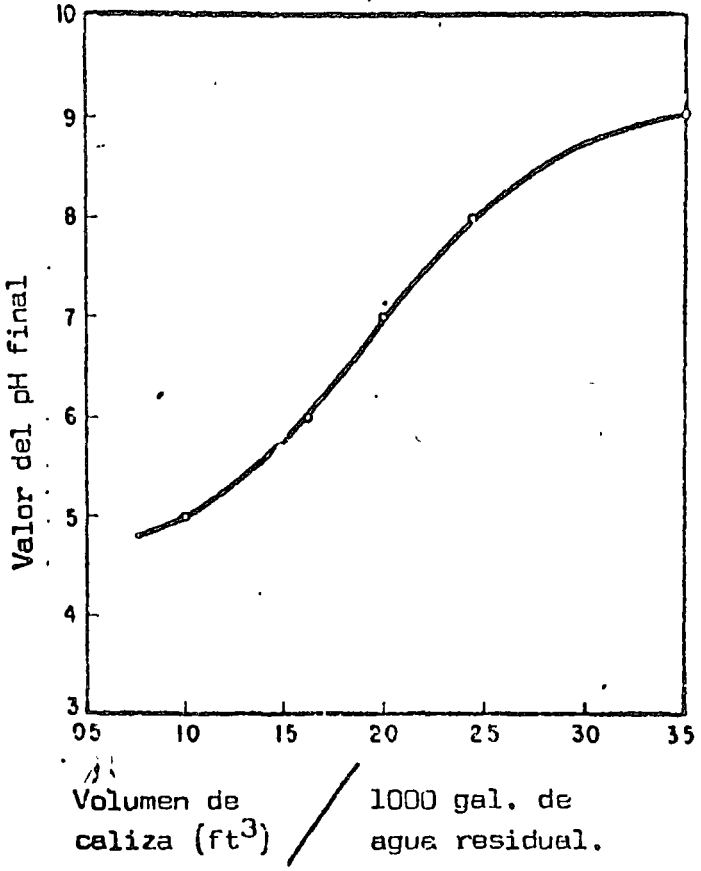


FIG. 4. Cantidad necesaria de caliza por volumen unitario de agua residual en función del pH final para una profundidad de lecho de 3 ft

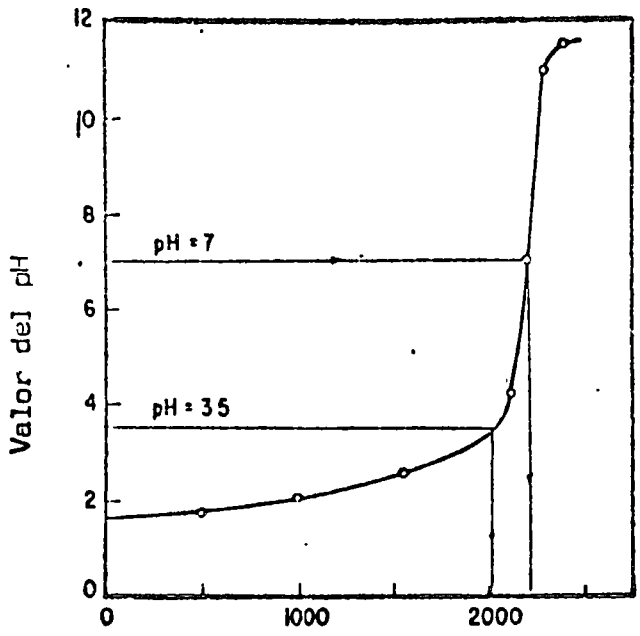


FIG. 5. Curva de neutralización.

TRATAMIENTO DE AGUAS RESIDUALES

FUENTES Y EFECTOS DE LA CONTAMINACION DEL AGUA

ING. EDMUNDO IZURIETA

FUENTES Y EFECTOS DE LA CONTAMINACION DEL AGUA. IMPORTANCIA DEL TRATAMIENTO.

Por: Ingeniero Edmundo Izurieta
Oficina Sanitaria Panamericana
Zona II

INTRODUCCION

De todos los problemas ecológicos del hombre moderno, los que más deberían preocuparnos son los relacionados con la explosión demográfica, urbanización e industrialización. La adaptación del hombre al fenómeno ecológico no es siemple, ya que se plantean dificiles problemas que requieren una profunda investigación, la misma que requerirá una actualización para adaptarla a la dinámica de la evolución social y tecnológica,

El control sanitario del ambiente en el que vivimos es muy importante, las condiciones insalubres han producido más muertes y enfermedades que cualquier otro factor. Por fortuna, la Ingeniería Sanitaria y las disciplinas actuales disponen, hoy en día, de técnicas suficientes para sanear cualquier tipo de ambiente habitado por el hombre. La aplicación de esos conocimientos es practicamente ilimitada, debiendo plantearse como meta a ser alcanzada por todas las comunidades no sólo como un objetivo sanitario sino como una característica de civilización.

La comparación de las condiciones presentes y futuras en las que vive y vivirá el hombre sirve de marco de referencia para calificar la calidad del ambiente en el que vivimos.

La contaminacion podría descibirse, en terminos generales, como la alteración desfavorables del medio que nos rodea, ocasionando problemas que tienden a gobernar.

la dinámica de la salud, de la economía y de los caracteres sociales del ser humano. La magnitud y complejidad de los problemas representan un desafío a todos los elementos constitutivos de la sociedad.

El mejoramiento de la calidad del ambiente requiere frecuentes innovaciones técnicas, así como también mucha imaginación para llevar a cabo efectivos programas de control. Además, es indispensable la comprensión y apoyo de la comunidad para poder interrelacionar la calidad del medio que se desea con el costo de las acciones.

Los desperdicios o residuos producto de la vida urbana, doméstica, social, agrícola, recreativa e industrial, que no son adecuadamente dispuestos ocasionan alteraciones físicas, químicas y biológicas en las características del aire, agua, suelo y la creación de problemas que deterioran los recursos materiales y naturales. Poco se conoce de las implicaciones a largo plazo que significan exponer al hombre a bajas concentraciones de sustancias tóxicas, en lo que respecta a aspectos fisiológicos y sicológicos. Estos y otros factores como el uso adecuado de la tierra, crecimiento industrial acelerado inducen al pronto establecimiento de programas adecuadamente administrados.

Tanto economistas, urbanistas y sanitaristas que tratan con el desarrollo social y económico, expresan su preocupación sobre el crecimiento demográfico y la distribución de la población. La urbanización es un fenómeno real que tiene caracteres de mayor o menor alarma, dependiendo del país.

A partir de los estudios demográficos se podrá estimar en forma cualitativa y cuantitativa los problemas ambientales que pueden derivarse del incremento de las concentraciones urbanas en determinadas regiónes del país. Será necesario evaluar con cifras el significado que tendrán esas grandes concentraciones humanas en las alteraciones que se produzcan tanto en el aire como en el agua y suelo.

El estudio y control de la contaminación requieren, de una acción conjunta o mancomunada entre todas las Instituciones Oficiales y a los diferentes niveles. Será indispensable planear las actividades en tal forma que nos permita la preparación de programas, adiestramiento del personal y búsqueda de métodos para financiar, diseñar y operar las facilidades o medios de tratamiento.

Por otro lado, será necesario establecer normas sobre la calidad del medio ambiente: aire, agua y suelo; para lo cual es indispensable disponer de información científica adecuada que nos permita definir los límites de calidad, integrar los estudios individualizados para poder relacionar los efectos existentes entre el medio y el hombre.

Será, asimismo, necesario definir la calidad del medio que se desea tener para determinar el costo de las medidas preventivas y de control.

II. CONTAMINACION DEL AGUA

Son innumerables los ejemplos que pueden citarse para ilustrar cómo el hombre ha usado y abusado de las

aguas superficiales, creando serias condiciones muchas veces sin el conocimiento de las autoridades interesadas. Por fortuna, la intervención de ciertas personas de visión ha impedido que la situación empeore y se produzca un grave deterioro de ese importante recurso natural.

Los pasos acelerados que se están dando en los países de la América para lograr su pronto desarrollo está estimulando vivamente la creación de nuevas industrias, sean éstas grandes, medianas o pequeñas. Esta actividad acompañada de la ilusión que significa figurar en la lista de países que están industrializándose, hace ignorar que ese desenvolvimiento debe ir acompañado de un profundo estudio sobre las posibles condiciones del medio, creado con el nuevo establecimiento industrial.

Aire, agua y suelo deberán ser motivo de investigación para concretar las nuevas situaciones que se crean. La ubicación de la industria no sólo es importante para satisfacer los requerimientos sanitarios, sino para lograr economías en el desplazamiento de la fuerza laboral, deberá tomarse en consideración el futuro inmediato y mediato de la industria para predecir los aspectos sociales y económicos derivados de su localización.

Por pequeña que sea una industria, en su proceso, se requiere la disposición de desechos gaseosos, líquidos y sólidos. Estos resíduos significan la adición de nuevos elementos al medio que modifican su composición, creando situaciones adversas y perjudiciales para el ambiente fabril y para elque tiene el hombre de las ciudades.

La urbanización, ese fenómeno real que viven todos los pueblos, producto de la atracción que siente el hombre por la ciudad, sea para satisfacer sus necesidades económicas buscando trabajo remunerativo o para satisfacer sus necesidades sicológicas y sociales, está generando, si no se la efectúa en forma ordenada y planeada, la creación de condiciones ambientales que tienden a degradar la calidad del medio. Resíduos líquidos y sólidos tienden a disponerse alsuelo o al agua, sin prever las implicaciones que eso acarrea si no se emplea la tecnología adecuada.

La contaminación del agua, aparte de producir situaciones inadecuadas para que el hombre pueda usar ese recurso en la satisfacción de sus necesidades domésticas, agrícolas o industriales, está originando una perturbación del medio en el que se desarrolla la comunidad o vida acuática. Esa alteración puede ocasionar que ciertas especies proliferen y otras tiendan a desaparecer. Por ejemplo, las especies de protozoarios que se alimentan de bacterias pueden aumentar cuando la carga bacteriana esalta. Más aún, la contaminación ocasiona el desarrollo de ciertas especies que pueden soportar o tolerar la perturbación o desequilibrio creado, tomando ventaja de las nuevas condiciones. Al mismo tiempo, aquellas especies que no puedan tolerar el nuevo régimen ecológico originado, tienden a reducirse.

La contaminación puede ocasionarse principalmente por la presencia de sólidos en suspensión, substancias tóxicas, cargas orgánicas y el calor.

Los sólidos en suspensión producen la reducción de la penetración de la luz en el agua. La luz es importante

en el proceso de fotosíntesis que aporta oxígeno y substituye al que es reducido por la respiración de los animales acuáticos. Se ha comprobado que la fotosíntesis es más importante que la turbulencia para obtener la reoxigenación del ecosistema acuático.

Siendo el oxígeno disuelto un elemento indispensable para lograr la estabilización de la materia orgánicadispuesta en el agua, lo lógico será establecer condiciones de equilibrio entre aquel y la demanda bioquímica del oxígeno. Esa relación nos da la pauta sobre la clase y grado de tratamiento que requiere un resíduo líquido doméstico e industrial.

En los anexos N°1 y N° 2 se presentan los principales orígenes de los contaminantes del agua (vivienda, industria, agricultura y minería) y su caracterización.

No siempre la contaminación del agua se debe unicamente a la carga orgánica, hay substancias químicas que producen alteraciones en el medio acuático, entre las principales tenemos: plaguicidas, herbicidas, fungicidas; fertilizantes que actúan a través del nitrógeno y fósforo como nutrientes produciendo fenómenos de eutroficación, detergentes y metales pesados.

Los plaguicidas constituyen un grupo muy variado de substancias tales como insecticidas, rodenticidas, molusquicidas, herbicidas, fungicidas. Su uso es muy variado y en forma poco técnica, sin ajustarse a las especificaciones que existen para cada uno de ellos. En la agricultura se emplean básicamente para la protección de las siembras (herbicidas para elarroz, maíz y caña de azúcar;

fungicidas para las patatas e insecticidas para una gran variedad de árboles); en los programas de salud pública para el control o erradicación de ciertos vectores responsables de la transmisión de enfermedades (paludismo, chagas y otras) o constituir molestias sanitarias.

Dada la enorme variedad de plaguicidas existentes se los clasifica en dos grupos "A" y "B", al primero pertenecen los organoclorados y organofosforados y al segundo principalmente ciertos herbicidas. Todos ellos son tóxicos en mayor o menor grado, dependiendo de la concentración. Se han logrado establecer normas sobre los niveles de concentración tanto en el agua de consumo doméstico, alimentos y como en el agua donde hay vida acuática productiva.

Para las aguas superficiales que se emplean como fuente de abastecimiento se han fijado algunos criterios:

PLAGUICIDAS	CONCENTRACION (mg/l)
Aldrín	0.017
Clordano	0.003
DDT	0.042
Dieldrina	0.017
Lindano	0.056

El uso de plaguicidas, principalente en la agricultura, determina que por escurrimiento del agua se produzcan concentraciones en lagos, estuarios, costas, etc.; hecho que reviste caracteres de toxicidad para una serie de especies acuáticas como ostras, camarones jóvenes y

otras económicamente importantes. Las ostras, por ejemplo, pueden vivir en presencia de DDT hasta niveles de 0.1 mg/l; pero, a niveles 1,000 veces menores (0.1 Microgramos/litro) la producción es 20% de la normal y las poblaciones de camarones sufren una mortalidad del 20%.

La toxicidad de una substancia se establece por el límite de tolerancia media (median tolerance limit = T Lm), que consiste en la cantidad o concentración necesaria para matar el 50% de los organismos en 96 horas o menos.

La toxicidad de los plaguicidas se determina respecto al camarón y los límites tolerables son los siguientes:

PLAGUICIDA	T Lm - 48 HORAS (µg/l)
Aldrín	0.04
BCH	2.00
Clordano	2.00
Lindano	0.20
DDT	0.60
Dieldrina	0.30

Otras substancias que desempeñan papel importante en la contaminación del agua son los detergentes. Su uso está muy generalizado tanto en la industria como en la vida doméstica.

Hasta la presente fecha se han empleado detergentes constituidos por fosfatos responsables del ablanda

miento del agua. Por el hecho de producir grandes cantidades de espuma dificultan el tratamiento de las aguas negras; además, son substancias de compleja composición molecular difícil de ser degradable por medio de las bacterias. Los detergentes comunmente empleados se les conoce como del tipo ABS (alkylben zene-sulfonate). Sus concentraciones en las aguas superficiales que se emplean como fuentes de abastecimiento doméstico se limita a 0.5 mg/1.

Estados Unidos e Inglaterra están realizando grandes esfuerzos para reemplazar los detergentes aniónicos por otros compuestos con menor contenido de fosfatos como el LAS, aún más, se ha determinado que el mejor substituto será el ácido nitrilo-triacetato (NTA). Este compuesto es 70 por ciento degradable por los procedimientos biológicos empleados en el tratamiento de aguas negras y las experiencias en animales revelan que no tienen efectos genéticos oevidencia de toxicidad.

Suecia, recientemente,dió a conocer haber producido un detergente que contiene 15 por ciento de citrato de sodio y es 100 por ciento biodegradable.

Existen otros elementos que alteran considerablemente la calidad del agua y por ello ocasionan su contaminación, estos son los metales pesados, que en altas concentraciones hacen indeseable al agua para el consumo doméstico o matan la vida acuática.

Entre los elementos tóxicos que juegan un papel importante tenemos el mercurio (Hg), plomo (Pb), níquel

(Ni), cadmio (Cd) y arsénico (As).

Existe una relación entre el contenido de cadmio y la dureza en los sistemas de abastecimiento de agua, con las enfermedades cardiovasculares.

Por otra parte, metales como zinc (Zn), magnesio (Mg), hierro (Fe), cobre (Cu), en concentraciones dos o tres veces mayores a los normales pueden producir daños que se hacen presentes solamente después de prolongados períodos.

Respecto al mercurio debemos recordar que por efecto de la luz solar hay reacciones de fotosíntesis con la presencia de la materia orgánica (plankton), que desempeña un papel catalizador y transforma los compuestos inorgánicos de mercurio en methyl-mercurio que es absorbido por los peces, creando intoxicaciones en las personas que los emplean como alimento.

En relación con el arsénico son muy conocidos los efectos que producen las altas concentraciones de ese elemento en el agua de consumo. Las normas establecen límites no mayores a 0.05 mg/l. Hay otro hecho importante respecto a este elemento y consiste en que hay varios detergentes de uso doméstico que contienen arsénico en cantidades variables. Un hecho evidente constituye los riesgos de contaminación a través de los residuos que quedan en la ropa lavada.

En el anexo N°3 se ha sintetizado los riesgos biológicos y químicos a los que está expuesto el hombre como consecuencia de ciertos contaminantes presentes en el agua; asimismo, se ha indicado las fuentes de procedencia de los principales.

El manejo de los residuos líquidos que son dispuestos en los cursos de agua, para que no sean dañinos al hombre y no produzcan degradación del ambiente, supone la ejecución de una serie de actividades que podrían resumirse así: análisis de los residuos, reconocimiento de las corrientes, control de las plantas industriales (modificación del proceso y reducción de los residuos y desperdicios), educación, cumplimiento de las disposiciones, tratamiento preliminar, control de los residuos líquidos, construcción y mantenimiento.

A los contaminantes se les clasifica en: causantes de enfermedades, conservativos y no conservativos. En estos tres grupos existen ocho categorías generales:

- agentes infecciosos
- residuos que demandan oxígeno
- nutrientes de plantas
- compuestos químicos orgánicos
- compuestos inorgánicos y minerales
- sedimentos
- materiales radioactivos
- calor

Entre los primeros se incluyen aquellos que se refieren a la salud pública. Los conservativos son estables y no se degradan por los procesos biológicos normales, como por ejemplo los compuestos inorgánicos, es el caso de los cloruros que pueden ser diluidos pero no reducidos encantidad. Los contaminantes no conservativos en el sistema acuático natural cambian sus características debido a las fuerzas físicas, químicas y biológicas. El residuo líquido (agua negra) es un desecho orgánico alta

mente inestable y puede convertirse en bióxido de carbono, materiales inorgánicos y substancias celulares.

La contaminación de las corrientes tiene efecto sobre la vida acuática. El tratamiento generalmente no es completo después de la estabilización de la materia por el proceso biológico, o después de que el residuo líquido haya recorrido los primeros kilómetros en la corriente de agua. El tratamiento será completo solamente cuando ya no se encuentren trazas de los materiales de desecho, en cantidades que puedan ser objetables a los usuarios del agua.

Al estudiar los cambios de una corriente de agua, por efecto de las descargas de materiales degradables, se tiene un nuevo sistema ecológico que debe adaptarse a las nuevas condiciones. Se produce primero una zona de degradación, seguida de una zona de descomposición y luego una de recuperación, en cada una de esas condiciones cambian el número y tipos de especies acuáticas . Los nutrientes disponibles proveen de alimentación a ciertos microorganismos, creando una demanda de oxígeno. Los microorganismos que metabolizan los alimentos y se reproducen bajo condiciones acróbicas requieren de la presencia de oxígeno gaseoso disuelto; por tanto, mientras más abundante sea el alimento los organismos requeren más oxígeno disuelto. En caso contrario, si el alimento disminuye las necesidades de oxígeno también disminuyen. Al producirse la reareación se restablece la concentración de oxígeno en la corriente. Anexo Nº 4.

La bioquímica del tratamiento aeróbico y anaeróbico puede verse en el Anexo Nº 5 .

Existen numerosos procesos para el tratamiento de los residuos líquidos, para su selección será necesario considerar las características del desecho y el grado de tratamiento requerido. En el anexo Nº 6 se indica la secuencia que tienen los diferentes procesos de tratamiento:

- pretratamiento
- tratamiento primario
- tratamiento secundario
- tratamiento terciario
- tratamiento de lodos
- disposición de lodos
- disposición de los líquidos tratados

IV. RESUMEN

La contaminación atmosférica tiene un profundo impacto en la salud y en la agricultura; por efecto de la corrosión produce daños profundos en muebles, automóviles, estructuras metálicas; afecta la limpieza de casas y edificaciones; ocasiona la devaluación de mercancías, deterioro de la ropa (el alquitrán disuelve la fibra sintética); por lo mismo, hay un marcado desperdicio de agua, jabón y detergentes.

Se podría medir monetariamente el impacto económico de la contaminación del aire, sin incluir los gastos debidos a muertes y reparación de enfermos, en la suma de 30 dol./persona/año.

Tenemos optimismo que una chimenea sea símbolo de progreso pero no de una indeseable contaminación. En los programas de desarrollo debe siempre asociarse progreso con salud.

En lo que respecta a la contaminación del agua y del suelo ya se ha mencionado la trascendencia que tiene su control y prevención en la salud, agricultura, industria, pesca, recreación, estética, etc. Resulta verdaderamente complejo valorar su impacto económico, ya que estará vinculado a la magnitud del daño que ocasione la contaminación y al grado de degradación que se produzca de ese recurso natural.

Es difícil establecer con precisión y en forma apriori los límites de la calidad del ambiente. Para entender mejor el por qué, imaginemos que los habitantes de una ciudad toman un vaso de agua conteniendo ciertas substancias tóxica. ¿Qué ocurrirá?, algunas personas morirán,

otras enfermarán leve o gravemente, y otras no resultarán afectadas. La cantidad de substancias que se administre permanentemente a las personas sin afectar su salud, constituirá el denominado "índice permisible".

La lucha contra la contaminación, sea ésta del aire, agua y suelo, requerirá una acción mancomunada y coordinada entre todas las instituciones públicas y privadas. Hay varios pasos previos que dar, pudiendo citar entre los principales: reglamentación, fijación de criterios claros para definir la calidad del ambiente que se desea obtener para esa forma determinar los parámetros, adiestramiento de personal tanto en el nivel normativo como en el aplicativo, para poner en marcha las medidas preventivas y correctivas.

CONTAMINACION DEL AGUA

ANEXO Nº 1

- ORIGENES DE LA CONTAMINACION
  - Aguas negras o residuos líquidos municipales.
  - Residios líquidos industriales: efluentes de las industrias de manufactura o procesamiento de productos de consumo (biológicos, químicos, metales pesados).
  - Residuos líquidos termales: termoeléctricas y refrigeración de la industria.
  - Residuos agrícolas: erosión de la tierra de cultivo, disolución y arrastre de sustancias químicas agrícolas (biocidas y residuos animales.).
  - Limo proveniente de: erosión natural de la tierra, tala de bosques, urbanizaciones, minería.
  - Petróleo y otras substancias: lugares de producción, transporte y distribución.
  - Residuos de minas: resultantes del proceso.
- CLASES DE CONTAMINANTES
  - Domésticos
  - Industriales
  - Materia orgánica (oxigenación para estabilizarla)
    - Demanda de oxígeno; demanda química de oxígeno (DQO) y demanda bioquímica de oxígeno (DBO).
    - Oxígeno disuelto: OD
  - Substancias Químicas
    - pesticidas, herbicidas, fungicidas
    - fertilizantes: nutrientes como N y P producen eutroficación
    - Detergentes
    - Metales pesados: Hg-Cu-Pb-Ni-Cd-Zn
    - Fotosíntesis del mercurio:

Hg+luz+plankton ⟶ Methyl mercurio
↓ catalizador ↓ compuesto absorbe

PRINCIPALES CONTAMINANTES DEL AGUA Y SU CARACTERIZACION

ANEXO N° 2

- VIVIENDAS (hombre) ⟶ aguas negras o domésticas
  - Lodos húmedos: 10 litros/persona/día
  - Sólidos secos: 50 Kg/persona/año
- CIUDADES ⟶ aguas municipales

materia orgánica: 200-500 mg/1 de DBO

- Compuestos orgánicos: Carbohidratos, proteinas, amino ácidos, ácidos grasos, esteres, jabones, detergentes aniónicos.
- Compuestos inorgánicos: sodio, potasio, calcio, magnesio, manganeso, cloruros, nitritos, nitratos, bicarbonatos, sulfatos y fosfatos.
- Parásitos, microorganismos y virus.

- INDUSTRIAS ⟶ aguas residuales
  - Materia prima, productos: intermedios, derivados y finales.
  - Detergentes, solventes, cianuros, metales pesados, blanqueadores, colorantes, ácidos: orgánicos y minerales, sustancias nitrogenadas, grasas, sales, agentes de curtiembre, sulfuros, amoniaco.

- AGRICULTURA ⟶ residuos agrícolas y ganaderos
  - Residuos de animales.
  - Material orgánico: DBO es 5 veces mayor a la producida por el hombre.
  - Material de erosión.
  - Sales inorgánicas y minerales diversos (irrigación).
  - Plaguicidas.
  - Nutrientes de plantas (fertilizantes).
  - Parásitos, microorganismos y virus.

EFECTOS DE ALGUNOS CONTAMINANTES DEL AGUA EN LA SALUD

ANEXO Nº 3

RIESGOS BIOLOGICOS

- Microorganismos patogénicos: cólera, disentoría bacilar, fiebres tifoidea y paratifoidea, gastroentoritis, diarreas infantiles, parálisis infantil, hepatitis infecciosa.
- Parasitosis: amibiasis, ascariasis, triquinosis, esquistosomiasis.
- Enfermedades producidas por vectores que se desarrollan en el agua.

RIESGOS QUIMICOS

- Nitratos y nitritos: metahemoglobinemia. No se produce cuando es menor de 45 mg/1.
- Fluoruros: fluorosis y ostiofluorosis.
- Arsénico: Presencia puede ser natural, industrial o de los plaguicidas. Límite permisible en el agua potable 0.05 mg/1. Aguas con concentraciones de 0.6~0.8 mg/1 en la América Latina ocasiona intoxicación endémica (acumulativo). Pie negro (black foot), cáncer.
- Selenio: el contenido de las aguas naturales 50-300 g/litro. En las plantas de tratamiento se lo elimina, como el arsénico, con precipitación química y adsorción.
- Mercurio: Contenido de las aguas naturales 0.01~0.3 µg/1., en el agua del mar 0.1 µg/1., en la atmósfera de las áreas industriales 1.0 µg/1. Origen: minas; industrias de la pulpa y papel, plástico, electrónica, agricultura y empleo combustibles fósiles. Límite permisible en el agua potable 0.001 mg/1. Toxicidad.
- Plomo: Contenido en las aguas naturales 0.01 ~ 0.03 mg/1. Origen: tuberías de plomo, plásticos, combustibles, industria de baterías. Se acumula en peces y mariscos. Límite permisible 0.1 mg/1
- Cadmio: Contenido en las aguas naturales 1µg/1, pero pueden ascender a 10µg/1. Origina en la industria, prosente en los sedimentos de tratamiento (contaminación del arroz en Japón, 1970). Toxicidad y posiblemente efectos cardiovasculares. Límite permisible en el a.p. 0.01 mg/1.
- Dureza del agua: la dureza baja del agua de consumo está asociada

ANEXO N°3

con la mayor prevalencia de enfermedades cardiovasculares, hipertensión, etc.

- Plaguicidas organo clorados: origen en la agricultura e industria. Compuestos de baja solubilidad, persistentes y permanecen sin cambio por muchos años. Ocasionan toxicidad aguda en concentraciones de 5 μg/l y menos, de ahí que se adopte 1/100 como factor de aplicación.

  En Estados Unidos las concentraciones medias varían de 0.2 ~ 28 nanogramos y en Gran Bretaña 1.6 ~ 64.6.

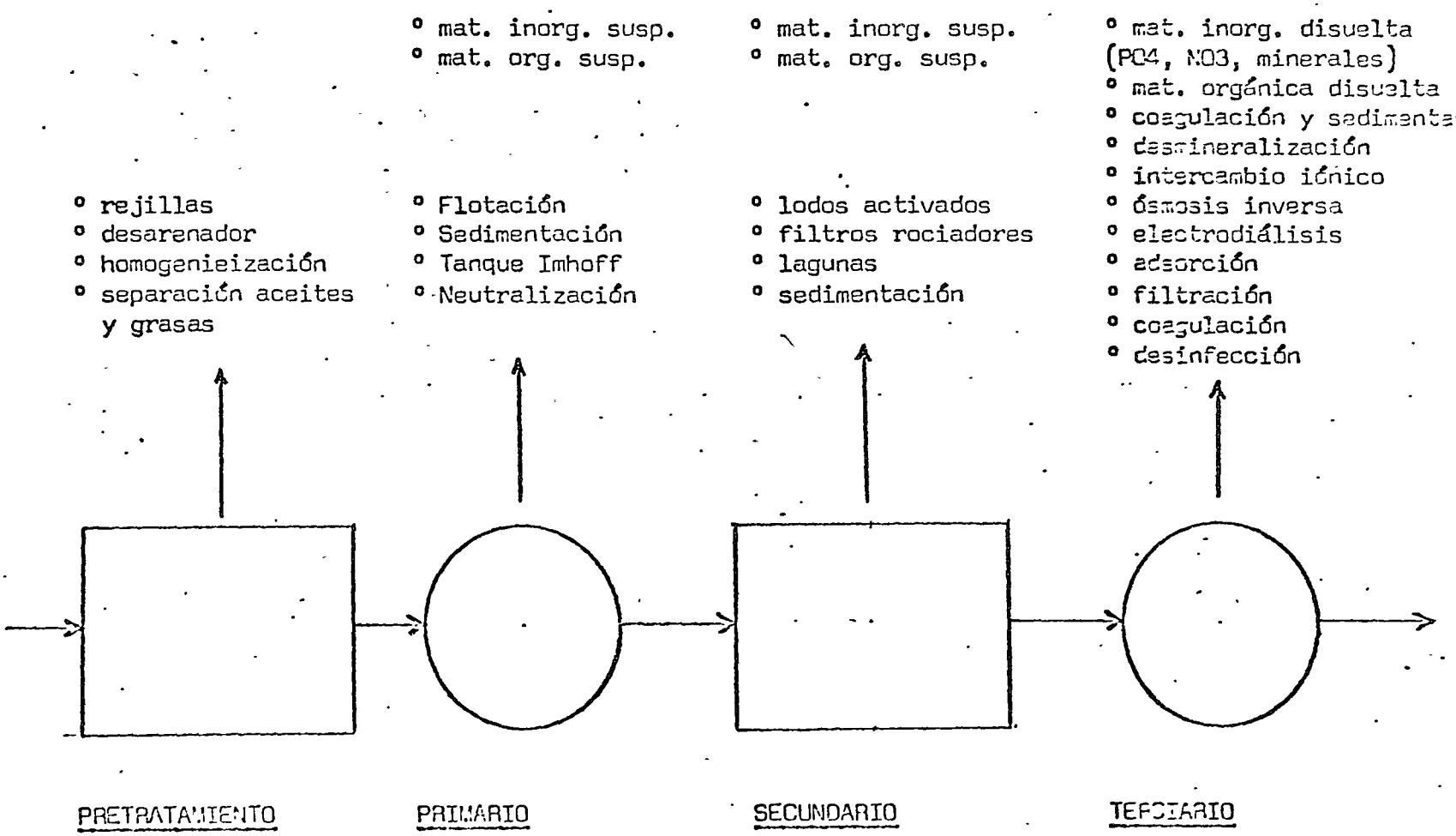
- Plaguicidas organofosforados: (diacinón, malatión, paratión, clortión, dipterex): Se hidrolizan más facilmente, persisten menos de un año, se degradan más facilmente, son más agresivos en invierno, producen mayor toxicidad a la fauna marina.

- Hidrocarburos aromáticos polinucleares: (HAP) En el ambiente se encuentra el benzopireno. Tiene caractores cancerígenos. Aguas subterráneas 0.001-0.010 μg/l, lagos 0.010 ~ 0.025 μg/l, aguas altamente contaminadas > 0.100 μg/l.

- Detergentes aniónicos: (ABS): causa espuma e interfiere con autopurificación y tratamiento. Los de la cadena Lineal son más biodegradables. Conc. deseable 0.2 mg/l.

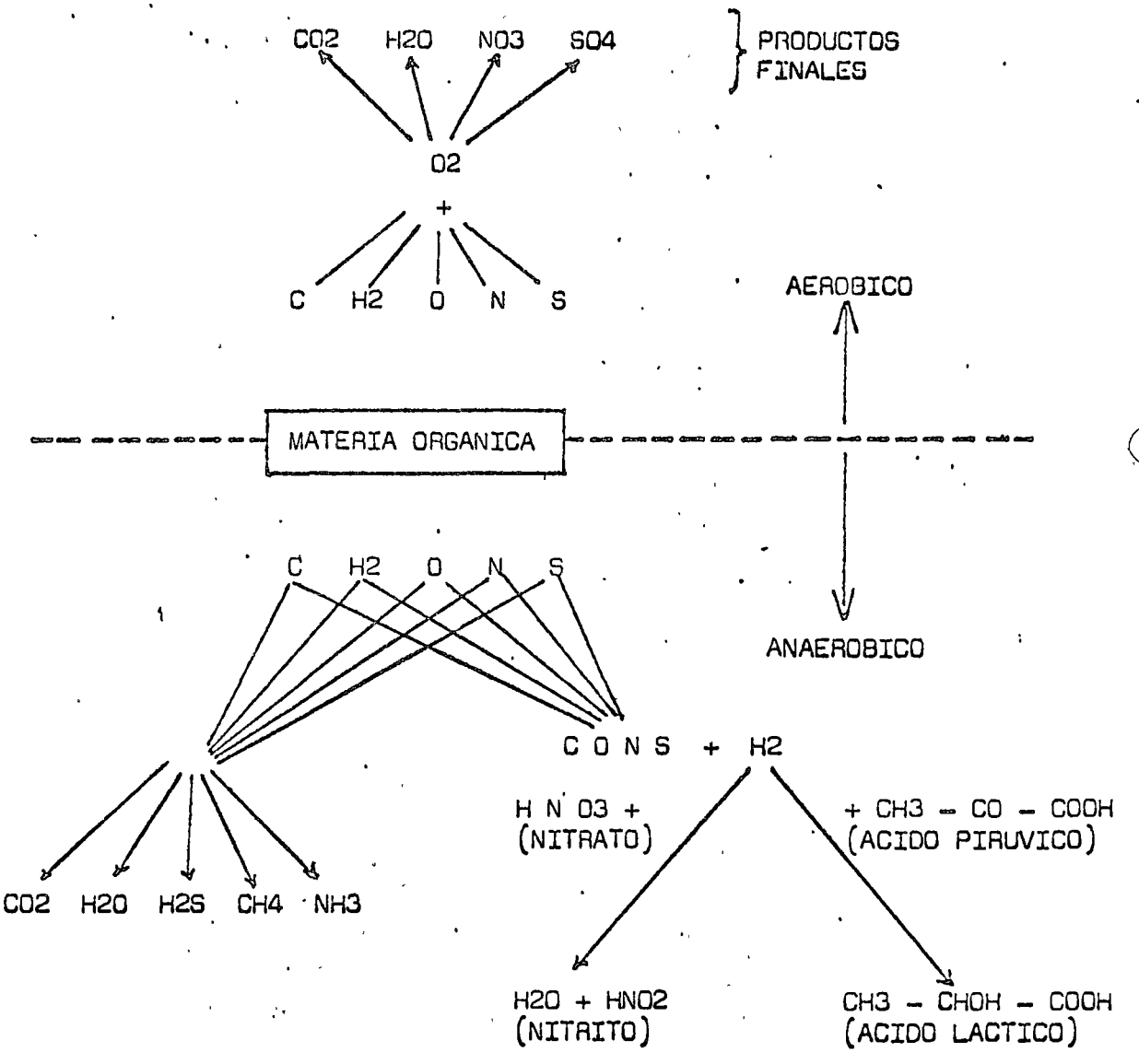
PROCESO DE TRATAMIENTO DE LOS RESIDUOS LIQUIDOS

ANEXO Nº 4



DEGRADACION DE LA MATERIA ORGANICA

ANEXO Nº 5



SECUENCIA EN EL TRATAMIENTO DE LOS RESIDUOS LIQUIDOS

ANEXO Nº 6

1. Pretratamiento

   1.a Rejillas
   1.b Desarenador
   1.c Homogeneización y almacenamiento.
   1.d Separación de aceites y grasas

2. Primario

   2.a Neutralización (Q)
   2.b Adición subst. químicas y floculación (Q).
   2.c Flotación (F)
   2.d Sedimentación (F)

3. Secundario

   3.a Lodos activados (SOD)
   3.b Lagunas anaeróbicas (SOD)
   3.c Filtros rociadores (SOD)
   3.d Lagunas aeradas (SOD)
   3.e Lagunas de estabilización (SOD)
   3.f Sedimentación (RSS)

4. Terciario

   4.a Coagulación y sedimentación
   4.b Filtración
   4.c Adsorción (carbón)
   4.d Intercambio iónico

5. Tratamiento de los lodos

   5.a Digestión
   5.b Filtración al vacio
   5.c Centrifugación
   5.d Lechos de secado o lagunamiento.

6. Disposición de los lodos

   6.a Incineración
   6.b Relleno del terreno
   6.c Disposición en el mar

7. Disposición de los líquidos tratados

   7.a Cuerpos receptores de agua
   7.b Transporte y descarga controlados
   7.c Disposición en el mar
   7.d Disposición superficial en la tierra (recarga de las aguas subterráneas)
   7.e Inyección en pozos profundos
   7.f Evaporación e incineración

Q = químico
F = Físico
SOD= substancias orgánicas disueltas
RSS= remoción de sólidos suspendidos

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TRATAMIENTO DE AGUAS RESIDUALES

INTRODUCTION-ENVIRONMENTAL GUIDELINES

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INTRODUCTION--ENVIRONMENTAL GUIDELINES

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Industrial wastewaters have a significant impact on the available water resources. The interrelated factors involving types of pollutants, source of pollution and impact of these constituents on water resources presents a complex problem. Expert knowledge is needed to understand the many industrial processes, options available for producing the required treatment and impact of residuals derived from treatment on the environment.

This paper discusses classification and characterization of industrial wastewaters, treatment technology and constituent removals, relationship between physical and biological environments, and role of environmental base line evaluations.

To the water resources planner, the answer to the above question becomes one of using sophisticated technology to solve a most complex problem. This evaluation involves an understanding of the industry, the waste constituents, the treatment options, the ultimate disposal limitations, the environmental base line as a societal monitor and the role of conceptual planning in residuals management.

Categorization of Industrial Wastewaters

The Standard Industrial Classification system (SIC) has been used in the United States for many years as a system for delineating industries according to product. Although such a system has many advantages for estimating industrial growth, statistical accounting, and economic assessment, it is severely limited when applied to industrial effluent classification. This is attributable to the many nonclassifiable factors which influence the quality of industrial effluents, such as plant age, feedstock, influent water quality, process

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characteristics, climatological conditions, operational practice, and water use patterns. In recognition of these factors, the U. S. Congress has listed a minimum number of industrial categories in recently enacted legislation which serves as the basis for effluent classification, quality limitations, and permit enforcement (1). These categories, which transcend many SIC numbers, are listed in Table 1.

Once an industrial categorization system is established, then the logical sequence of predicting industrial effluent loads to a defined body of water would involve:

(a) estimating raw waste loads generated in the present and future manufacture of product;
(b) predicting the portion of this load that can be removed using demonstrated treatment technology; and
(c) projecting the implementation schedule for applying this demonstrated technology.

Raw waste loads, as a practical matter, are usually estimated from historical characterization data of the total effluent discharged from many production components within an integrated industrial plant. If it were possible to obtain such information from singular production units, the wastewater profiles could be developed on a "building block" or cumulative approach for complex systems. However, there are many factors such as water recycle and reuse, changes in water quality when mixed with other sources, and water use not directly associated with production which prevent this form of developing raw waste loads.

Classification of Raw Waste Loads

The impact of raw waste loads may be depicted in terms of various potential impacts; namely, oxygen depletion, eutrophication, toxicity, and general nuisance. It is recognized that many constituents commonly found in industrial effluents transcend this classification system.

Oxygen Depletion Potential: Certain inorganic compounds and many organic compounds commonly found in industrial wastewaters exert an oxygen demand in water. This demand can be either chemical or biological and it can be measured in terms of:

(a) biochemical oxygen demand (5 day or ultimate--BOD_5, BOD_u);
(b) Chemical oxygen demand (COD);

Table 1. Classification for Industrial Effluents

Pulp and paper mills	Inorganic chemicals manufacturing
Paperboard, builders paper and board mills	Plastic and synthetic materials manufacturing
Meat product and rendering processing	Soap and detergent manufacturing
Dairy product processing	Fertilizer manufacturing
Grain mills	Petroleum refining
Canned and preserved fruits and vegetables processing	Iron and steel manufacturing
Canned and preserved seafood processing	Nonferrous metals manufacturing
Sugar processing	Phosphate manufacturing
Textile mills	Steam electric powerplants
Cement manufacturing	Ferroalloy manufacturing
Feedlots	Leather tanning and finishing
Electroplating	Glass and asbestos manufacturing
Organic chemicals manufacturing	Rubber processing
	Timber products processing

(c) total oxygen demand (TOD);

(d) Total organic carbon (TOC); and

(e) immediate oxygen demand (IOD).

Oxygen demand using one of these parameters is convenient for indirectly estimating the environmental and water use effects of a particular industrial wastewater. It may be difficult to relate the oxygen demand of an industrial wastewater to the dissolved oxygen pattern of a receiving water. Many industrial effluents exhibit high COD, TOC or TOD, but very low BOD values. Such characteristics indicate the presence of a high concentration of organic materials, but wastes which are not oxidized biochemically under the test conditions. The BOD_5/COD ratio is indicative of the organic fraction subject to biological degradation and oxygen utilization, and typical values for industrial effluents are tabulated in Table 2. It should be noted that neither the BOD_5 nor COD reflect the total oxidation potential of ammonia. Nitrification can significantly reduce the dissolved oxygen.

Dissolved oxygen depletion is not only a function of the quantity of oxygen-demanding material present in the water but also depends on:

(a) natural reaeration due to the transport of oxygen from the atmosphere across the air-water interface;

(b) mixing and dispersion of the oxygen-demanding materials in the water column; and

(c) oxygen production by the physiological activities of photosynthetic plants, principally phytoplankton.

Thus, the physical and biological properties of the receiving waters are equally as important as the oxygen demand of a wastewater effluent when estimating the impact of the effluent on the dissolved oxygen concentration in the receiving water.

The primary purpose for establishing dissolved oxygen criteria for receiving waters is to protect aquatic organisms. Secondarily, low dissolved oxygen concentrations can cause nuisance conditions and may endanger terrestrial wildlife by permitting the growth of anaerobic, pathogenic microorganisms in bottom sediments (2).

The dissolved oxygen criterion commonly used for fresh surface waters is based on the needs of native fish populations and associated aquatic life. It is reasonable to assume that the requirements for fish would serve the remainder of the aquatic community since a fish population would not remain in

Table 2. BOD_5/COD Ratios for Selected Chemical Groups

Chemical Group	BOD_5/COD
Aliphatics	
Methanol	1.00
Ethanol	0.75
Ethylene glycol	0.32
Isopropanol	0.08
Maleic acid	0.80
Acetone	0.39
Methyl ethyl ketone	0.82
Ethyl acetate	0.80
Oxalic acid	0.89
Aromatics	
Toluene	0.61
Benzaldehyde	0.82
Benxoic acid	0.74
Hydroquinone	0.55
O-Cresol	0.74
Nitrogenous Organics	
Monoethanolamine	0.65
Acrylonitrile	0.01
Aniline	0.61
Refractory	
Tertiary - butanol	0.01
Diethylene glycol	0.14
Pyridine	1.00
Wastewater	
Acrylonitrile	0.19
Ammonia	0.06
Ammonia	0.55
Ammonia + Utilities	0.37
Butadiene-Styrene	0.05
Chlorine-Soda	0.03
Cumene	0.12
EDC-Direct	0.49
EDC-Oxyhydrochlorination	0.64
Ethylene oxide	0.35
Olefins	0.25
Polystyrene	0.44
Polyvinylchloride	0.10
Propylene oxide	0.45
Propylene glycol	0.48
Propylene tetramer	0.34
Sewage	0.37
Synthetic rubber	0.51
Urea	0.79
Vinyl Chloride	0.04

an area devoid of an adequate food supply. Much more information is available for fresh water fishes and organisms than for estuarine and marine organisms. However, sufficient data are available to establish preliminary critera for the latter groups.

A dissolved oxygen (D.O.) concentration greater than 5.0 mg/l provides a suitable environment for a diversified warm water biota, including game fish. Natural D.O. variability due to the biological and physical characteristics of a particular body of water may require that the established criterion permit deviations below this value of as much as 1.0 mg/l of D.O under extreme low flow and temperature conditions.

Because of the natural variability inherent in estuarine environments, estuarine organisms have adapted themselves to a wider range of dissolved oxygen concentrations than most fresh water organisms. Thus, a dissolved oxygen criterion of 4.0 mg/l minimum, with provision for short term variations of as much as 1.0 mg/l, is generally promulgated for estuarine waters (2).

Eutrophication Potential: The proliferation of aquatic plant life in waters which receive effluents from municipalities and many industries is commonly attributed to the enrichment of waters by the addition of nitrogen and phosphorus. Eutrophication, the term used to describe this phenomenon, is a complex process and often chemical compounds other than nitrogen and phosphorus are significant factors in promoting it; specifically, trace metals and carbon dioxide. Severe eutrophication represents an unstable aquatic ecosystem exhibiting extreme diurnal fluctuations in D.O., pH, and alkalinity. These conditions can result in fish kills due to oxygen depletion or toxicity, visually displeasing algal growth, and taste and odor problems in receiving waters. In addition, algae-laden fresh water supplies are not suitable for municipal and industrial uses without extensive and costly treatment.

The main precursors to eutrophication have been attributed to inorganic phosphorus and nitrates (3). However, more complex forms of inorganic phosphorus as well as organic phosphorus can stimulate aquatic plant life. Similarly, nitrogen derived from ammonia and subsequent fixation of gaseous nitrogen by algae can enhance eutrophication. This diversity of nutrient utilization, combined with complex interactions between nutrients and various physical, chemical, and biological variables clouds the establishment of any definitive threshold concentration responsible for eutrophication. This makes it difficult to establish specific nitrogen and phosphorus limitations for industrial effluents.

Toxicity Potential: The term toxicity may include the effects of pH, dissolved oxygen depletion, high salt concentrations, elevated temperature, soluble metals, and a host of other physical-chemical-biological interactions.

Toxicity is directly related to the dosage of the chemical taken into an organism. The mode of intake is not important. In water, the toxic effects of a compound can best be described in terms of a concentration threshold; the concentration above which some type of physiological damage will occur to the organism or its progeny.

It is useful to distinguish between classes of toxic action. A classification is usually based on the rate of toxic action of the toxic compound, the duration of the symptoms, and the rate of intake of the compound. Acute toxicity is characterized by the onset of negative physiological effects, frequently resulting in death shortly after exposure. Chronic toxicity is manifested by the appearance of negative physiological effects after extended periods of exposure to sub-acute chemical dosages. Typical chronic toxicity manifestations include: mortality, malignancies, inability to reproduce, and genetically mutated progeny. The purpose of toxicity criteria is to eliminate compounds with this potential from both the aquatic environment and from any potential uses of the water involving human or animal consumption.

Relatively few of the many compounds found in industrial wastewaters which are potentially toxic to aquatic life have been sufficiently studied to allow an accurate definition of their maximum allowable concentrations. Numerical criteria have been established for some common chemical constituents discharged in industrial wastewaters. However, toxicity bioassays, in which indigenous aquatic organisms are exposed to known concentrations of the wastewater to be discharged in order to observe deleterious physiological effects, are the only means for establishing the toxicity of other less common or unknown substances. Unfortunately, toxicity bioassays measure only acute toxicity and chronic toxic effects of the tested effluent may remain unknown. The chronic toxicity of certain compounds, notably the heavy metals and radioactive compounds, are sufficiently understood so that criteria have been established for these materials.

Ammonia-nitrogen, which exists either as free ammonia or an ammonium ion in water, exhibits several important effects in the aquatic environment in a toxicological sense. The class of toxic action of ammonia-nitrogen involves acute rather than chronic toxicity.

In most aquatic systems, the biological conversion of ammonia to nitrate is relatively rapid, so ammonia concentrations will tend to decrease with time

of exposure. Evidence indicates that ammonia or ammonium concentrations greater than 1.0 mg/l adversly affect many aquatic populations, the exact lethal concentration being a function of the pH and the D.O. of the water. Ammonia-nitrogen concentrations lower than 1.0 mg/l should be safe for most aquatic populations although some phytoplankton species may be affected at concentrations of 0.5 mg/l (4).

Heavy metals found in many industrial effluents exhibit both acute and chronic toxic effects in aquatic and terrestrial ecosystems. Thus, public health effects are equally as important as environmental impacts when criteria are set for the various metals found in effluents and natural waters. An important property of heavy metals is that many organisms, both aquatic and terrestrial, tend to accumulate certain metals in various organs of the body until toxic conditions inevitably result. In fact, a lower food chain organism may show little or no toxic effect from a particular metal while the predators of this organism may, upon eating large quantities of the contaminated organism, demonstrate chronic or acute toxicity. The biological properties of heavy metals and their extreme toxicity are such that stringent criteria for their concentration in receiving waters must be established to avoid adverse consequences to public health and the environment resulting from excessive discharges of these materials. The criterion for each metal is based on suitability of the water for human consumption and is a function of its toxicity, its persistence in toxic form, and its tendency to accumulate in the food chain. The criteria for the heavy metals in drinking water as referenced to a background concentration in sea water is given in Table 3 (3,4,5).

Table 3. Receiving Water Quality Criteria and Natural Water Quality for Selected Heavy Metals

Element	Criterion (mg/l)	Natural Concentration in Sea Water (mg/l)
Mercury	0.005	0.0001
Chromium (hexavalent)	0.05	0.00004
Lead	0.05	0.00002
Copper	1.0	0.001
Zinc	5.0	0.002

To eliminate the possibility of acute toxic effects resulting from the discharge of a wastewater effluent into a receiving water, a toxicity bioassay is generally recommended. The bioassay consists of placing the most sensitive native organisms of the proposed receiving waters in varouis dilutions of the wastewater and the receiving waters and observing any toxic effects which occur in the sample population during a specified time period. Common time periods used are 40 and 96 hours and the bioassay results are usually defined in terms of a median tolerance limit (TL_m) for the organisms being evaluated. The TL_m is that concentration or dilution of the toxic waste or compound which sults in 50 percent mortality in the test organism sample during the specified time period. This TL_m is applied to the wastewater using an application factor which is some fraction of the TL_m and is designed to account for the persistence or cumulative effect of the toxic compounds. Non-persistent compounds, those that degrade rapidly under natural conditions, generally have an application factor of 1/10 while for more persistent or toxic compounds, an application factor of 1/20 to 1/100 is used.

General Nuisance Potential: Many constituents found in industrial wastewaters have nuisance potential. Phenolic compounds are particularly common to many industrial effluents and impart a taste to drinking water, even in minute concentrations. Floating materials such as oils, grease, and chemical surfactants have an adverse affect both in terms of aesthetics and atmospheric reaeration.

Oils have a wide range of effects on water resources. Extremely small quantities of oil can cover large surface areas. Oil slicks are visible at concentrations as low as one litre of oil per hectare. Free oils and oil emulsions may interfere with the respiration of aquatic organisms. Many oils contain soluble fractions which are toxic to aquatic life and other fractions may impart taste and odors to the flesh of fish. Oils can also produce displeasing sludges on beaches and may destroy benthic biota. Due to the chemical complexity of chemicals frequently called oils, it is difficult to establish numerical criteria. Current practice for fresh, estuarine, and marine receiving waters is to prohibit discharge of oils and greases which:

(a) result in a visible film or sheen;
(b) is detectable by odor;
(c) cause a "tainting" of the flesh of edible fish or macro-invertebrates;
(d) form an oil sludge deposit on beaches or bottom sediments; and
(e) become effective toxicants to aquatic organisms.

Color and turbidity are undesirable properties of some waste effluents. Color and turbidity diminish light penetration in natural waters, and also affect the domestic and industrial reuse of water. This removal process often adds undue expense to water treatment costs.

Settleable and suspended solids, both organic and inorganic substances, are frequently associated with industrial wastes. The settleable and suspended material in a water or wastewater sample is generally estimated on the basis of the following parameters; total suspended solids (TSS), volatile suspended solids (VSS), and settleable matter, all measured in mg/l. The inorganic solids consist of sands, silts, clays, inorganic precipitates, and dusts while the organic fraction may be extremely heterogeneous with regard to its chemical content. Factors affecting the settleability of suspended solids include the turbulence in the receiving waters, chemical or physical agglomeration of the particles, and the relative density of the particles in relation to the water.

Settleable solids may adversely affect the aquatic biota by covering the bottom with a blanket of material that destroys the benthic biota or spawning areas of fish. Organic bottom deposits may deplete benthic dissolved oxygen and produce hydrogen sulfide, methane, carbon dioxide, or other noxious gases. Some settleable solids can cause damage by direct mechanical action, such as clogging of the fish gills. Suspended solids increase the turbidity of the receiving waters and may reduce photosynthetic activity by reducing the depth of sunlight penetration in the water column. Suspended matter may also clog the gills of fish and can increase the cost of treating the receiving waters for municipal and industrial uses. Suspended solids also serve as a vehicle for transporting sorbed toxic materials and pathogenic microorganisms.

Dissolved inorganic ions in industrial effluents are difficult to categorize but usually dissolved solids present a problem when the level is significantly different than the receiving water. In fresh waters, for example, a dramatic increase in dissolved solids can upset the osmotic balance of the indigenous aquatic organisms as well as reduce the use for drinking purposes. The effect is less severe when estuarine waters are involved as estuarine organisms are generally adapted to wide fluctuations in dissolved ion content due to natural salinity variation.

Treatment Technology

Raw waste loads in most cases can not be completely eliminated, and treatment of the wastewater becomes necessary. Treatment technology is dynamic, and

processes for improved constituent removal are being developed. The efficacy of selected processes for reducing industrial effluent constituents to desired levels, however, must usually be estabished by pilot plant or laboratory testing procedures (6).

The treatment of wastewaters discharged from industries encompasses the removal of diverse pollutants, with most attention historically focused on organic removal (7,8). Recently, however, removal of eutrophying and potentially toxic substances has been emphasized by pollution control and regulatory agencies.

It is recognized that as environmental stresses become more acute, the concepts of pollution control will by necessity become more sophisticated.

Table 4 presents a classification and application of necessary treatment processes. A commonly accepted treatment classification is as follows:

a. in-plant
b. primary
c. intermediate
d. secondary
e. tertiary
f. quaternary

A general listing of these processes and their applicability of removing the industrial waste loads is presented in Table 4. A removal profile of these constituents is shown in Fig. 1. Removal efficiencies depend on waste characteristics, adequacy of design, operational effectiveness, and environmental conditions.

Prediction of treatment plant effluent characteristics can be estimated on the adequacy of the following:

a. in-plant surveys
b. waste characterization
c. laboratory treatability studies
d. pilot plant studies
e. plant design
f. construction inspection
g. maintenance and operation

Table 5 provides estimates of possible constituent residuals. It is these concentrations that must be evaluated for their impact on receiving waters, properly considering dispersion patterns and receiving water quality. It is on this basis that associated costs to reduce the industrial waste loads can be predicted and the results integrated into a cost-effective/benefit format for making decisions in water quality management.

Relationship Between Physical and Biological Environments

Efficient and acceptable use of natural water systems for the disposal of residual wastewaters requires knowledge of the processes by which the contaminants are mixed and dispersed throughout the receiving waters. Of the many factors which influence the quality of receiving waters, mixing and dispersion are among the most important. These factors effect the ecology of the waters,

Table 4. Classification and Application of Treatment Processes

CONTAMINANTS	IN-PLANT	PRIMARY	INTERMEDIATE	SECONDARY	TERTIARY	QUATERNARY
Oil	Segregation Concentration Housekeeping	API Separator Tilted Frame Separator	Air Flotation Mechanical Flotation Media Filtration			
Soluble COD	Housekeeping		Chemical Precipitation Flotation or Gravity Separation Equalization Waste Stabilization Ponds	Activated Sludge Aerated Lagoon Chemical Oxidation Waste Stabilization Ponds	Media Filtration Carbon Adsorption	Reverse Osmosis
Hardness	Segregation				Chemical Precipitation	Ion Exchange
Other TDS	Segregation					Ion Exchange Reverse Osmosis Electrodialysis
Ammonia-nitrogen	Substitution Segregation Steam Stripping		Trickling Filter	Activated Sludge	Denitrification	Ion Exchange
Phosphorus	Segregation Substitution			Activated Sludge Aerated Lagoon	Chemical Precipitation	
Heavy Metals	Housekeeping Substitution Segregation	Ponding			Chemical Precipitation Chemical Oxidation Media Filtration	Ion Exchange
Sulfides	Segregation Steam Stripping				Chemical Oxidation	
Cyanides				Alkaline Chlorination Electro-Dialysis		Incineration

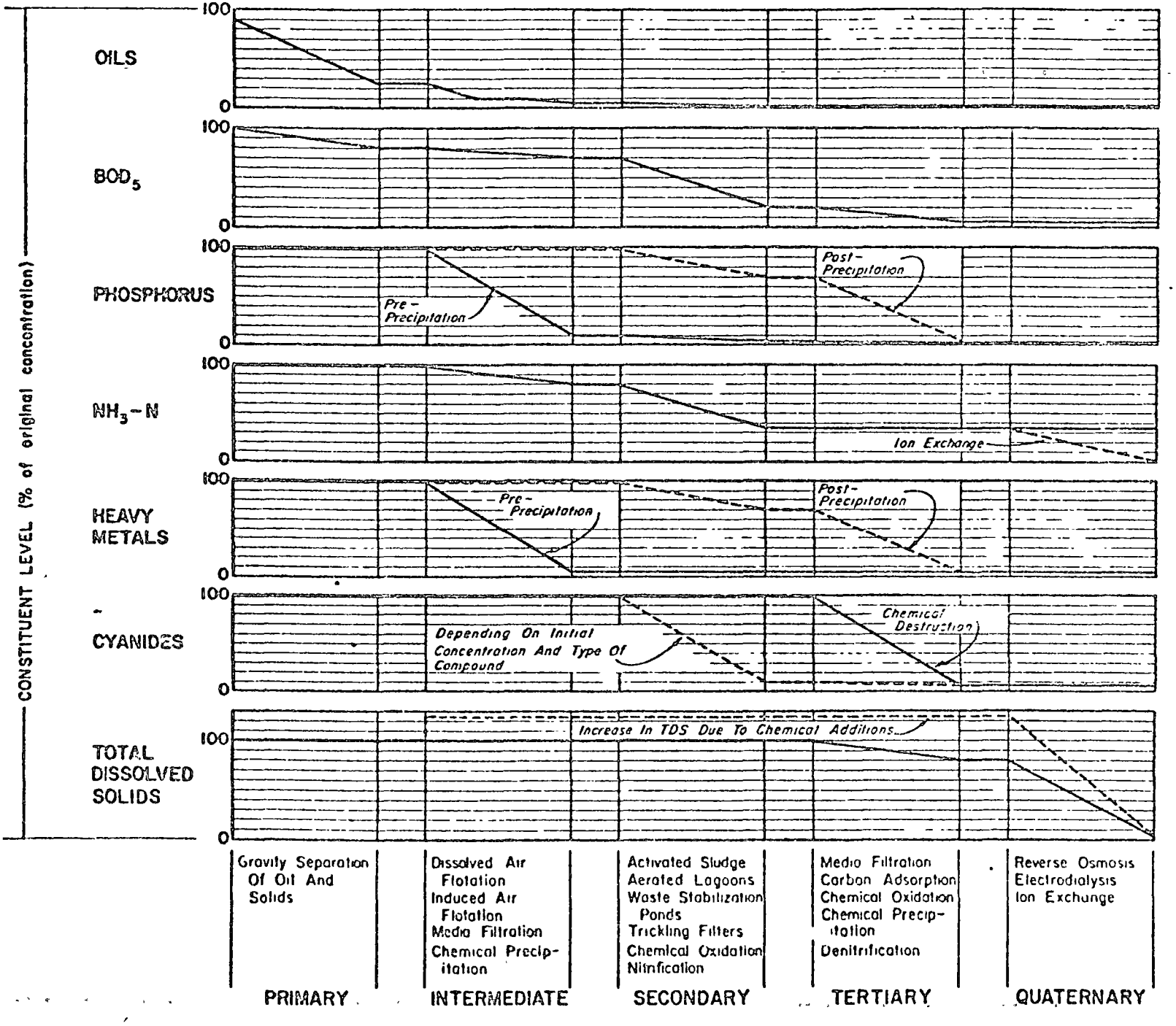

FIG. 1. FATE OF INDUSTRIAL WASTE WATER CONSTITUENTS IN TREATMENT PROCESSES.

Table 5. Generalized Levels of Constituent Residuals

Constituent	Range for Selected Industrial Raw Waste Loads (total effluent)	Secondary Effluent	Tertiary Effluent	Quaternary Effluent	General Remarks
COD	500-700 mg/l	100-200 mg/l	50-200 mg/l	<100 mg/l	Exact COD residuals vary with complexity of industry & design contact times in the Act.S. and Carbon Treatment Plants.
BOD_5	250-350 mg/l	20-50 mg/l	5-20 mg/l	<5 mg/l	BOD residual depends on BOD/COD ratio which characterizes relative biodegradability of wastewater.
Phenols	10-100 mg/l	<1 mg/l	<1 mg/l	<1 mg/l	Phenols(ics) are generally amenable to biological and sorption removal.
Heavy Metals	5-100 mg/l	1-50 mg/l	<1 mg/l	<1 mg/l	Heavy metals concentrated to some extent in biological sludge and removed with sludge wastage. Chemical precipitation at high pH level effective for reducing most metallic ion to less than 1 ppm.
SS	50-200 mg/l	20-50 mg/l	<10 mg/l	<10 mg/l	Primary effluent solids depend on design and operation of oil removal units. Act.S. effluent solids depend on effectiveness of secondary clarifier. Low effluent solids characterize carbon column effluent.
TDS	1500-3000 mg/l	1500-3000 mg/l	1500-3000 mg/l	<300 mg/l	TDS is essentially unchanged through all three treatment systems.
NH_3-N	15-150 mg/l	5-100 mg/l	1-5 mg/l	<1 mg/l	Exact concentration depends on pre-stripping facilities, nitrogen content of raw materials corrosion additive practice and biological nitrification.
P	1-10 mg/l	<1-7 mg/l	<1 mg/l	<1 mg/l	Only removal attributed to biological synthesis.
Cyanides	1-200 mg/l	~.05 mg/l	-	-	Simple cyanides can be reduced to less than 50 ppb with proper treatment and process application.

and the net result is reflected in the benefits which may be expressed in terms of the economic value derived from the waters. The biological, ecological and economic analyses can be considered only as partially complete until integrated with mixing and transport characteristics of the receiving waters.

The mixing process in any body of water is three-dimensional; vertical, lateral and longitudinal. By assuming complete mixing in the vertical and lateral dimensions, estimates of longitudinal concentration variations can be constructed (9). The complexity of the model and potential for errors may be illustrated by examining the physical processes external to an estuary:

(a) tidal action at the estuary mouth;
(b) fresh water inflow;
(c) radiation balance; and
(d) meteorological conditions.

These processes are of importance in developing the velocity fields and turbulence in the estuary.

However, using adequate data and simplified one-dimensional models it is possible to predict incremental changes at various distances from a point of discharge (10). Such results are shown in Fig. 2.

Role of Environmental Baselines

The impact of industrial discharges on receiving waters represents a high degree of uncertainty until baseline information is developed. Sampling stations should be established at predefined locations around the discharge points, and water qulaity, sediment, and species diversity numbers obtained at sufficient frequency to establish statistically reliable baseline environmental information. The sampling chronology should take into account the factors of parametric variation, hydrodynamic and hydrographic factors, and seasonal influence. Both *in situ* and laboratory analyses are required.

A typical schedule of analysis for a baseline study being conducted in an estuary which will receive a large volume of treated petrochemical wastewater is shown in Table 6 (11). Background information must be determined as per this schedule before and after the effluent is discharged to the estuary. These data will provide the necessary information to accurately evaluate the response of the existing aquatic ecosystem and receiving water quality to the proposed discharge.

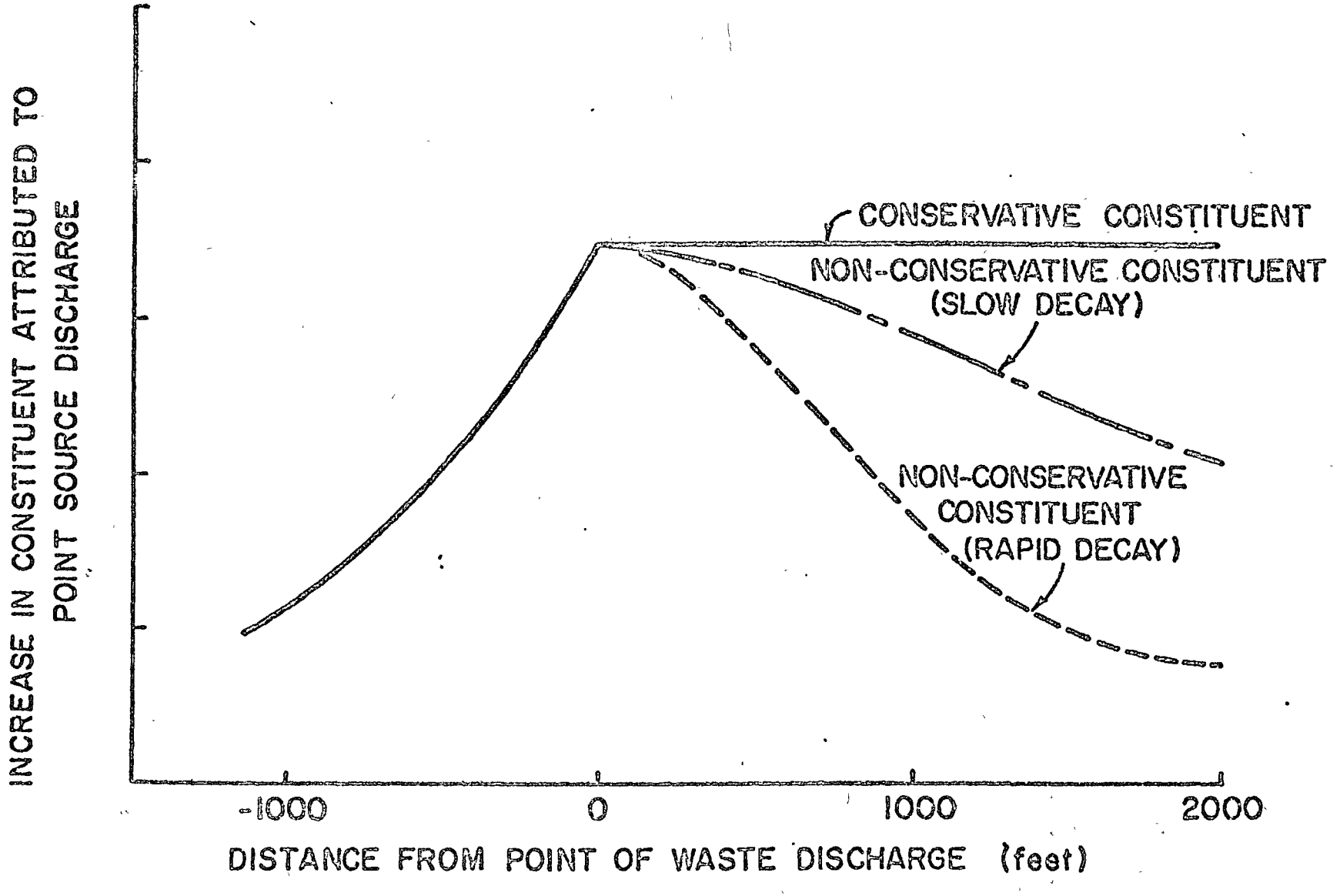

FIG. 2. MATHEMATICALLY PREDICTED DISPERSION PATTERNS.

Table 6. Schedule of Analyses for Baseline Study

Constituent	Type of Sample	Frequency	Analytic Method
Receiving Water			
pH	P*	W*	DR*
Dissolved Oxygen (DO)	P	W	DR
Temperature	P	W	DR
Conductivity	P	W	DR
Transparency (Secchi)	S	W	DR
Salinity	P	W	CN
Density	P	W	CN
Biochemical Oxygen Demand (BOD)	D	M	LA
Chemical Oxygen Demand (COD)	C	M	LA
Total Organic Carbon (TOC)	D	M	LA
Kjeldahl Nitrogen	D	M	LA
Ammonia Nitrogen (NH_3)	D	M	LA
Nitrite Nitrogen ($NO_2^$)	D	M	LA
Nitrate Nitrogen ($NO_3^$)	D	M	LA
Reactive Phosphate (PO_4)	D	M	LA
Phenols	D	M	LA
Mercury	D	M	LA
Phytoplankton	D	M	LA
Coliforms (total and fecal)	D	M	LA
Sediments			
Classification	D	Q	FA
Chemical Oxygen Demand (COD)	D	Q	LA
Hexane Extractable Materials	C	Q	LA
Hexavalent Chromium	C	Q	LA
Mercury	C	Q	LA
Lead	C	Q	LA
Particle Size Distribution	D	Q	LA
Cyanide	C	Q	LA
Dissolved Sulfide	C	Q	LA
Kjeldahl Nitrogen	C	Q	LA
Benthic Organisms	D	Q	LA

*P - Profile at 1.0 meter intervals witn in situ equipment.
D - Discrete grab sample for laboratory analysis
S - Single, in situ, analysis
C - Composite of duplicate grab samples with laboratory analysis
W - Weekly
M - Monthly
Q - Quarterly
DR- Direct reading instrument
CN- By calculation
LA- Laboratory analysis
FA- Field analysis

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INTRODUCTION--EXAMPLE

CONTROL OF REFINERY AND PETROCHEMICAL WASTEWATERS AND RESIDUALS [1]

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This paper considers a spectrum of factors which reflect on the control of wastewaters and residuals derived from the refining and processing of crude petroleum and petrochemicals. The source of waste, analyses of wastewater and residuals management, typical wastewater characteristics and treatment of wastewaters are discussed. Emphasis is directed to those treatment units which are capable of removing oil.

Experimental and field data are provided describing process waste sources, boiler and cooling tower blowdowns, runoff from combined process and storm sewer systems, and ballast water. Oil removal through the use of gravity separators, dissolved air flotation, coagulation and precipitation and coalescers are stressed. Brief discussion is presented on the topic of soluble organics removal by biological action.

The control of wastewaters will depend on a thorough understanding of all industrial processes contributing to the waste stream, options available for producing the required treatment and finally the impact of residuals derived from the total treatment process on the environment.

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Terminology and Target Dates

In the USA, governmental agencies are using a new set of terminology to define industrial processes and waste sources. Today, industry must be concerned with best practical technology (BPT), best available technology (BAT) and new source standards as defined in the Environmental Protection Agency's (EPA) standards effluent guidelines. The latter represent levels of wastewater treatment which industry will be required to implement by specific dates, Table 1.

The applicable Standard Industrial Classification (SIC) numbers related to the topics under discussion include:

SIC 2911 Petroleum Refining
SIC 2815 Cyclic Intermediates, Dyes, Organic Pigments, and Crudes
SIC 2818 Organic Chemicals
SIC 2819 Inorganic Chemicals Derived from Petroleum
SIC 2821 Plastic Materials and Resins

The detail of each SIC is illustrated by listing the twelve processes which define SIC 2911:

1. Storage and Transportation
2. Crude Desalting
3. Fractionation
4. Cracking
5. Hydrocarbon Rebuilding
6. Hydrocarbon Rearrangement
7. Solvent Extraction or Refining
8. Hydrotreating
9. Grease Manufacturing
10. Asphalt Production
11. Product Finishing
12. Auxiliary Activities

These products include kerosene, gasoline, distillate fuel, residual fuel oil, and a host of miscellaneous products. This list grows as petrochemicals are added to the list.

Source of Wastes

The present and future levels of wastewaters and residuals depend on the sources and management of these inputs. Figure 1 depicts the six general sources as process streams, utility wastes, sewage, contaminated storm water, ballast water and miscellaneous discharges.

Table 1. EPA Target Dates

	TYPE OF SOURCE	LEVEL OF TECHNOLOGY	DATE EFFECTIVE	BY WHOM ESTABLISHED	ENFORCEMENT MECHANISM	SCOPE
Water Quality Standards	NOT a "source" rivers, streams, lakes-all surface waters	Not level of technology-water which provides for recreation in & on water	July 1983	States / EPA	Permits / State programs for non-point sources	All surface waters, (except those specifically approved by EPA for less stringent classifications)
Best Practicable Technology	Industry major feedlots (existing)	Level I average of the best technology currently available	July 1977	EPA	Permits	Add-on treatment technology-includes process changes
Best Available Technology	Industry major feedlots (existing)	Level II very best economically Achievable technology	July 1983	EPA	Permits	Add-on treatment technology-greater emphasis on production changes
New Source Standards	Industry major feedlots (constructed after May 1974)	Level III very best technology to be contructed	May 1974	EPA	Permits	Add-on, in process controls, plant-design, raw materials, -all aspects-
Pretreatment Effluent Standards	Industries introducing wastes into publicly owned treatment works	Not a precise level of technology -generalized unit processes	July 1976 existing plants / May 1974 New plants	EPA / Municipalities	No permits -monitoring-	-Unlimited- any unit process controls needed to prevent excess of pollutants into treatment plant
Toxic Effluent Standards	All sources	Not a level of technology -whatever is needed to get out toxics	January 1975	EPA	Permits	-Unlimited- any changes needed to prohibit/limit toxics
Secondary Treatment (Public treatment plants)	Publicly owned treatment plants (constructed by July 1974)	Average of well-run waste treatment plants using secondary treatment	July 1977 existing / July 1978 plants constructed prior to 6/30/74	EPA / States	Permits	Add-on tightening process control
Best Practicable Waste Control Technology (Public treatment plants)	All publicly owned treatment plants	Average of best advanced treatment systems	July 1983	EPA	Permits	Construction of new treatment systems and additional process controls

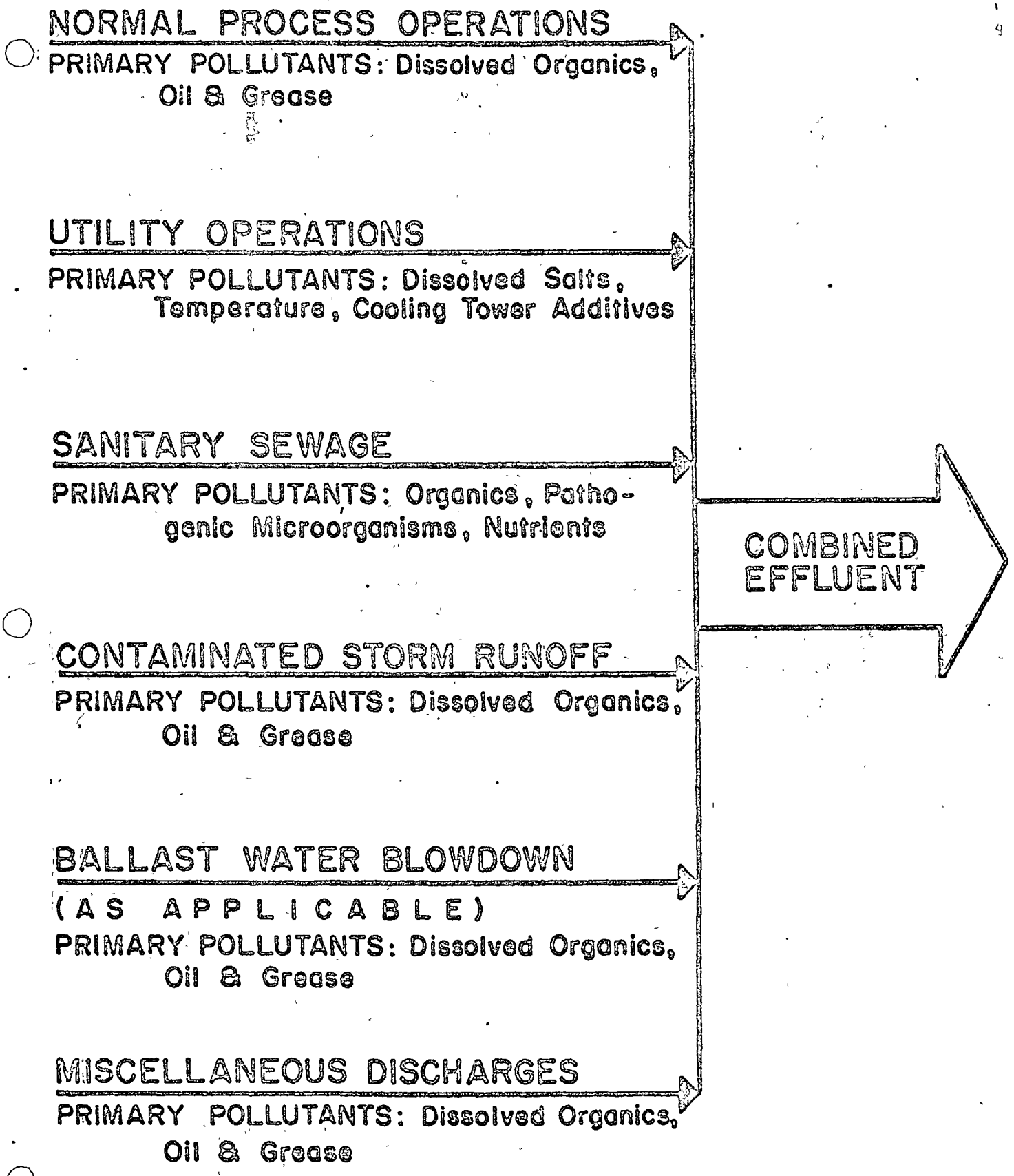

FIG. 1. GENERAL SOURCES of WASTES.

Analysis of Wastewater and Residuals Management

Treatment and solids disposal is usually required because there is no such thing as zero discharge. However, process designs, waste treatment and all other industrial decision-making processes must relate reuse and recycling with effluent levels and cost. Hopefully, some of the money required to treat the residual wastes can be derived from credits obtained through better engineering of the production facilities, i.e., reduction of the waste load through the use of more efficient production units.

The effectiveness of handling refinery and petrochemical wastewaters usually depends on the efficient utilization of several treatment processes:

Primary Treatment - Gravity Separation

Intermediate Treatment - Neutralization

Dissolved Air Flotation	Chemical Coagulation-Sedimentation
Filtration	

Final Treatment (Biological/Physical/Chemical) -

Activated Sludge	Cooling Tower Oxidation
Aerated Lagoons	Filtration
Trickling Filters	Carbon Adsorption
Waste Stabilization Ponds	Reverse Osmosis

The problem is to delineate costs for meeting various levels of environmental quality. Costs will reflect such considerations as:

(a) production variables;
(b) liquid residual reduction and its impact on secondary residuals production, energy requirement, and land requirement for sludge disposal;
(c) effects of air quality controls on liquid residuals;
(d) effect of residuals modification measures on consumptive use of water;
(e) variability in residuals generation and performance of treatment plant; and
(f) effect of rainfall on probability of achieving zero discharge.

Figure 2 shows an example where reducing variability in discharge require increased cost. In this case, lagoon and/or spray irrigation systems are examples, which are sensitive to both temperature and precipitation. Although the generalized cost increases greatly, this curve represents only one of many variables in residuals generation and residuals discharge.

The response of an individual industrial plant to effluent controls may be illustrated by an analysis of a 150,000 barrels per day petroleum refinery (1). Table 2 depicts the sizes of process units and magnitudes of product output. Table 3 illustrates the residuals generated with treatment limited to oil-water separators and sour-water scrubbers. As shown in Fig. 3, discharges of BOD sulfide, phenols, and ammonia decrease rapidly over the range of charges from 1 cent to 7 cents per pound, which represents reduction of 70% of BOD, 82% of phenol, 48% ammonia and 74% sulfide. As the BOD reduction increases to about 95% the charge increases to about 25 cents. For this example, the cost of reducing BOD by 75% is about $0.002 per barrel of crude processed or about 0.045% of daily cost.

Typical Wastewater Characteristics

Once an industrial categorization system is established, then the logical sequence of predicting industrial effluent loads to the treatment facility and environment are:

(a) estimating waste loads generated in the present and future manufacture of product;
(b) predicting the portion of this load that can be removed using demonstrated treatment technology; and
(c) projecting the implementation schedule for applying this demonstrated technology.

Raw waste loads, as a practical matter, are usually estimated from historical characterization data of the total effluent discharged from many production components within an integrated industrial plant. If it were possible to obtain such information from singular production units, the wastewater profiles could be developed on a "building block" or cumulative approach for complex systems. However, there are many factors such as water recycle and reuse, changes in water quality when mixed with other sources, and water use not directly associated with production which prevent precise predictions of raw waste loads.

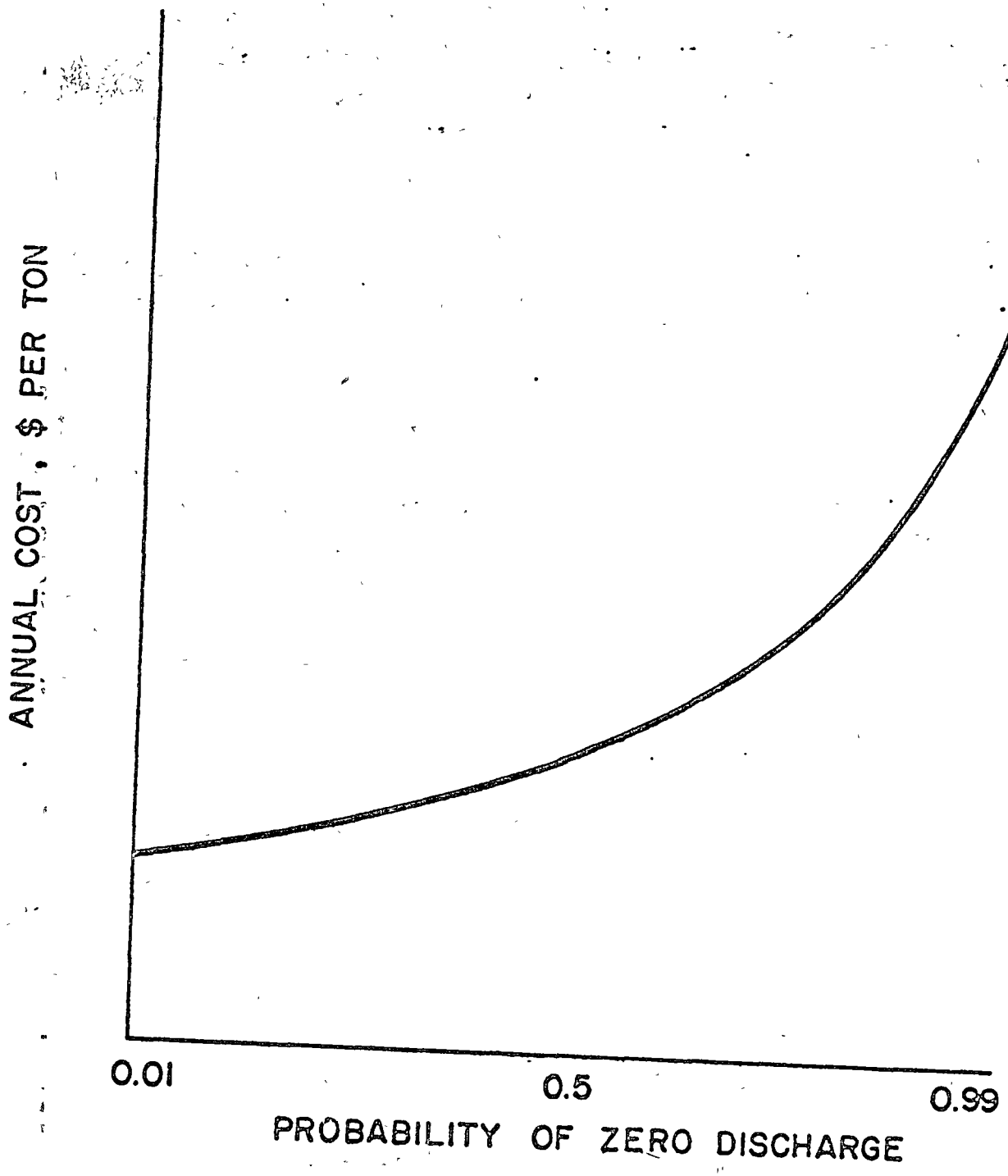

FIG. 2. RELATIONSHIP BETWEEN COST AND PROBABILITY OF ZERO DISCHARGE

Table 2. Process Units and Product Outputs, 150,000[1] Barrels Per Day Petroleum Refinery

PROCESS UNITS (Barrels per barrel of crude charged)	
Desalting	1.00
Atmospheric Distillation	1.00
Coking	.133
Hydrotreating	.139
Reforming	.139
Catalytic cracking	.466
Alkylation	.076
Sweetening	.393

PRODUCT OUTPUTS (Quantity per day)		
Products sold		
Refinery gas		2.944×10^6 lbs.
Kerosene/diesel oil		15,760 barrels
Distillate fuel oil		17,400 barrels
Low sulfur	8,880 B	
Medium sulfur	8,230 B	
High sulfur	290 B	
Polymer		660 barrels
Premium gasoline[2]		35,100 barrels
Regular gasoline[3]		51,150 barrels
Residual fuel oil		3,000 barrels
Straight run gasoline sold as petrochemical feed		16,360 barrels
Recovered sulfur		40.0 long tons
Products used internally		
Hydrogen (burned)		100,250 lbs.
Sweet coke (burned)		1,180,000 lbs.
Sour coke (burned)		260,000 lbs.
Coke burned in catalyst regeneration		1,540,000 lbs.

[1] Crude charged: 111,000 barrels East Texas (low sulfur)
39,000 barrels Arabian Mix (high sulfur)
Total 150,000 barrels per day

[2] Octane $\geq$ 100; tetraethyl lead content $\leq$ 2.5 cc/gal.

[3] Octane $\geq$ 94; tetraethyl lead content $\leq$ 2.5 cc/gal.

Table 3. Residuals Generation per Barrel in a 150,000 Barrels per day Petroleum Refinery

RESIDUAL	GENERATION (Lbs. per barrel)
Gaseous	
Particulates	0.423
SO_2	1.429
Liquid	
BOD_5	0.060
Oil	0.047
Phenols	0.032
Ammonia	0.021
Sulfide	0.003
Heat, 10^6 Btu	0.300

Assumptions:

Cost of water withdrawals:
- Cooling, $.015/1000 gal.
- Desalter, $.025/1000 gal.
- Process steam, $.15/1000 gal.

Cost of purchased fresh heat:
- 0.5% Sulfur, $.477/$10^6$ Btu
- 1.0% Sulfur, $.593/$10^6$ Btu
- 2.0% Sulfur, $.661/$10^6$ Btu

Price of Recovered Sulfur: $20/long ton

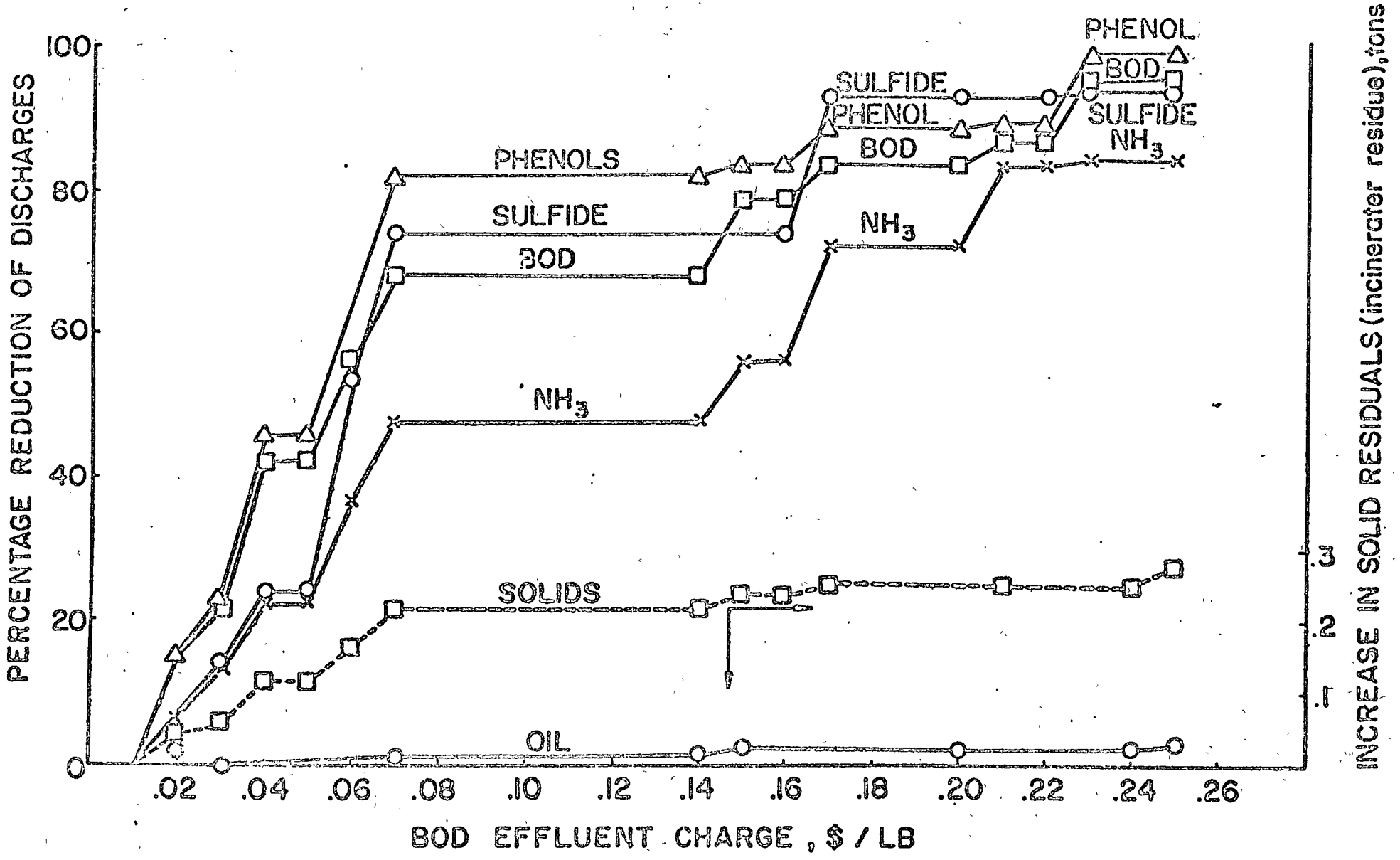

FIG. 3. RESPONSE TO BOD EFFLUENT CHARGE, 150,000 BARRELS/DAY PETROLEUM REFINERY.

The impact of raw waste loads on the environment may be depicted in terms of various potential impacts; namely, oxygen depletion, eutrophication, toxicity, and general nuisance. Characterization of wastes for treatment plant design usually requires a detailed analysis of the following:

(a) Flow;
(b) Solids (SS, TDS, VSS);
(c) Nutrients (N, NH_3, P);
(d) pH;
(e) Biodegradability and oxygen requirements (BOD_5, BOD_u, COD, TOC);
(f) Toxicity (heavy metals, cynides, phenols);
(g) Additional physical-chemical characteristics; and
(h) Rate relationships for treatment facilities design.

Process Sources: An estimate of the amount of wastewater derived from a plant might be obtained by comparisons with other installations (2) or relating the quantity and quality of pollutant produced by a unit process to production units. For example, the American Petroleum Institute Refinery Effluent Profile (3) has tabulated process flow in terms of production units for the five refinery classifications, Table 4.

Table 4. Wastewater Discharge as a Function of Crude Throughput

Refinery Classification	No. Refineries Reporting	Gal. Effluent/bbl Crude Throughput		
		Max.	Min.	Avg.
A	15	499.8	0.4	57.5
B	70	1658.6	2.1	116.3
C	20	1399.9	17.6	181.0
D	18	759.4	14.8	143.4
E	4	1700.2	32.8	410.1

The organic content can be expressed in terms of biochemical oxygen demand (BOD), chemical oxygen demand (COD), or some other form of carbon source and oxygen demand. It is estimated that 90% of the BOD is derived from eight process units. The source and range of BOD levels are: naptha treater (3,000-4,000 mg/l); MEK stripper (3,000 mg/l); furfural stripper (2,200 mg/l); lube distillation unit, atm. (1,100 mg/l); crude desalter (500 mg/l); sour condensates (60 mg/l); lube hydrotreater (300 mg/l); and lube vacuum, distill. (300 mg/l).

Similarly, the COD load as derived from seven process units may have the following characteristics: delayed coker (6,000 mg/l); FCCU (6,000 mg/l); crude unit (2,000 mg/l); paraxylene (1,200 mg/l); styrene (1,000 mg/l); platformer Udex (800 mg/l); and alkylation (500 mg/l). The oil, as the COD is largely derived from kerosene and diesel hydrotreating (about 50%). The FCCU and crude units may contribute 20% to 30% each, while the delayed coker, unsaturated gas plant, ultrafiner and untraformer and others contribute less than 5% each of the total contribution. Wastewater characteristics associated with some petrochemical products are listed in Table 5. Typical spent caustic and acid waste streams in petroleum refineries are given in Tables 6 and 7, respectively. The type of wastes derived from primary conversion and refining processes are depicted in Table 8.

Boiler Sources: It has been recommended that the water within steam drums (for pressures between 300 to 750 psig) not exceed dissolved solids levels of 3,500 to 2,000 mg/l, suspended solids levels of 300 to 100 mg/l, and alkalinity (as $CaCO_3$) levels of 700 to 400 mg/l. Typical analysis of boiler blowdown wastewaters and residuals is shown in Table 9 (5).

Cooling Towers: Most of the wastewater of the utility blowdown and frequently a sizable portion of the combined plant flow will be derived from cooling towers. All of the utility blowdown streams contain organic materials, although the pollutants may exist at low concentrations (6). In addition to the incoming dissolved salts, the cooling tower blowdown will contain sulfuric acid, inorganic chromate salts (300 to 2,000 mg/l), inorganic and organic phosphates and polyphosphates (2 to 30 mg/l), organic chromates (5 to 20 mg/l CrO_4 and 5 to 20 mg/l organics), chlorinated phenols (300 to 400 mg/l), chlorine or bromine, and quaternary ammonia copper complexes (200 mg/l). See Table 10.

Ballast Water: Ballast water quality can be expected to vary considerably. [illegible] of a ballast water survey from two refineries are shown in Table 11 (5). Usually the underflow from a ballast holding tank must be given further t[illegible]ment.

Table 5. Wastewater Characteristics Associated With Some Chemical Products (3)

Material	Flow (gal/ton)	BOD (mg/L)	COD (mg/L)	Other Characteristics
Primary Petrochemicals				
Ethylene	50- 1,500	100- 1,000	500- 3,000	phenol, pH, oil
Propylene	100- 2,000	100- 1,000	500- 3,000	phenol, pH
Primary Intermediates				
Toluene	300- 3,000	300- 2,500	1,000- 5,000	
Xylene	200- 3,000	500- 4,000	1,000 8,000	
Ammonia	300- 3,000	25- 100	50- 250	oil, nitrogen
Methanol	300- 3,000	300- 1,000	500- 2,000	oil
Ethanol	300- 4,000	300- 3,000	1,000- 4,000	oil, solids
Buthanol	200- 2,000	500- 4,000	1,000- 8,000	heavy metals
Ethyl benzene	300- 3,000	500- 3,000	1,000- 7,000	heavy metals
Chlorinate hydrocarbons	50- 1,000	50- 150	100- 500	pH, oil, solids
Secondary Intermediates				
Phenol, cumene	500- 2,500	1,200-10,000	2,000-15,000	phenol, solids
Acetone	500- 1,500	1,000- 5,000	2,000-10,000	
Glycerin, glycols	1,000- 5,000	500- 3,500	1,000- 7,000	
Urea	100- 2,000	50- 300	100- 500	
Acetic anhydride	1,000- 8,000	300- 5,000	500- 8,000	pH
Terephtalic acid	1,000- 3,000	1,000- 3,000	2,000- 4,000	heavy metals
Acrylates	1,000- 3,000	500- 5,000	2,000-15,000	solids, color, cyanide
Acrilonitrile	1,000- 10,000	200- 700	500- 1,500	color, cyanide, pH
Butadiene	100- 2,000	25- 200	100- 400	oil, solids
Styrene	1,000- 10,000	300- 3,000	1,000- 6,000	
Vinyl chloride	10- 200	200- 2,000	500- 5,000	
Primary Polymers				
Polyethylene	400- 1,600		200- 4,000	solids
Polypropylene	400- 1,600		200- 4,000	
Polystyrene	500- 1,000		1,000- 3,000	solids
Polyvinyl chloride	1,500- 3,000	50- 500	1,000- 2,000	
Cellulose acetate	10- 200	500- 2,000	1,000- 5,000	
Butyl rubber	2,000- 6,000	800- 2,000	2,500- 5,000	
Dyes and Pigments	50,000-250,000	200- 400	500- 2,000	heavy metals, color, solids, pH
Miscellaneous Organics				
Isocyanate	5,000- 10,000	1,000- 2,500	4,000- 8,000	nitrogen
Phenyl glycine	5,000- 10,000	1,000- 2,500	4,000- 8,000	phenol
Parathion	3,000- 8,000	1,500- 3,500	3,000- 6,000	solids, pH
Tributyl phosphate	1,000- 4,000	500- 2,000	1,000- 3,000	phosphorus

Table 6. Typical Spent Caustic Stream Characteristics (4)

Characteristics	Benzene Sulfonation Scrubbing	Ortho-phenyl-phenol Washing	Alkylate Washing	Polymerization
Alkalinity (mg/l)	33,800	18,400	46,250	209,330
BOD (mg/l)	53,600	18,400	256	8,440
COD (mg/l)	112,000	67,600	3,230	50,350
H_2S (mg/l)	-	-	-	-
pH	13.2	9-12	12.8	12.7
Phenols (mg/l)	8.3	5,500	50	22.2
NaOH (wt %)	1	0.2-0.5	-	-
Na_2SO_4 (wt %)	1.5-2.5	-	-	-
Sulfates (mg/l)	3,760	2,440	-	-
Sulfides (mg/l)	-	-	2	3,060
Sulfites (mg/l)	7,100	4,720	-	-
Total Solids (mg/l)	90,300	40,800	-	-

Table 7. Typical Acid Waste Characteristics (4)

Characteristic	Acid Wash-Alkylation	Acid Wash-Phenol Still Bottoms	Acid Wash-Orthophenyl-phenol	Sulfite Wash Liq. OP-phenol Distillation
Acidity (mg/l)	1,105-12,325	-	24,120	675
BOD (mg/l)	31	20,800	13,600	105,000
COD (mg/l)	1,251	248,000	23,400	689,000
Dissolved Solids (mg/l)	-	340,500	81,300	176,800
Oil (mg/l)	131.5	-	-	-
pH	0.6-1.9	1.0	1.1	3.8
Phenols (mg/l)	-	3,800	1,500	16,400
Sulfate (mg/l)	-	-	54,700	-
Sulfite (mg/l)	-	34,800	2,920	74,000
Total Solids mg/l)	-	403,200	81,600	176,900

Table 8. Typical Process Waste Characteristics of Primary Conversion and Refining Processes (4)

Characteristic	Crude Desalting	Catalytic Cracking	Naphtha Cracking	Sour Condensates from Distillation, Cracking, etc.
Ammonia (mg/l)	80	-	-	135-6,550
BOD (mg/l)	60-610	230-440	-	500-1,000
COD (mg/l)	124-470	500-2,800	53-180	500-2,000
Oil (mg/l)	20-516	200-2,600	160	100-1,000
pH (mg/l)	7.2-9.1	-	-	4.5-9.5
Phenols (mg/l)	10-25	20-26	6-10	100-1,000
Salt (as NaCl) (wt %)	0.4-25	-	-	-
Sulfides (mg/l)	0-13	-	-	390-8,250 (H_2S)

Table 9. Typical Boiler Blowdown Analyses

Parameter	Number of Analysis	Mean	Standard Deviation
pH	22	12	0.34
Total Suspended Solids (mg/l)	22	40	24
Volatile Suspended (mg/l)	22	25	16
Settleable Matter (mg/l)	22	19	23
Immediate Oxygen Demand (mg/l)	13	12	8
Biochemical Oxygen Demand$_5$ (mg/l)	7	61	27
Chemical Oxygen Demand (mg/l)	22	201	70
Oil and Grease (mg/l)	22	14	5
Temperature (°C)	22	174	8
Chromium (mg/l)	3	0.8	0.3
Phenols (mg/l)	19	0.1	0.2
Fluorides (mg/l)	15	7	9
Total Residue (mg/l)	8	4950	300
Ammonia (mg/l)	10	3	2
Oxygen Demand Index (mg/l)	9	69	46

Table 10. Analysis of Cooling Tower Blowdown (24 hr. Composits)

Parameter	Mean	Standard Deviation
pH	7.3	0.3
Total Suspended Solids (mg/l)	34	-
Volatile Suspended Solids (mg/l)	26	-
Biochemical Oxygen Demand$_5$ (mg/l)	33	35
Chemical Oxygen Demand (mg/l)	140	98
Oil and Grease (mg/l)	7	3
Temperature (°C) (Grab Samples)	27	3
Sulfides (mg/l) (Grab Samples)	0	0
Chromium (mg/l)	12	-
TKN (mg/l)	12	18
Total Phosphate (mg/l)	5	0.9
Total Dissolved Solids (mg/l)	7,630	2,430
Dissolved Organic Carbon (mg/l)	60	59

Table 11. Ballast Water Characteristics

	High Value (mg/l)	Low Value (mg/l)	Mean (mg/l)
Refinery No. 1:			
COD	472	207	342
BOD_5	389	23	168
Oil	148	9	44
Chlorides	18,500	14,200	16,900
Refinery No. 2:			
COD	1,600	1,173	1,456
Oil	280	147	183

The quantity of ballast water required during calm weather is about 1.5 barrels (63 gallons) per ton of tanker deadweight displacement, but the actual amount may vary greatly. Since only the most modern tankers have separate ballast holds, there is little clean ballast.

Furthermore, the unloading operations are extremely varied. Deballasting at port, by necessity, is rapid.

Other Discharges: Additional contributors to the overall waste load are: storm waters, sanitary wastes, tank cleaning, product spills, off-specification product dumps, equipment malfunction, turnarounds, and cleaning operations. The storm waters can be a very significant contributor to the waste load.

For storm water analyses it is necessary to know the probable volume which will be collected, quality characteristics and the peak flows (7). Storm water studies at large refinery and petrochemical facilities throughout the United States have indicated a general relationship between runoff volumes and contamination. This relationship is depicted in Fig. 4. During the course of a given storm, one runoff reaches a peak flow commensurate with the concentration time of the installation. Following this peak, if no further rainfall occurs, a slow decline in flow is experienced as stored rainfall drains off. For large installations, this period of declining flow can last several days. The removal of contaminant mass, however, appears to be a much more rapid process. Peak contaminant loadings generally occur near the peak flow and die off rather quickly to a consistent base level. Additionally, the analysis of numerous storm flow versus

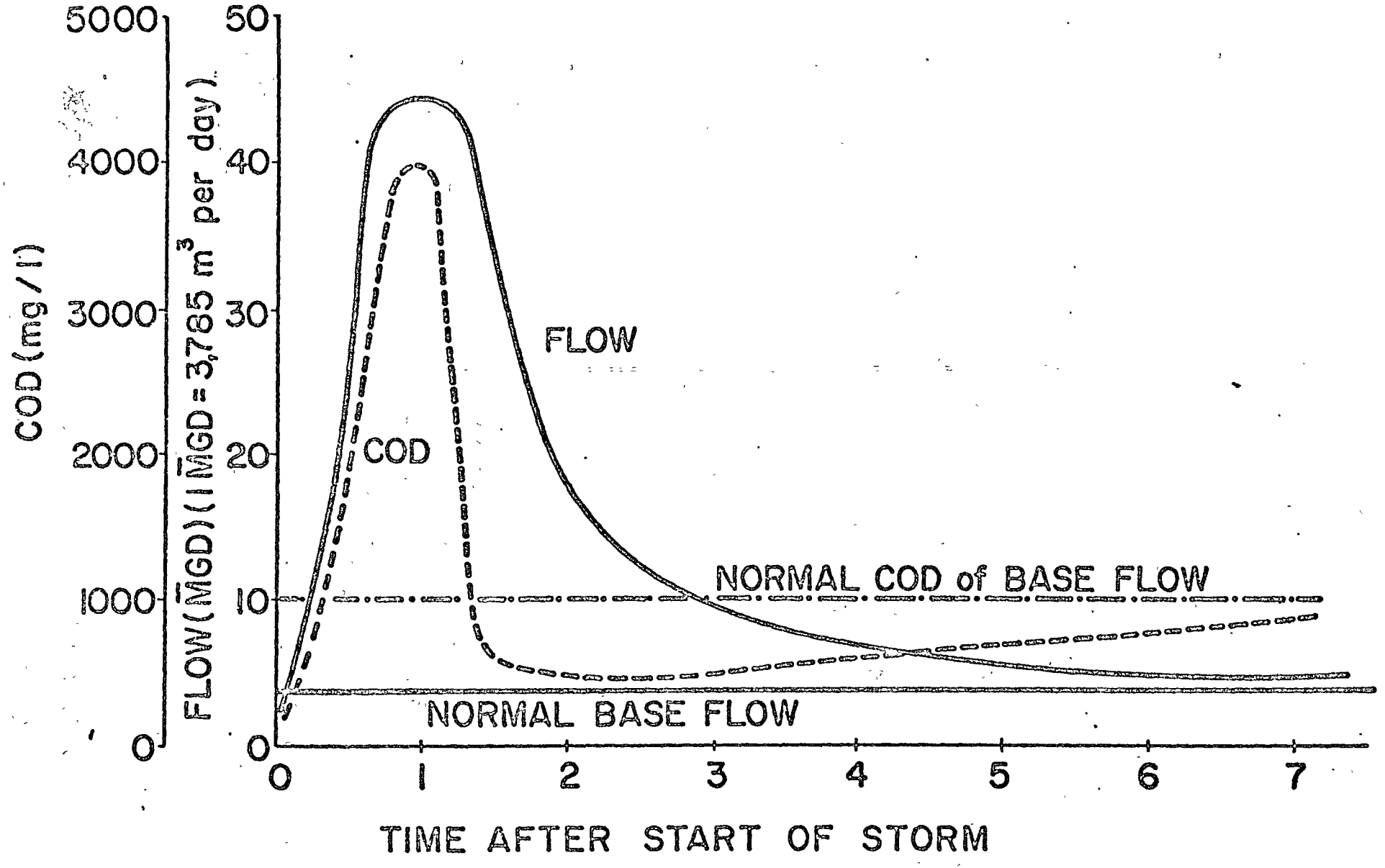

FIG. 4. STORM RUNOFF FLOW AND QUALITY CHARACTERISTICS FOR TYPICAL REFINERY / PETROCHEMICAL INSTALLATIONS.

contamination relations has indicated that between 60 and 80 percent of the contaminant mass is washed out during a one-hour period centered about the time of peak flow.

Treatment of Wastewaters

Each refinery-petrochemical facility produces its own unique waste, but there are some generalities that can be developed. Pretreatment is usually required to equalize the load, remove suspended solids and free oil, and possibly remove soluble organics (8). Secondary treatment usually involves biological treatment in conjunction with some form of physical-chemical treatment to polish the effluent and reduce the volume of residual solids.

Equalization: While equalization does not normally reduce the concentration of pollutants, most waste treatment processes depend on a relatively high degree of uniformity in load. The size and mixing features depend on waste characteristics, plant schedule, and cyclic fluctuations. If sufficient flow and quality information can be obtained from a wastewater survey, a rational basis for designing the equalization facility can be developed. One approach is the use of the following equation (29):

$$x_{(t + \Delta t)} = C_t\left[1 - \exp\left(-\frac{Qt}{v}\right)\right] + x_t\left[\exp\left(-\frac{Qt}{v}\right)\right]$$

where:

t = Time increment chosen for the numerical step-by-step calculation
C_t = input concentration averaged over Δt
x_t = basin concentration before addition of the increment of flow at concentration of C_t
$x_{(t + \Delta t)}$ = basin concentration after addition of increment of flow
Q = volumetric flow rate
v = basin volume
t = time, varies between zero and Δt in the equation. The expression need only be evaluated at $t = \Delta t$.

Using this model, the concentration of pollutant in a mixed equalization basin or the effluent can be calculated. This assumes that the critical pollutant in the industrial discharge was measured at time intervals of sufficient

frequency to accurately define the variation. The standard deviation of the equalized concentration will decrease with increasing basin retention time. The relationship then can be used for selecting the retention time which corresponds to the maximum fluctuation that can be tolerated in the biological system. As shown in Fig. 5, the standard deviation for COD loading without equalization for a petrochemical wastewater discharge is approximately 8,000 lb/day. Using a residence time of two days, the standard deviation is reduced by 50% (9).

Oil Removal: Oil separation is usually accomplished by gravity separators, dissolved gas flotation (DAF) and coalescers. In some cases, it may be necessary to use emulsion breakers and other chemical aids. The importance in controlling the oil concentrations is shown in Table 12 (9,10). Activated carbon beds and biological systems are particularly sensitive to the problem of free oil.

Table 12. Acceptable Levels of Oil in Treatment Units

Treatment Process		Application (ppm)
Gravity	API	> 150 *
	CPI	> 50
	TPI	> 73
DAF	Full or Partial Pressurization	200 to 90
	Chemical Treatment Recycle Flow	200 to 15
	Chemical Treatment Multicell, Eductor	200 to 10
Coalescers	Granular Media	150 to 80
	Granular Media with Chemicals	130 to 5
	Vacuum Precoat Filtration, Chemicals	100 to 5
Biological Treatment		100 to 0
Activated Carbons		5 to 0

*Oil contents > 80 ppm are considered to be free oil
Oil contents < 80 ppm are considered to be emulsified or soluble

Gravity Separators: Gravity separation using API separators is basic to treatment of oily wastes. Typical oil removal efficiencies from refinery wastes may range from 50 to 90%. See Table 13. Generally the two most significant factors which influence separation of free oil from water are flow rate and influent oil concentration. The impact of surges of flow through an API separator is shown in Fig. 6. A similar pattern exists for surges of oil.

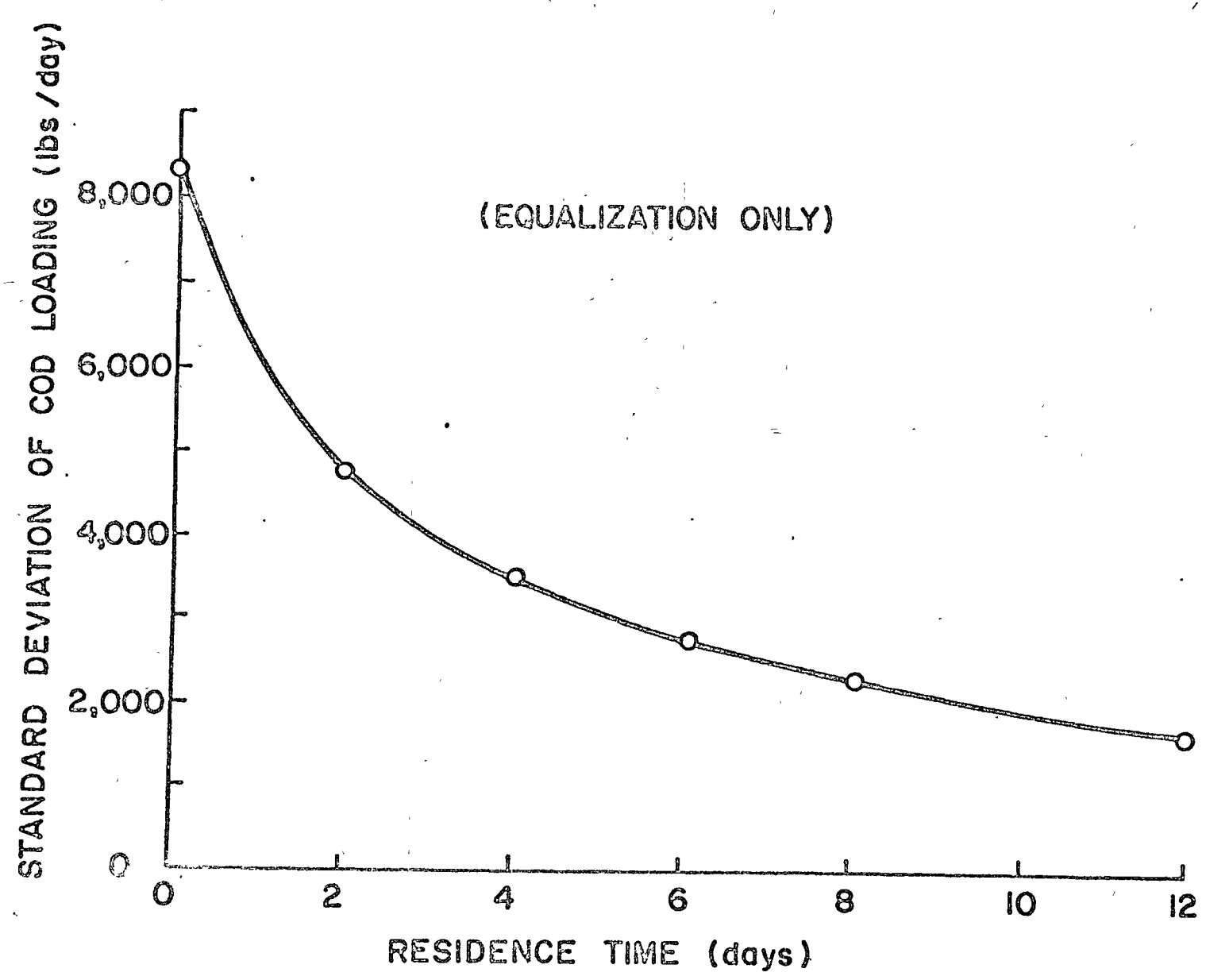

FIG. 5. STATISTICAL EVALUATION OF EQUALIZATION EFFICIENCY.

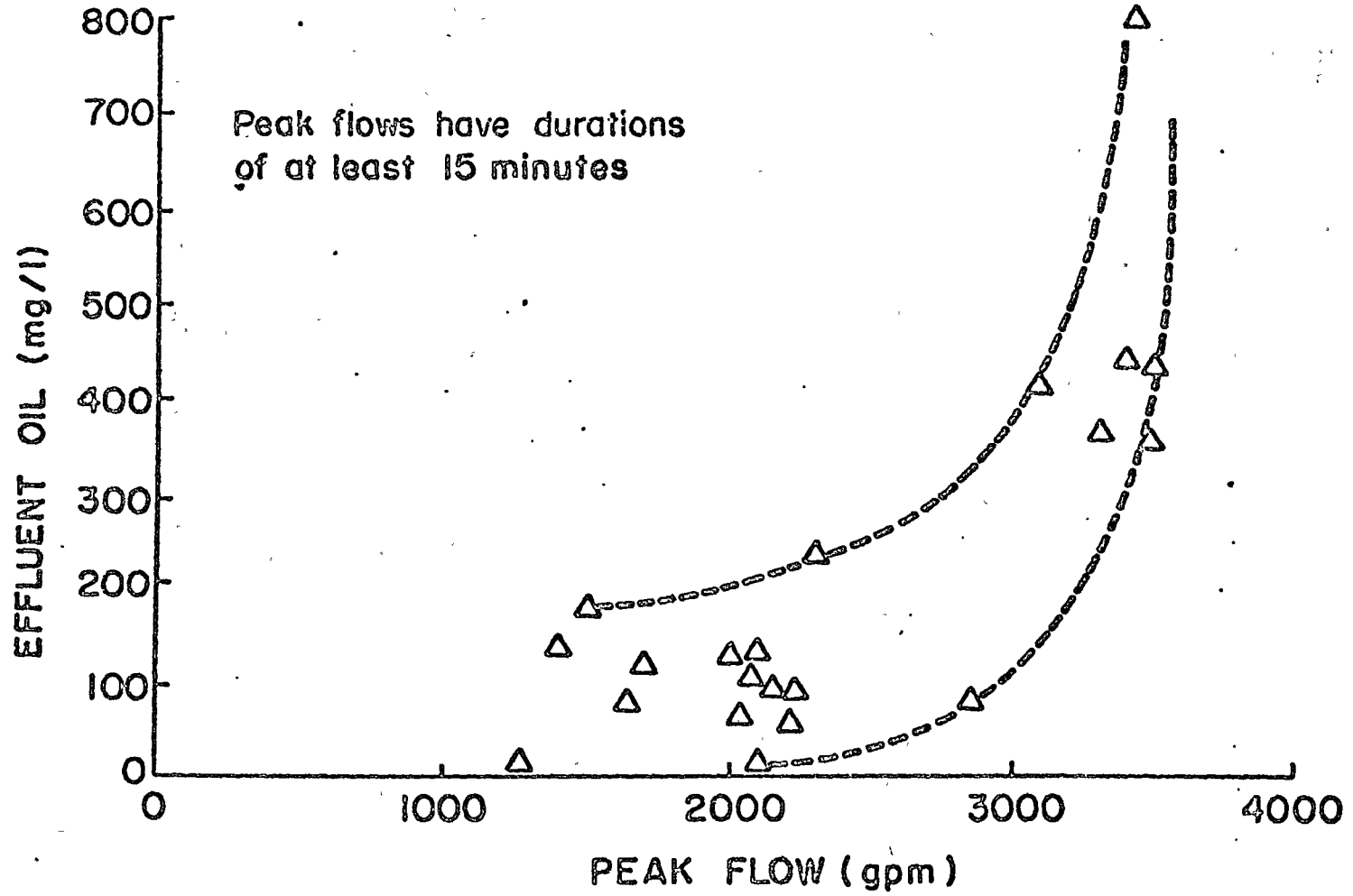

FIG. 6. INFLUENCE OF PEAK FLOWS ON EFFLUENT OIL CONCENTRATION.

Table 13. Gravity Separation of Oil

Oil Content Influent (mg/l)	Oil Content Effluent (mg/l)	Oil Removed (%)	Type	COD Removed (%)	SS Removed (%)
300	40	87	Parallel Plate	-	-
220	49	78	API	45	-
108	20	82	Circular	-	-
108	50	54	Circular	16	-
98	44	55	API	-	-
100	40	60	API	-	-
42	20	52	API	-	-
2,000	746	63	API	22	33
1,250	170	87	API	-	68
1,400	270	81	API	-	35

Dissolved Air Flotation (DAF): Special oil removal units are usually required following API separators or final clarifiers. DAF units are frequently capable of meeting these needs. Table 14 provides a listing of oil removal efficiencies that have been reported. In this table all cases, with one exception, were operated with chemical addition. The design flow rate ranged between 1.5 to 3.0 gpm per ft^2, and all units used pressurized recycle systems.

Table 14. DAF Oil Removal Performance

Influent oil (mg/l)	Effluent oil (mg/l)	Removal (%)	Chemicals*	Configuration
1930 (90%)*	128 (90%)	93	Yes	Circular
** 580 (50%)	68 (50%)	88	Yes	Circular
** 105 (90%)	26 (90%)	78	Yes	Rectangular
68 (50%)	15 (50%)	75	Yes	Rectangular
170	52	70	No	Circular
125	30	71	Yes	Circular
100	10	90	Yes	Circular
133	15	89	Yes	Circular
94	13	86	Yes	Circular
638	60	91	Yes	Rectangular
153	25	83	Yes	Rectangular
75	13	82	Yes	Rectangular
61	15	75	Yes	Rectangular
360	45	87	Yes	Rectangular

* Parenthesis denotes probability of occurrence
** Alum most common, 100-130 mg/l
Polyelectrolyte, 1-5 mg/l occasionally added

The results of a detailed study, involving a rectangular DAF unit operated in series with an API separator, is given in Fig. 7. The oil concentration in

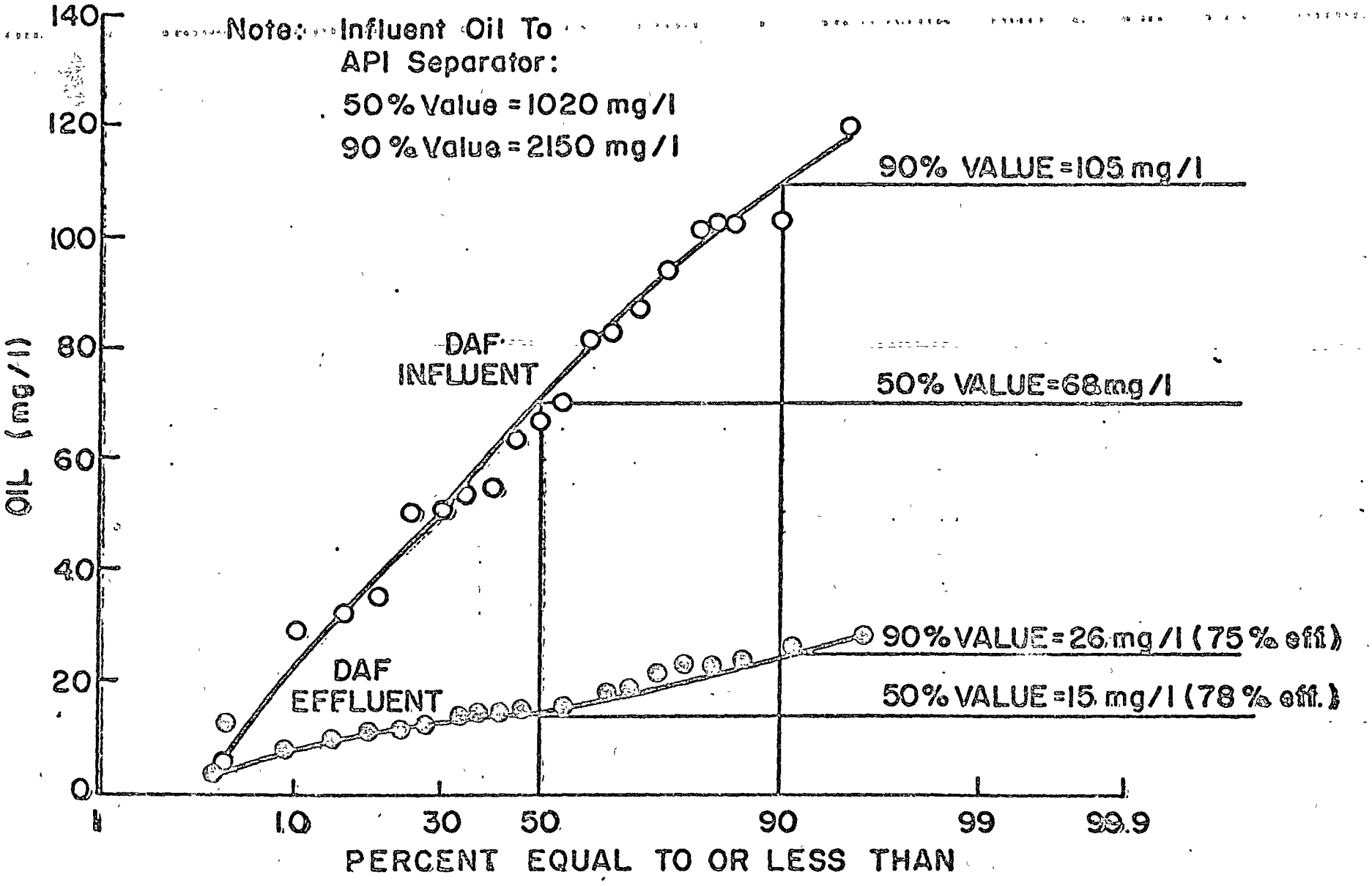

FIG. 7. PROBABILITY OF OIL REMOVAL IN DAF UNIT.

the influent to the separator was 1,020 mg/l (50% probability) and 2,150 mg/l (90%). The DAF reduced the total oil from 68 mg/l to 15 mg/l for 50% probability and from 105 mg/l to 26 mg/l for the 90% probability level.

Figure 8 shows the relationship between the influent and effluent oil concentration in a DAF unit. The oil removal efficiencies vary from 60% to 95%. The major factors in oil removal are oil concentration and form of the oil.

Table 15 provides a qualitative comparison between three pressurized and one induced DAF systems. Each type has some advantages and disadvantages. In all cases, if a significant amount of the oil is in the emulsified form, chemicals will have to be added to insure acceptable DAF performances.

Table 15. Comparison of DAF Processes (11,12)

Process	Advantages	Disadvantages
I PRESSURIZED SYSTEMS		
(a) Full Stream	More gas/hr dissolved, & improved separation.	Influent must be pumped; emulsification will occur; and high power requirements.
(b) Partial Stream	Lower power required as compared to full stream pressurization	Less gas/hr. dissolved; influent must be pumped; and can emulsify oil in influent.
(c) Recycle Stream	Need not pump influent solids; possible to optimize floc formation; influent oil not emulsified; and employs simpler control.	Requires larger flotation cell
II INDUCED	Lower capital cost;	higher corrected power requirements;
	smaller space requirements;	need strict hydraulic control;
	efficient in removing oil and SS; and	less flexibility in chemical addition flocculation; and
	can use multicells in series	3 to 7 times more volume of float skimmings.

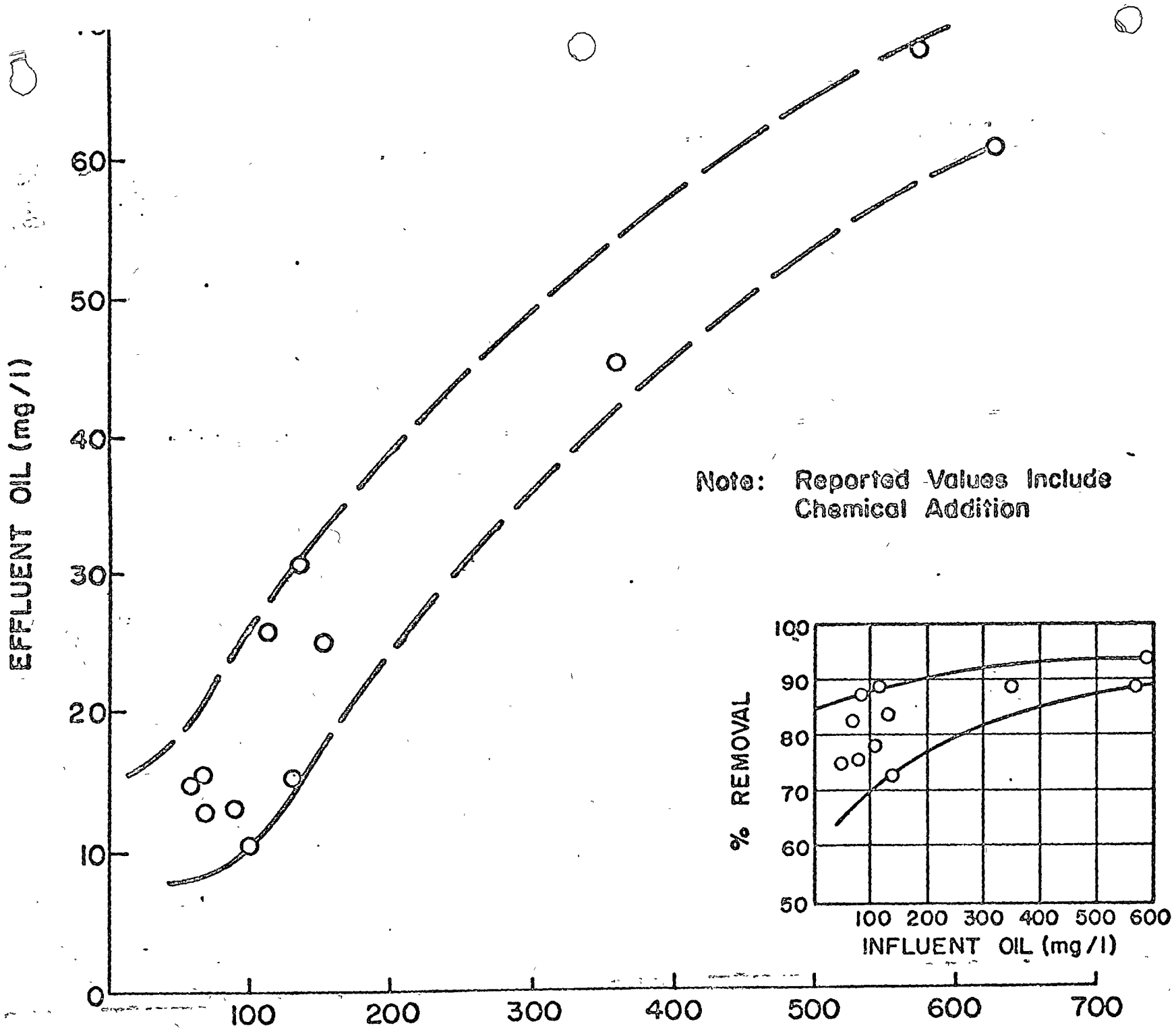

FIG. 8 OIL REMOVAL BY

Coagulation and Precipitation: This process is effective in reducing nutrient concentrations such as phosphates, in precipitating heavy metals as metallic hydroxides, and in removing water soluble materials such as alkyl-Aryl sulfonates by forming insoluble precipitates.

Soluable organic removals by lime pretreatment are illustrated in Table 16.

Table 16. Soluble Organic Removals by Lime Pretreatment*

Results	BOD_5	COD	TOC
Mean filtered infl. (mg/l)	168	464	201
Mean filtered effl. (mg/l)	131	408	155
Mean removal (mg/l)	37	56	46
Mean removal (%)	24	13	23

* All data from filtered samples

These wastes were derived from a proposed regional treatment system containing effluents from chemical plants and petroleum refineries. The mean overall BOD_5 and soluble removals respectively, were 37% and 24%.

Figure 9 depicts a case involving an integrated refinery and petrochemcial facility where air flotation on a bench scale was unsuccessful. However, it was found that a flocculant suspension could be developed at a pH above 8.0. A lime dosage of 350 mg/l was required.

Massive lime addition did present a potential problem in that the available natural alkalinity was insufficient to precipitate all of the calcium and the unstable effluent interfered with subsequent treatment steps. Concern over the fate of these excess calcium ions together with anticipated problems in controlling the pH of the mixed liquor prompted the addition of soda ash. Drastic pH reductions to below four had occurred during bench-scale biological treatability studies. This low pH problem is a fairly common occurrence when treating some refinery wastes. It was hoped that the soda ash would precipitate the excess calcium ions, enhance the settleability of the floc, and buffer the biological process against detrimental pH changes. It was found that the natural biological reduction in pH from an influent of 8.5 to a mean of 7.0 shifted the carbonate-bicarbonate balance and reduced the carbonate ions available for calcium carbonate precipitation to approximately one-twenty fifth of that entering the aeration basin. The result being that the primary effluent was rendered more stable by biological treatment and soda ash addition was not required for this purpose.

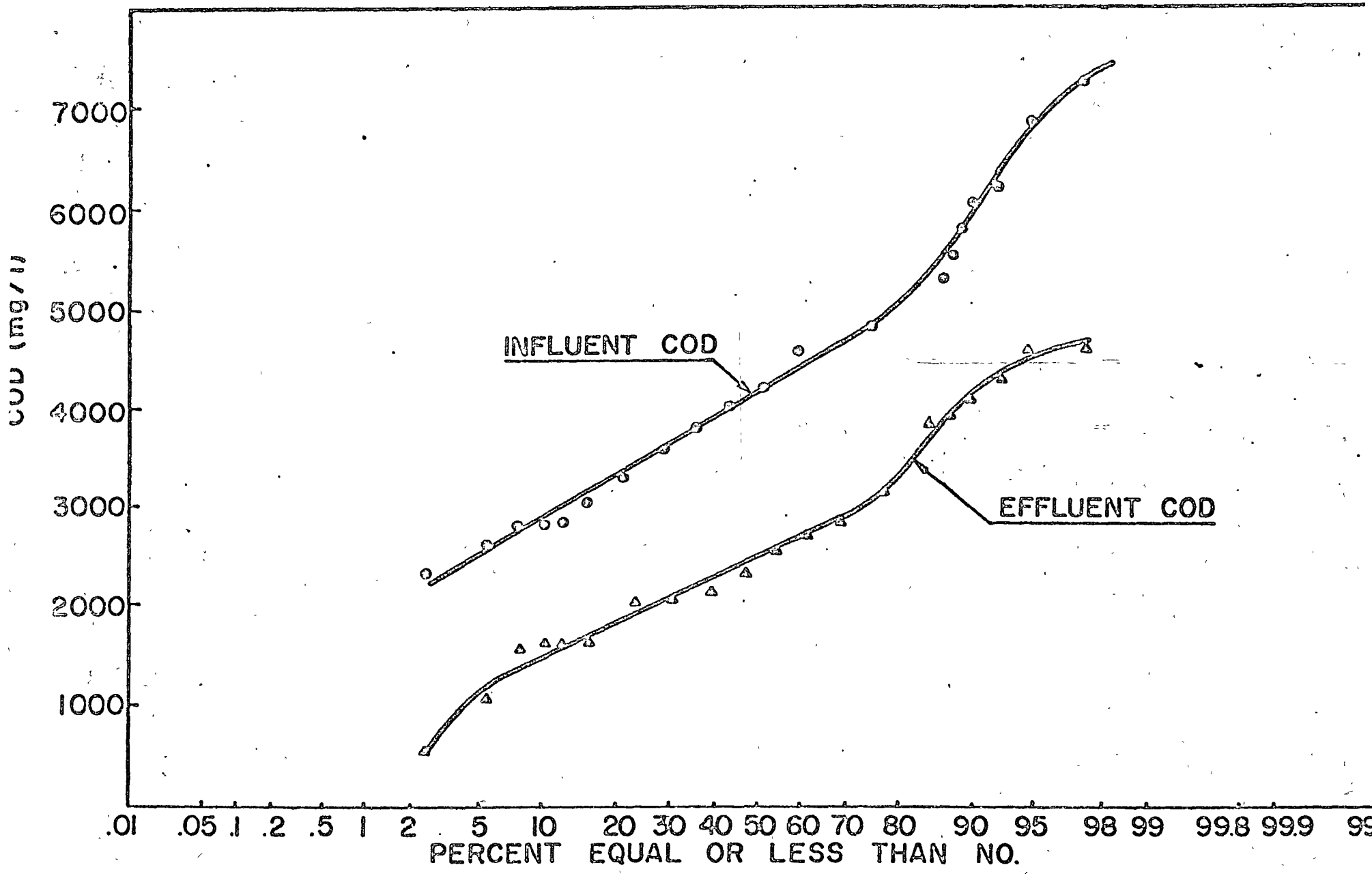

FIG. 9. EFFECTIVENESS OF PRIMARY TREATMENT FOR INTEGRATED REFINERY / PETROCHEMICAL FACILITY.

Drastic pH shifts did not occur in the pilot unit and soda ash proved to be unnecessary as a buffer. Furthermore, cost analysis indicated that a weighting agent could be applied more effectively in the form of powdered limestone.

The primary clarifier was operated for approximately two months at overflow rates ranging between 400 to 1,100 gpd/ft^2. The pilot unit could be operated either as a reactor clarifier or in the conventional centerfeed configuration.

Actual performance can best be characterized by extended periods of high efficiency punctuated by periodic gross discharges of oily sludge. Each failure could be traced to abnormally high influent oil concentrations. Normally, the influent oil remained less than 200 mg/l but on occasion jumped to over 700 mg/l which in turn triggered a clarification failure. This problem was eventually overcome by operating the unit at an overflow rate of approximately 600 gpd/ft^2 and adding massive quantities of weighting agent when influent oil levels rose significantly.

After the appropriate operational techniques had been perfected, effluent oil and suspended solids concentration could be maintained consistently below 50 mg/l. Removals of COD in the primary treatment unit are shown in Fig. 9. Approximately 40 percent of the influent loading, or a total of 1,700 mg/l of COD was removed. Oil and grease removal ranged from 100 to 5,000 mg/l with a mean of approximately 500 mg/l.

Considering the characteristics of the waste streams, it is believed that lime coagulation followed by sedimentation offered the only workable alternative for effective oil and suspended solids removal. Furthermore, this technique provided the added attraction of taking advantage of co-precipitation to assist in the removal of significant quantities of dissolved organics.

Coalescers: Coalescers are useful in breaking some types of oil emulsions, and may be classified as plate, fibrous media and loose media. Plate coalescers employ gravity separation and parallel plates to improve separation. Fibrous media units have a fixed filter element such as fiber glass. Loose media coalescers usually use some type of multigrade sand or other filtering media.

The oil removal efficiency is related to two major factors:

(a) variations in type of oil, degree of emulsion, droplet sizes, and suspended solids; and

(b) fluctuations in flow rates, influent oil concentrations and equipment upsets.

The advantages of coalescers are the compactness of the units and flexible operation. Some disadvantages include problems with solids, stabilized oil emulsions and suspended solids which may reduce the efficiencies that are no better than gravity separation. However, some have reported up to 95% removal of oils at design flow rates. The amount of input oil, Table 12, is limited to about 150 ppm.

Secondary and Tertiary Treatment: Biological processes for removing soluble organics from wastewaters is well documented, and considerable experience is being accumulated in physical-chemical techniques for polishing the final effluents (13,14). Table 17 summarizes typical experience derived from eight refinery and petrochemical plants in which activated sludge and activated carbon treatment were tried. Each waste stream has its own peculiar characteristics and any process sequence can be determined only after a thorough investigation using continuous flow pilot systems. Temperature and biotoxicity are of particular importance to biological systems. Cooling might be required during the summer months. Biotoxicity may be controlled by proper use of equalization basins and reducing excessive levels of known biotoxicants such as chromates, sulfides, ammonia, free oil, etc.

The design organic load for most activated sludge systems ranges from 0.10 lbs BOD_5/day/lb MLSS (extended aeration) to as high as 0.8 - 1.0 lbs BOD_5/day/lb MLSS. Higher loadings can be imposed, but generally at the expense of poorer efficiency and higher organic levels in the treated effluent.

Oil and grease are of paramount importance when designing activated sludge systems for wastewaters such as those discharged from petroleum refinery and petrochemical installations. Hexane extractables adversely affect a biological

Table 17. Effluent Quality from Activated Carbon and Activated Sludge Units

Constituent	Mean Value Range Primary Effluent	Total Carbon Effluent	Combined Activated Sludge-Carbon Effluent	Remarks
COD	500-700 mg/l	100-200 mg/l	30-100 mg/l	Exact COD residuals vary with complexity of refinery & design contact times in the Act.S. & Carbon Treatment Plants
BOD_5	250-350 mg/l	40-100 mg/l	5-30 mg/l	BOD residual depends on BOD/COD ratio which characterizes relative biodegradability of wastewater.
Phenols mg/l	10-100 mg/l	<1 mg/l	<1 mg/l	Phenols(ics) are generally amenable to biological and sorption removal.
pH	8.5-9.5	7-8.5	7-8.5	pH drop in Act.S. systems attributed to biological production of CO_2 and intermediate acids. pH change in carbon columns depends on preferential absorption of acidic and basic organics.
SS	50-200 mg/l	<20 mg/l	<20 mg/l	Primary effluent solids depend on design and operation of oil removal units. Act.S. effluent solids depend on effectiveness of secondary clarifier. Low effluent solids characterize carbon column effluent.
TDS	1500-3000 mg/l	1500-3000 mg/l	1500-3000 mg/l	TDS is essentially unchanged through all three treatment systems.
NH_3-N	15-150 mg/l	10-140 mg/l	2-100 mg/l	Exact concentration depends on prestripping facilities, nitrogen content of crude charge, corrosion additive practice and biological nitrification.
P	1-10 mg/l	1-10 mg/l	<1-7 mg/l	Only removal attributed to biological synthesis.

system as the concentration in the mixed liquor approaches 50 to 75 mg/l. A recent study conducted for the Environmental Protection Agency indicated that an activated sludge system will perform satisfactorily with a continuous loading of hexane extractables of 0.1 lbs/lb MLSS. It is recommended that the influent to the biological system should contain less than 75 mg/l hexane extractables and preferably less than 50 mg/l. The most significant problem related to oils in biological systems seems to be attributable to lowering of the floc density to a level where the sludge settling properties are destroyed.

Summary

The spectrum of wastewater derived from refinery and petrochemical plants may range from innocuous, readily biodegradable organics to highly toxic metallic complexes. Each combination of process units, operational procedures and flows deserves its own unique solution which satisfies the technical, economical and even local institutional constraints.

The modern waste treatment system may include: improved in-plant control and treatment units; storm water collection system; gravity-type oil separator; equalization basin; gravity-type clarifiers; dissolved air flotation system; secondary biological treatment; biological and chemical sludge disposal systems; and physical-chemical polishing units to remove excess suspended solids, oil, color, organics, metals, and toxic or other unwanted residuals. Each treatment process has its limitations.

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in-plant transport of solid waste materials. Significant pollutants will result from hot lye peeling, sorting, slicing, etc., washing and cooling of cans and plant clean up. The range of waste quantities from these operations are summarized in Table 1. (FWPCA, 1967).

The distribution of water use in cannery operation is summarized in Table 2.

Typical canning wastes characteristics are summarized in Table 3.

The average waste characteristics from frozen food preparation are 0.62, 0.63, and 0.50 lbs BOD, SS and TDS/case respectively with a daily wastewater volume of 125 gal.

Typical survey data of a peach canning operation showing the flow, and solids produced per case of No. 303 cans is given in Table 4. Table 5 shows the probability data of the same data.

Figure 1 shows an example of waste sources from a corn cannery. The BOD load is derived from washing, cutting, reels and blanching.

The EPA, Doc. 440/1-74-027-a, March 1974 provides considerable information on apple products (except caustic peeled and dehydrated products), citrus products (except pectin and pharmaceutical products), and frozen and dehydrated products. These products are classified S.I.C. 2033, 2034, and 2037. Tables 6, 7 and 8, respectively, provide data on water usage and waste characterization in the apple, citrus and potato processing industries.

The average BOD and flows for various apple, citrus and potato products, respectively, is shown in Tables 9, 10 and 11.

The waste loadings for BOD and SS from 12 plants representing the apple processing industry range in size from 3,700 to 43,100 kilograms/hour (4.1 to 47.5 tons per hour). The water usage of these plants varied from 1190 liters per thousand kilograms (285 gallons per ton) to 14,800 l/kkg (3550 G/T) with an average flow of 3,660 l/kkg (875 G/T). The plant using 14,800 l/kkg (3550 G/T) was far removed from the other with the next closest one using 6,050 l/kkg (1450 gallons per ton). The BOD ranged from 1.4 to 10.1 kilograms per thousand kilograms (2.8 to 20.2 lbs per ton) and again the high water user had the highest BOD. The average BOD for the 12 plants was 5.0 kg/kkg (10.0 lb/ton). Suspended solids ranged from 0.15 to 1.05 kg/kkg (0.3 to 2.1 lb/ton) with the average being 0.5 kg/kkg (1.0 lb/ton).

Table 1. Daily Waste Quantities from Unit Processes

Process	Wasteload, lb/day/case			Wastewater Volume
	BOD	SS	TDS	
Washing	0.050-0.3	0.05 -0.4	300- 1,500	08.0- 25.0
Belt Conveyor	0.003-0.001	0.01 -0.02	30- 100	01.0- 05.0
Sorting, Pitting Slicing, etc.	0.005-0.06	0.015-0.070	100- 500	01.0- 0.75
Blanching and/or Peeling	0.1 -0.4	0.10 -0.4	2,000- 4,000	06.0- 25.0
Exhausting of cans	0 -0.015	0 -0.015	0 - 200	0 - 02.5
Processing	0.005-0.06	0.005-0.0450	40- 1,200	01.0- 05.0
Cooling of Cans	0.005-0.06	0.005-0.0300	300- 1,000	06.0- 30.0
Plant Cleanup	0.032-0.12	0.030-0.15	230- 1,000	06.0- 20.0
Box Washing	0.01 -0.025	0.015-0.04	200- 500	02.0- 05.0
TOTAL	0.26 -1.05	0.23 -1.17	3,200-10,000	31.0-125.0
AVERAGE	0.7	0.8	7,500	075.0

Table 2. Water Reuse

Operation	Gross Water Use	
	Range (%)	Average (%)
Raw Production Preparation (including peeling)	25-55	34
Syrup and Brine	2-10	6
Steam and Sterilization	10-20	14
Cooling	6-60	35
Clean-up	5-25	8
Other	1- 6	3

Table 3. Typical Canning Wastes

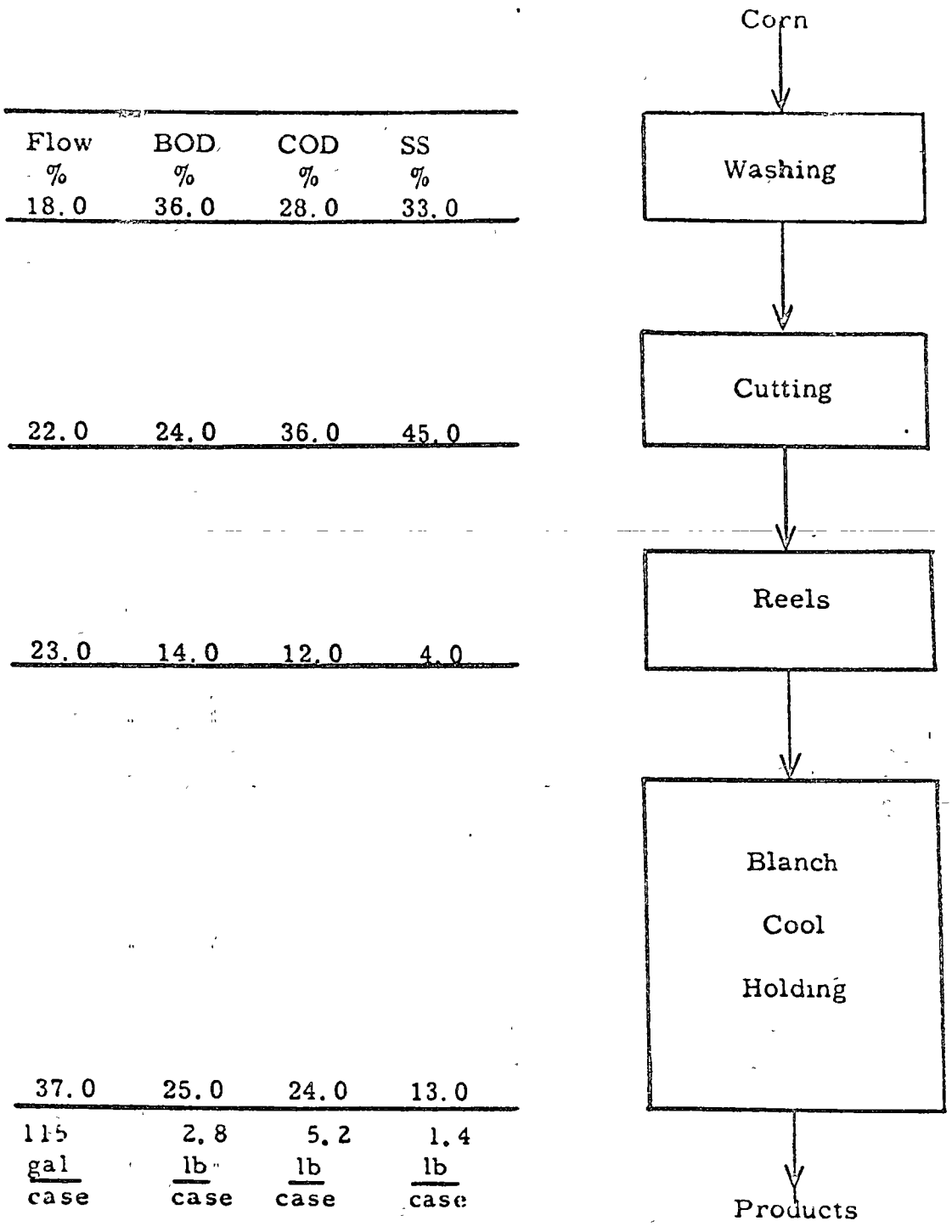
Product	Waste Volume (gal/case)	5-Day BOD (mg/l)	5-Day BOD (lb/case)	Suspended Solids (mg/l)	Suspended Solids (lb/case)
Apples	29- 46	1,680- 5,530	0.64-1.31	300- 600	0.10-0.20
Apricots	65- 91	200- 1,020	0.15-0.56	200- 400	0.14-0.25
Cherries	14- 46	700- 2,100	0.16-0.50	200- 600	0.05-0.14
Cranberries	11- 23	500- 2,250	0.10-0.21	100- 250	0.02-0.05
Pineapples	74	26	0.002	--	--
Peaches	51- 69	1,200- 2,800	0.69-1.20	450- 750	0.24-0.34
Asparagus	80	16- 100	0.01-0.07	30- 180	0.02-0.12
Beans, Baked	40	925- 1,440	0.31-0.48	225	0.07
Beans, Green/Wax	30- 51	160- 600	0.15-0.67	60- 150	0.02-0.04
Beans, Kidney	20- 23	1,0[illegible]0- 2,500	0.19-0.45	140	0.02
Beans, Lima, Dried	20- 33	1,740- 2,880	0.30-0.60	160- 600	0.05-0.10
Beans, Lima, Fresh	57-294	190- 450	0.21-0.47	420	0.20-1.02
Beets	31- 80	1,580- 7,600	1.00-2.00	740-2,220	0.50-1.00
Carrots	36	520- 3,030	0.11-0.67	1,830	0.40
Corn, Cream Style	28- 33	620- 2,900	0.17-0.66	300- 675	0.07-0.17
Corn, Whole Kernel	29- 80	1,120- 6,300	0.74-1.50	300-4,000	0.20-0.95
Mushrooms	--	76- 850	4.77-53.38	50- 240	3.14-15.07
Peas	16- 86	380- 4,700	0.27-0.63	270- 400	0.06-0.20
Potatoes, Sweet	90	1,500- 5,600	1.10-4.40	400-2,500	0.31-1.95
Potatoes, White	--	200- 2,900	--	990-1,180	--
Pumpkin	23- 57	1,500- 6,880	0.72-1.31	785-1,960	0.38
Sauerkraut	3- 20	1,400- 6,300	0.10-0.30	60- 630	0.01-0.10
Spinach	180	280- 730	0.42-1.11	90- 580	0.14-0.88
Squash	23	4,000-11,000	0.76-2.09	3,000	0.57
Tomatoes	3-114	180- 4,000	0.11-0.17	140-2,000	0.06-0.13

Table 4. Waste Loadings From Peach Canning Operations

Flow (gals)	Cases (#303)	gal/case	Total Solids (mg/l)	Suspended Solids (mg/l)	TS lb/1000 gal	SS lb/1000 gal	TS (lb/case)x10^{-2}	SS (lb/case)x10^{-3}
119,280	3,500	34.1	1750	60	14.595	0.5	49.77	17.05
78,120	1,700	46.0	2045	120	17.055	1.0	78.45	46.00
99,720	2,381	41.9	-	-	-	-	-	-
143,560	1,940	74.0	-	-	-	-	-	-
45,840	8,150	5.6	2905	155	24.228	1.29	13.57	6.67
74,280	1,460	50.9	2330	450	19.432	3.75	98.91	190.87
85,800	2,200	39.0	-	-	-	-	-	-
69,840	1,485	47.0	2010	25	16.763	0.21	78.78	9.87
54,600	1,045	52.2	1585	150	13.219	1.25	69.00	65.25
58,580	796	73.6	2065	250	17.222	2.08	126.75	153.09
89,520	1,655	54.1	1895	335	15.804	2.79	85.50	150.94
124,560	4,460	27.9	-	-	-	-	-	-
171,840	4,940	34.8	1430	250	11.926	2.08	41.50	72.38
170,520	4,860	35.1	1495	165	12.468	1.38	43.76	48.44
153,600	4,970	30.9	2005	305	16.722	2.54	51.67	78.48
125,400	4,810	26.1	2175	240	18.139	2.0	47.34	52.20
170,280	4,200	40.5	-	-	-	-	-	-
168,600	5,030	33.5	2010	75	16.763	0.63	56.15	21.10
140,040	4,900	28.6	1660	95	13.844	0.79	39.59	22.59
156,120	4,900	31.9	1975	125	16.471	1.04	52.54	33.17
139,680	5,370	26.0	1895	425	15.804	3.54	41.09	92.04
131,040	4,860	27.0	-	-	-	-	-	-
157,560	4,580	34.4	1665	90	13.886	0.75	47.77	25.80
77,520	1,840	42.1	1915	130	15.971	1.08	67.23	45.47
146,400	5,100	28.7	2015	345	16.805	2.88	48.23	82.65

Table 5. Probability Data From Peach Canning Operations

Probability gal/case			Probability TS, S_5			
Rank	gal/case	$\frac{m}{n+1}$	Rank	(lbs/case)x10^{-2}	(lbs/case)x10^{-3}	$\frac{m}{n+1}$
1	5.6	1.92	1	13.57	6.67	2.5
2	26.0	5.77	2	39.59	9.87	7.5
3	26.1	9.62	3	41.09	17.05	12.5
4	27.0	13.46	4	41.50	21.10	17.5
5	27.9	17.30	5	43.76	22.59	22.5
6	28.6	21.15	6	47.34	25.80	27.5
7	28.7	25.00	7	47.77	33.17	32.5
8	30.9	28.85	8	48.23	45.47	37.5
9	31.9	32.69	9	49.77	46.00	42.5
10	33.5	36.54	10	51.67	48.44	47.5
11	34.1	40.38	11	52.54	52.20	52.5
12	34.4	44.23	12	56.15	65.25	57.5
13	34.8	48.08	13	67.23	72.38	62.5
14	35.1	51.92	14	69.00	78.48	67.5
15	39.0	55.77	15	78.45	82.65	72.5
16	40.5	59.61	16	78.78	92.04	77.5
17	41.9	63.46	17	85.50	150.94	82.5
18	42.1	67.31	18	98.91	153.09	87.5
19	46.0	71.15	n = 19	126.75	190.87	92.5
20	47.0	75.00				
21	50.9	78.85				
22	52.2	82.69				
23	54.1	86.54				
24	73.6	90.38				
n = 25	74.0	94.26				



Flow	BOD	COD	SS
%	%	%	%
18.0	36.0	28.0	33.0
22.0	24.0	36.0	45.0
23.0	14.0	12.0	4.0
37.0	25.0	24.0	13.0
115 gal/case	2.8 lb/case	5.2 lb/case	1.4 lb/case

Figure 1. Potential Pollution Sources - Corn Cannery

Table 6. Water Usage and Waste Characterization in Apple Processing

Process Step	Water Usage		BOD5		Suspended Solids	
	l/kkg	G/T	kg/kkg	lb/T	kg/kkg	lb/T
Washing	142	34	0.09	0.18	0.03	.06
Peeling						
Mechanical	104	25	0.16	0.31	0.015	0.03
Slicing	638	158	2.49	4.97	0.182	0.36
Deaeration	71	17	2.21	4.42	0.12	0.24
Cooking	267	64	0.14	0.27	0.05	0.10
Cooling (1)	58	14	0.02	0.03	0.005	0.01
Transport	58	14	0.02	0.03	0.005	0.01
Clean-up	1,558	372	1.90	3.80	0.30	0.60

(1) 95% recirculated

Table 7. Water Usage and Waste Characterization in Citrus Processing

Process Steps	Water Usage		BOD5		Suspended Solids	
	l/kkg	(G/T)	kg/kkg	(lb/T)	kg/kkg	(lb/T)
Fruit Cleaning	303	(73)	0.08	(0.16)	0.04	(0.07)
Extracting	389	(93)	0.40	(0.79)	0.27	(0.54)
Pasteurizing/Homogenizing	62	(15)	0	(0)	0	(0)
Cooling (1)						
Juice Products	221	(53)	0.03	(0.05)	0.02	(0.03)
Segments			0.01	(0.02)	0.01	(0.02)
Juice Condensing	400	(96)	0.06	(0.12)	0.02	(0.03)
Barometric Condensing (2)						
Juice Products	50	(12)	0.07	(0.13)	0.09	(0.17)
Waste Heat Evaporator	71	(17)	0.15	(0.29)	0.09	(0.18)
Peeled Fruit Washing	129	(31)	0.04	(0.07)	0.01	(0.01)
Caustic Treatment	1	(0.3)	0.01	(0.02)	0.01	(0.01)
Centrifuging	144	(35)	3.07	(6.14)	0.51	(1.02)
Container Washing	75	(18)	0		0	(0)
Waste Heat Evaporator Condensate	334	(80)	0.33	(0.66)	0.11	(0.22)
Waste Heat Evaporator Scrubber Effl.	351	(84)	0.22	(0.43)	0.08	(0.15)
Oil Lean Residue From Separator	126	(30)	0.16	(0.32)	0.25	(0.49)
Boiler Blowdown	60	(14)	0.01	(0.02)	0.01	(0.02)
Regeneration Brine	13	(3)	0	(0)	0	(0)
Cleanup						
Juice Products	705	(169)	0.16	(0.32)	0.16	(0.31)
Segments	371	(89)	0.36	(0.72)	0.07	(0.13)
Peel Products	484	(116)	0.07	(0.14)	0.11	(0.22)

(1) 90% recirculated
(2) 2% cooling tower blowdown

Table 8. Water Usage and Waste Characterization in Potato Processing

Process Steps	Water Usage		BOD5		Suspended Solids	
	l/kkg	G/T	kg/kkg	lb/T	kg/kkg	lb/T
Washing	1,102	264	0.676	1.35	1.383	2.76
Peeling						
Dry Caustic	1,448	347	7.325	14.62	9.569	19.1
Wet Caustic	3,000	719	20.245	40.41	28.662	57.2
Steam	2,391	573	15.215	30.37	13.427	26.8
Trimming	793	190	0.777	1.55	0.26	0.52
Slicing						
Dehydrated	764	183	0.296	0.59	0.701	1.4
Frozen	1,519	364	2.630	5.25	1.303	2.6
Blanching						
Dehydrated	175	42	0.701	1.40	0.601	1.2
Frozen	1,043	250	5.461	10.9	2.104	4.2
Cooling	668	160	1.172	2.34	-	-
Cooking	448	117	1.192	2.38	-	-
Dewatering	513	123	0.471	0.94	0.351	0.70
Fryer Scrubber	417	100	-	-	-	-
Fryer Belt Spray	417	100	-	-	-	-
Refrigeration	1,602	384	-	-	-	-
Transport Water	292	70	0.261	0.52	-	-
Cleanup	951	228	2.725	5.44	-	-

Table 9. Average (Range) of BOD and Flow For Various Apple Product Styles

PRODUCT STYLE	NUMBER PLANTS	FLOW 1/kkg AVERAGE (RANGE)	FLOW gal/T AVERAGE (RANGE)	BOD kg/kkg AVERAGE (RANGE)	BOD lb/T AVERAGE (RANGE)
Juice Only	3	2880 (1880-3540)	690 (450- 850)	2.05 (1.6- 2.55)	4.1 (3.2- 5.1)
Sauce Only	3	3400 (1380-6050)	815 (330-1450)	5.35 (3.4- 7.5)	10.7 (6.8-15.0)
Sauce & Juice	3	1690 (1190-14800)	405 (285-3550)	6.85 (5.8- 8.5)	13.7 (11.6-17.0)
Apple Products (except Juice Only)	9	3920 (1190-14800)	940 (285-3550)	6.0 (1.4-10.1)	12.0 (2.8-20.2)
All Apple Products	12	3660 (1190-14800)	875 (285-3550)	5.0 (1.4-10.1)	10.0 (2.8-20.2)
Slices with Apple Products	3	6635 (1790-14800)	1595 (430-3550)	5.85 (1.4-10.1)	11.7 (2.8-20.2)

Table 10. Average (Range) of BOD and Flow For Various Citrus Product Styles

PRODUCT STYLE	NUMBER PLANTS	FLOW 1/kkg AVERAGE(RANGE)	FLOW gal/T AVERAGE(RANGE)	BOD kg/kkg AVERAGE(RANGE)	BOD lb/T AVERAGE(RANGE)
Segments Only	2	7455(4340-10570)	1790(1040-2535)	3.5 (2.65-4.35)	7.0(5.3- 8.7)
Citrus Products without Segments	19	10160(710-24950)	2440(170-5980)	3.15(0.45-8.5)	6.3(0.9-17.0)
Citrus Products with Segments	6	10850(4380-19180)	2600(1050-4600)	3.3 (1.4 -5.6)	6.6(2.8-11.2)
Citrus Products without Oil	5	7570(4340-10570)	1820(1040-2535)	3.35(1.45-5.6)	6.7(2.9-11.2)
Citrus Products with Oil	22	10690(710-24950)	2560(170-5980)	3.2 (0.45-8.5)	6.4(0.9-17.0)
Citrus Products without Feed	9	7570(1630-24950)	1820(390-5980)	3.15(0.7 -6.4)	6.3(1.4-12.8)
Citrus Products with Feed	18	11380(710-24740)	2730(170-5930)	3.25(0.45-8.5)	6.5(0.9-17.0)
All Products	27	10110(710-24950)	2425(170-5980)	3.2 (0.45-8.5)	6.4(0.9-17.0)

Table 11. Average (Range) of BOD and Flow For Various Potato Product Styles

PRODUCT STYLE	NUMBER PLANTS	FLOW 1/kkg AVERAGE(RANGE)	FLOW gal/T AVERAGE(RANGE)	BOD kg/kkg AVERAGE(RANGE)	BOD lb/T AVERAGE(RANGE)
Frozen Products	13	11320(4090-15510)	2710(980-3720)	22.9 (4.45-36.95)	45.8(8.9-73.9)
Dehydrated Products	7	8770(6530-12010)	2100(1565-2880)	11.05(7.75-15.2)	22.1(15.5-30.4)
Frozen & Dehydrated Products	3	9260(6380-12800)	2220(1530-3070)	13.8(13.65-13.95)	27.7(27.3-27.9)
All Potato Products	23	10270(4090-15510)	2460(980-3720)	18.1 (4.45-36.95)	36.2(8.9-73.9)

The BOD average ranged from 2.05 kg/kkg (4.1 lb/ton) for juice to 6.85 kg/kkg (13.7 lb/ton) for the sauce and juice group. The BOD averages for all the groups compared favorably to the BOD of 5.0 kg/kkg (10.0 lb/ton) for all apple products with the exception of the plants producing juice. The flow averages ranged from 1690 to 6,635 l/kkg (405 to 1595 G/T) with the average for all apple products being 3,660 l/kkg (875 G/T).

Waste waters from citrus processing plants contain organic carbon and matter in suspended and dissolved form. The quantity of fresh water intake to plants ranges between 710 and 24,950 liters per thousand kilograms (170 and 5,980 gallons per ton) of raw material. Fresh water use is highly contingent upon in-plant conservation practices and reuse techniques and averages approximately 10,110 l/kkg (2425 G/T) of citrus processed. The nature and amounts of these water reuses as influenced by in-plant controls and operational practices have a substantial effect on resulting waste water quantities and characteristics.

About two-thirds of the total solids in citrus juices are sugars and the same may be said of the waste water. Because of this citrus wastes are highly putrescible. Citrus wastes contain pectic substances which interfere with settling of the suspended solids. Primary clarification of citrus waste water is not as effective as with most other wastes. Citrus waste water contains a small amount of the essential oil that occurs mostly in the fruit peel. This oil is bacteriostatic but usually does not interfere with treatment procedures unless it accumulates in an anaerobic sludge digester. Citrus wastes are deficient in nitrogen and phosphorus compounds; treatment by biological procedures may be accelerated by adding these nutrients. Citrus waste water usually is somewhat acid because of the citric acid it contains. However, alkaline materials used in cleaning the equipment and lye-bath water from sectionizing operations tend to make the waste water alkaline, and at times very strongly so.

The volume of citrus waste water fluctuates through the harvesting season. The production of frozen orange concentrate is a continuous operation, running twenty-four (24) hours per day until it becomes necessary to clean the equipment. On the other hand, the other processing operations are mostly a one or two shift operation daily, and may shutdown completely on weekends or holidays, depending on fruit supply and market demand. The volume of waste water changes markedly when the production run is over and clean-up operations begin.

The changes in strength, volume, and pH are such that biological treatment of the waste is rendered difficult unless fluctuations are leveled out. This is accomplished by a surge tank with suitable mixing facilities placed ahead of the treatment plant or with treatment plant design to handle these fluctuations.

In a survey of 23 plants ranging in size from 180 to 1630 kkg (200 to 1800 tons), the BOD ranged from 4.45 to 36.95 kg/kkg (8.9 to 73.9 lb/ton) with an average of 18.1 kg/kkg (36.2 lb/ton). Suspended solids ranged from 3.8 to 45.5 kg/kkg (7.6 to 91.0 lb/ton) with an average of 15.9 kg/kkg (31.8 lb/ton). Water usage ranged from 4090 to 15,510 l/kkg (980 to 3720 G/T) with an average of 10,270 l/kkg (2460 G/T).

Case History

1. Spray Irrigation

(a) Description -- The Paris, Texas plant of Campbell Soup Company, whose building complex extends over an area of 22 acres, produces a complete line of heat processed soups, plus beans and spaghetti type products. Waste water from the processing areas is collected by two drainage systems. One, containing the grease from the cooking areas, is first routed through a gravity grease separator at the waste screening building before it joins the second waste stream from the vegetable trimming area. Together the merged streams pass through revolving drum type 10-mesh screens to remove large pieces of vegetable matter which are then conveyed to a storage hopper for later removal as animal feed. The wastewater falls into a 100,000 gallon surge tank from where it is pumped at high pressure to the spray irrigation field.

Pumping is accomplished by five 75 HP vertical turbines each capable of 1000 gpm at 200 feet TDH. The selection of vertical turbines over horizontal centrifugal pumps is the result of cost considerations over a long period of time. While these pumps are more expensive at the outset, the cost of mounting, the efficiency of operation, the accessibility for maintenance, and their reliability makes them a less expensive pump in the long run. A liquid level system controls the starting of each pump so that each is energized in turn as the water rises in the surge tank. Tied electrically to the starting circuit of each pump is a timing device which controls the operation of pneumatically controlled valves in the field, which in turn activate the sprinklers. Each sprinkler line is assigned a position in an operating group and each operating group is balanced to the discharge rate of the pump. In general, all lines discharge the same quantity of water on a per-acre basis so that the rate of application is adjusted by the duration of the sprinkling time. A switching arrangement has been provided so that the groups of lines operating from a given pump may be rotated from time to time.

For example, assume that pump "A" is operating Group II sprinklers. When the water rises in the pit, Pump "B" comes on, energizing Group V sprinklers. In the meantime, Group II finishes its allotted time and turns off, but Pump "A" continues to operate and Group III sprinklers come on automatically. When Pump "B" has lowered the liquid level in the surge tank, it turns off and Group V sprinklers are shut down. The system continues to recycle as long as there is flow from the factory.

Periodic samples secured at the outfall of the system indicated a consistent reduction in BOD of 99 percent with most samples indicating a BOD of 3 to 6 ppm.

(b) Key Design Parameters

(1) Length of Slope -- The Paris system was designed on the basis that the downhill slope should be between 200 and 300 feet. Basically, the downslope area requirement is 50 feet beyond the perimeter of the sprinklers.

(2) Degree of Slope -- The pitch of slopes in Paris ranges from less than one percent to more than twelve percent. The investigation led to the conclusion that a flat slope encouraged puddling and subsequently anaerobic conditions, while the retention time on a steep slope was insufficient for complete degradation at normal application rates. This established a design criterion of no more than six percent but not less than two percent for any slope.

(3) Hydraulic Loading -- In Paris, the design was based upon an application rate of .25" per day in winter and .50" per day in summer based upon an estimated wetted area coverage of approximately 75 percent. As it turned out, the actual wetted area was considerably less than the estimate, but the disposal capacity per wetted acre was much greater. The greater hydraulic load capacity combined with more efficient land utilization results in a more compact system requiring less acreage. The application to wetted watershed in the test areas was normally 0.6" per day or 3.0" for a five-day week. During the summer of 1968 the duration of the sprinkling cycle was increased from 6 to 8 hours per day, while hay harvest was in progress.

(4) Hay Harvest -- Reed Canary Grass will yield a large quantity of exceptionally high quality hay which according to nutritional analysis approximates the value of first

CANNED & PERSERVED FISH AND SEAFOODS PROCESSING INDUSTRY

E. F. Gloyna

Fish and shellfish industry is an integral part of the food processing industry. The industry world-wide uses some of the oldest and newest technologies. Harvesting techniques employ; netting, trapping, dredging, and live fishing. Fishing vessels either take their catches directly to the processor or ice down the catch for later delivery. Wastes from butchering and evisceration are usually dry captured, or screened from the wastewater, and processed as a fishery by product. Unless the seafood is prepared for the fresh market, most catches of sea food receive some form of precooking or blanching which facilitates removal of skin, bone, shell, gills, and other wastes. The fish is prepared in its final form by picking or cleaning to separate the edible portions. Bacterial growth is arrested at temperatures below -9 °C. Preservation by canning at about 115 °C for 30 to 90 minutes, depending on can size.

Typical fisheries processing plants in the USA include: catfish, blue crab, shrimp and tuna. The following data (figures and tables) are derived from EPA Draft Document, "Development Document for Effluent Limitations Guidelines and Standards of Performance for the Canned and Preserved Fish and Seafoods Processing Industry".

Catfish

About 45% of the whole catfish is waste but about 45% of the rendered offal is protein, Table 1.

Table 1. Proximate Analysis of Raw Catfish Offal (,1970)

Constituent	Level
Moisture	58.6%
Crude fat	25.5%
Ash	3.1%
Crude protein	12.8%

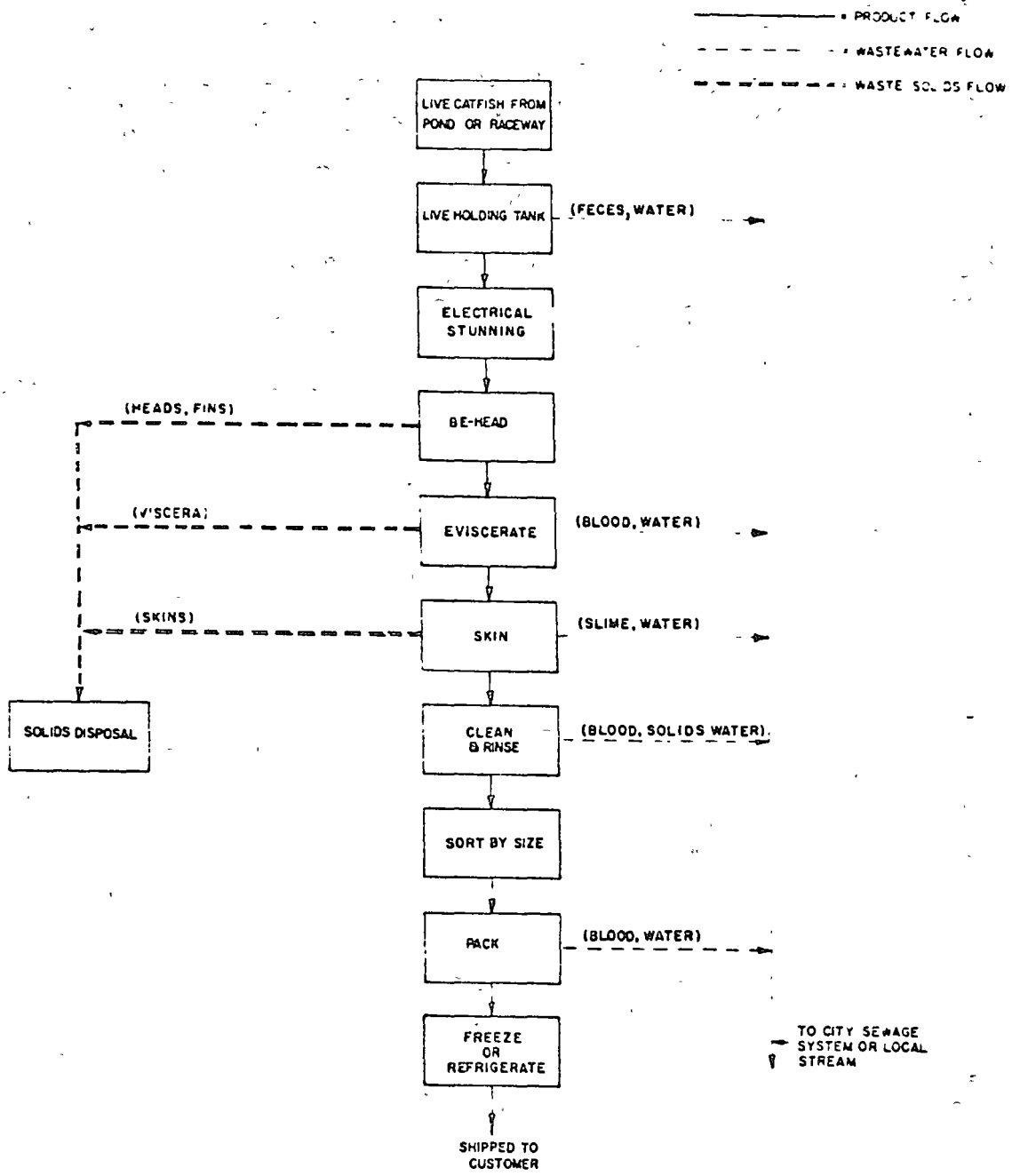
Table 2 shows the waste characteristics from typical catfishing processing plants.

Table 2. Catfish Processing Wastewater Characteristics (Malkey and Sargent, 1972)

Parameter	Level			
	kg or l / 1000 fish	lb or gal / 1000 fish	kg or l / kkg raw mat'l	lb or gal / ton raw mat'l
Flow	7570	(2000)	135	(3912)
BOD	3.6	(8.0)	7.83	(15.65)
COD	4.9	(10.8)	10.57	(21.12)
TSS	2.3	(5.1)	5.00	(9.98)
TVSS	2.0	(4.5)	4.40	(8.80)
Grease and Oil	0.8	(1.7)	1.67	(3.33)

A typical flow diagram for a catfish processing facility is given in Fig. 1.

Fig. 1. Catfish Process



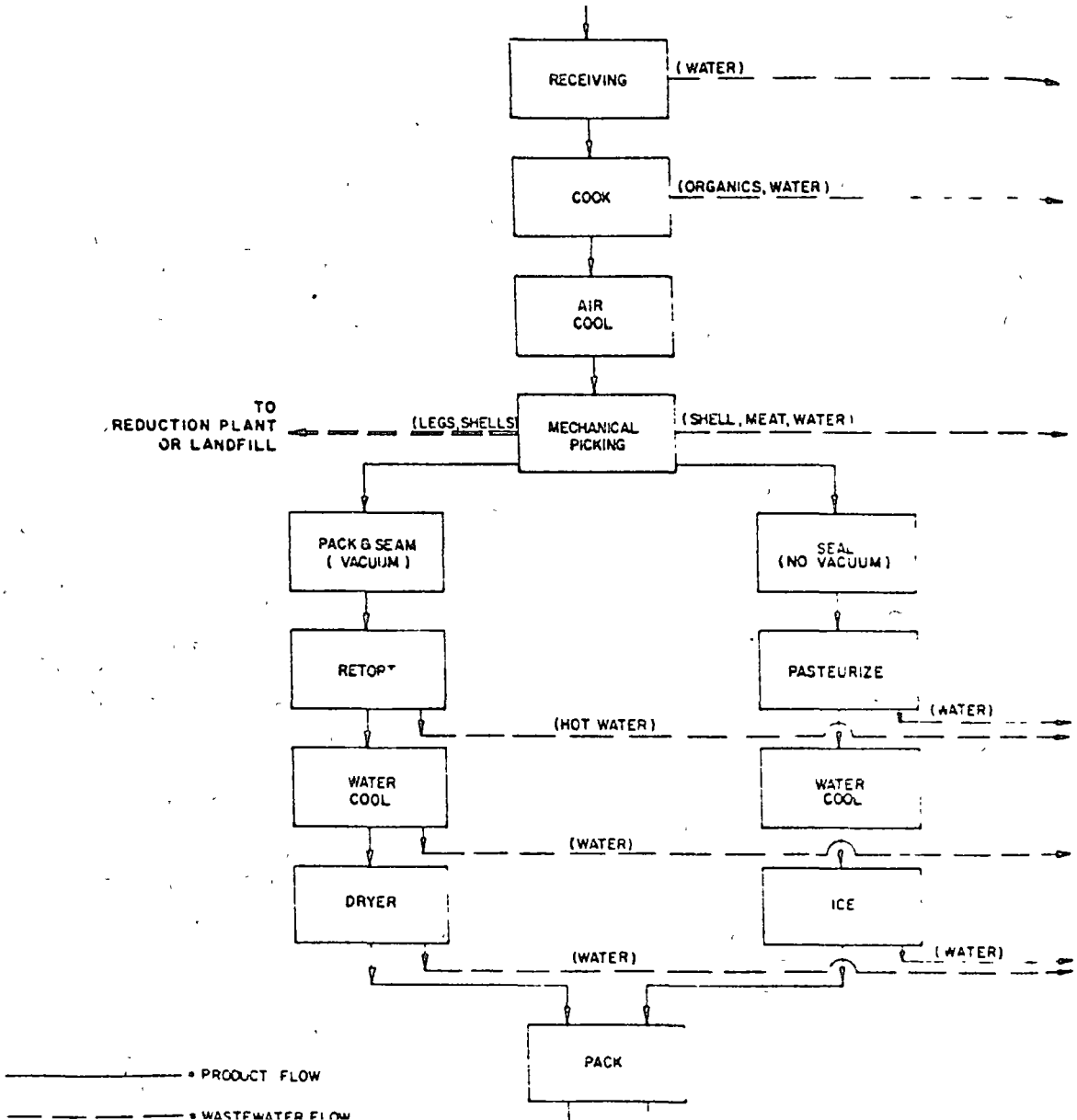
Blue Crab

The major part of the blue crab is not edible. The waste consist of body juices, shell and entrails. The loss may be as high as 86% of the crab weight. About 35% of the total loss may be lost in cooking. Because much of the waste is exoskeleton the protein concentration of these wastes are low as compared visceral fish wastes.

About 35% of the live weight of the crab is lost in the steam cooking process. These condensates from the crab cookers exhibit BOD's of 12,000 to 14,000 mg/l. Plant clean up waters may have organic strenghts of 1,400 mg/l. Also, in canning, additives such as EDTA, Alum, Citric Acid and other organic acids are used in small amounts.

The blue crab handling process is shown in Fig. 2. A typical mechanized plant utilizes the mechanical picker 5 to 10 hours per week or more.

Fig. 2 Mechanized Blue Crab Process



The major portion of the Alaskan (King Crab) is wasted in processing. About 80% is wasted. The waste in primarily protein, chitin and calcium carbonate, Table 3.

Table 3. Typical Crab Meat Composition

Species	Source	Composition		
		Protein (%)	Chitin (%)	$CaCO_3$ (%)
king crab	picking line	22.7	42.5	34.8
tanner crab	leg and claw shelling	10.7	31.4	57.9
tanner crab	Body butchering and shelling	21.2	30.0	48.8

A study by Oregon State University (Soderquist, et al., 1972a) conducted in 1970 and 1971, characterized the wastewaters from the processing of several fuits and vegetables in terms of organic load. The study found that green bean processing generates about 3.5 kg COD/kkg (7 lbs/ton) of raw product, whereas royal ann cherry processing generates 14 kg/kkg (28 lbs/ton); and red beets, 37.5 kg/kkg (75 lbs/ton). The Dungeness crab plants surveyed, by comparison, produced 11.0 kg/kkg (22.0 lbs/ton) of raw product processed. This, surprisingly, was lower than all but on of the fruit and vegetable commodities mentioned above.

This comparison is made all the more interesting when viewed in the light of water usage. Whereas, the range of water usage for the fruits and vegetables mentioned above was 3.75 to 12.07 cu m/kkg (900 to 2900 gallons per ton), water use in the Dungeness crab processing industry was about 15.0 to 21.2 cu m/kkg (3600 to 5100 gallons per ton).

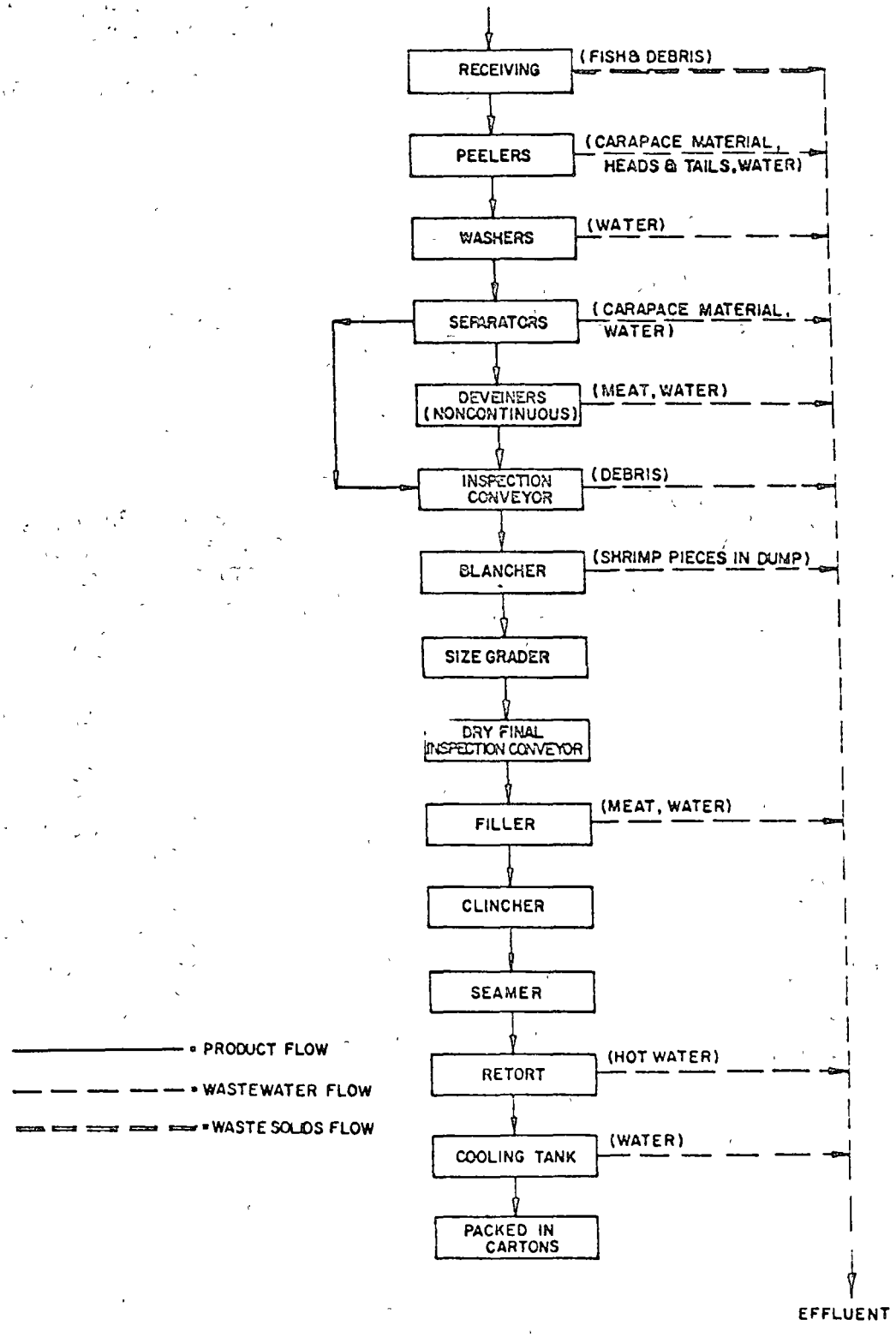
Shrimp

The process for canned or frozen shrimp is fairly uniform throughout the United States (see Figure 3). On the lower Pacific Coast, shrimp are brought to the processing plant frequently (1-2 days). Very seldom are the shrimp held at sea more than a few days. After netting, the shrimp are brought onto the deck of the ship and the majority of the larger fish and debris is removed at that time. The shrimp are then stored whole in the hold of the boat. These shrimp are laid in a two to three inch mat with about an inch or more of ice put properly, spoilage will occur quite rapidly. Although trash fish are removed from the catch prior to returning to port, approximately one percent of the delivered load still consists of trash fish and debris, and must be manually separated at the processing plant.

In the Gulf of Mexico and South Atlantic fishery, the boats normally do not bring their catch directly to the processing plant. They commonly dock at central locations (buying stations) and unload their catch into waiting trucks. The shrimp are then iced down and hauled to the processing plant. Unlike other areas, the Gulf and South Atlantic shrimp fishery dehead a significant portion of the catch at sea. This is done to minimize degradation of the product and permits extension fishing trips. Also, the breaded shrimp industry pays a higher price for deheaded shrimp

due to certain types of machinery that can only handle this type of product. In a few instances, heads-on shrimp are brought to the unloading point where they are deheaded prior to being loaded onto the truck, for transport to the processing plants. In the New England area, the shrimp are delivered fresh daily to the processing plant, heads on. At the plant dock they are inspected and foreign material is removed; then they are weighed and iced.

Fig. 3. Gulf and East Coast Shrimp Canning Process



Wastes Generated

Jensen (1965) estimated that 78 to 85 percent of the shrimp is wasted in mechanical peeling. Using a value of 80 percent, the quantity of shrimp waste generated in Alaska in 1971 was calculated to be 4500 kkg (5000 tons).

Vilbrandt and Abernathy (1930) mentioned that the shrimp heads comprised 43 to 45 percent of the whole raw shrimp. Thus, the estimated total shrimp waste would be reduced to approximately 77,000 kkg (85,000 tons) if all the catch in the Gulf and South Atlantic states were beheaded at sea.

The wastes consists of about 25% protein, 50% chitin and 25% calcium carbonate.

Tuna

The four main tuna species of interest to the tuna processors are the yellow fin (Neothunus macropterus), blue fin (Thunnus thynnus), skipjack (Katsuwonus pelamis), and Albacore (Thunnus germo). These species are divided into the white meat variety, exclusively Albacore, of which there is a limited catch, and the light meat varieties of blue fin, yellow fin and skipjack, the latter two of which comprise the majority of the tuna canned in the United States. White meat tuna is considered the "premium" product of the industry, because of its characteristically white color, firm texture and delicate flavor as compared with the darker, fuller flavored light meat.

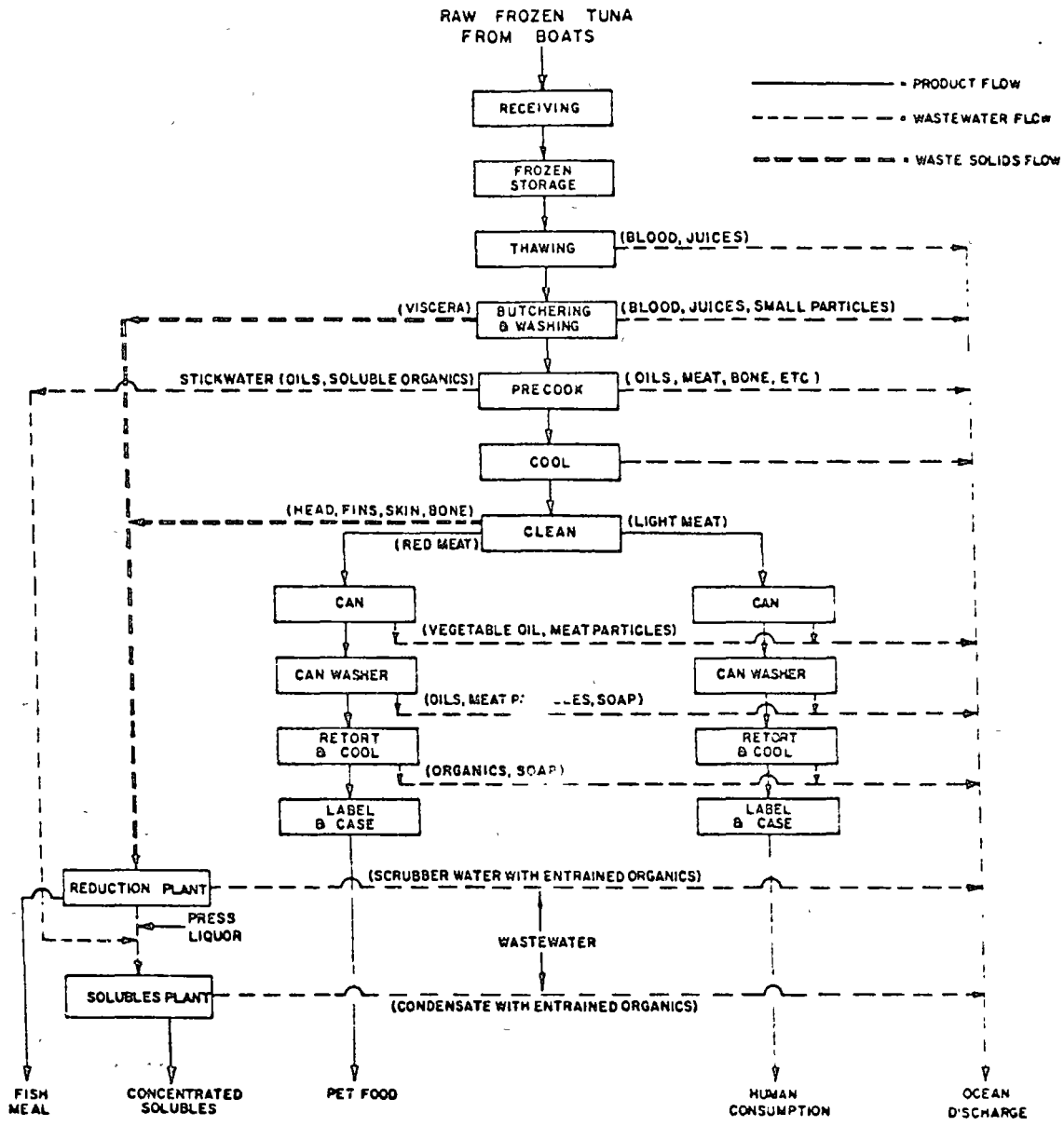
Harvesting with pole and line has given way in the past 20 years to the use of the purse seiner, which permits the catching of a large volume of fish in about one-fourth the time. (Albacore are primarily harvested with pole and line because they don't school). After locating a school of tuna, the fish are encircled with a large net which is then drawn closed at the bottom. The fish are subsequently crowded together and dipped out of the enclosure into the hold of the boat. Fish harvested locally, i.e., near the processor, are held in refrigerated cargo holds or wells in the ship.

The processing of tuna is divided into several unit processes, specifically; receiving, thawing, butchering, precook, cleaning, canning, retorting, and finally, labeling and casing. Product flow, wastewater flow, pet food production, and waste utilization is shown schematically in Figure 4.

The tuna are precooked to favilitate the removal of edible from inedible portions. The pre-cook process involves 3 main steps: 1) the steam cooking of the fish, 2) removal of the steam condensate or "stickwater," and 3) the cooling of the fish prior to cleaning.

No part of the tuna which enters the processing plant is regarded as waste by the industry.

Fig. 4. Tuna Process



Waste Characterization

Various summaries are provided depicting the raw waste loodings and average flows. Table 4,5,6, respectively provides process summaries for catfish, mechanized blue crab, shrimp and tuna processing.

Table 4. Catfish Process Summary (5 plants)

Parameter	Mean	Standard Deviation	Coefficient of Variation (% of mean)	Range
Flow Rate, cu m/day[1]	109	43	39	42 - 153
(mgd)	(0.029)	(0.011)	39	(0.011- 0.0
Flow Ratio, l/kkg[2]	19,000	7,000	32	12,000 - 29,000
(gal/ton)	(4600)	(1700)	32	(2900 - 6900)
Settleable Solids, ml/l	0.6	0.4	59	0.3 - 1.2
Settleable Solids Ratio, l/kkg	10.6	10.2	96	1.6 - 27.6
Screened Solids[3], mg/l	305	179.8	59	117.9 - 476.6
Screened Solids Ratio, kg/kkg	6.7	3.4	50	3.5 - 10.2
Suspended Solids, mg/l	445	204	46	274 - 756
Suspended Solids Ratio, kg/kkg	8.3	4.2	51	3.3 - 12.9
5 day BOD[4], mg/l	511	152	30	212 - 1006
5 day BOD Ratio, kg/kkg	8.3	5.3	63	5.0 - 16.2
20 day BOD, mg/l	--	--	--	-- - --
20 day BOD Ratio, kg/kkg	--	--	--	-- - --
COD, mg/l	891	432	48	496 - 1600
COD Ratio, kg/kkg	15.5	6.1	40	10.2 - 25.7
Grease and Oil, mg/l	257	121	47	114 - 448
Grease and Oil Ratio, kg/kkg	4.5	2.0	44	2.9 - 7.2
Organic Nitrogen[4], mg/l	32.7	12.3	38	20.7 - 49.8
Organic Nitrogen Ratio, kg/kkg	0.5	0.2	31	0.3 - 0.8
Ammonia-N[4], mg/l	0.8	0.4	52	0.5 - 1.4
Ammonia-N Ratio, kg/kkg	0.01	0.007	53	0.006 - 0.0
pH[5]	6.4	0.6	9	5.8 - 7.0

1 day = 8 hrs
2 weight of raw product
3 based on three observations
4 based on four observations
5 laboratory pH

Table 5. Mechanized Blue Crab Process Summary
(2 plants)

Parameter	Mean	Range
Flow Rate, cu m/day[1] (mgd)	178 (0.047)	76 - 279 (0.020 - 0.073)
Flow Ratio, l/kkg[2] (gal/ton)	36,900 (8860)	29,000 - 44,900 (6960 - 10760)
Settleable Solids, ml/l	2.5	2.4 - 2.6
Settleable Solids Ratio, l/kkg	92	77 - 107
Screened Solids, mg/l	--	-- - --
Screened Solids Ratio, kg/kkg	--	-- - --
Suspended Solids, mg/l	331	398 - 496
Suspended Solids Ratio, kg/kkg	11.7	11.5 - 22.3
5 day BOD, mg/l	650	496 - 796
5 day BOD Ratio, kg/kkg	22.7	22.3 - 23.0
20 day BOD, mg/l	--	-- - --
20 day BOD Ratio, kg/kkg	--	-- - --
COD, mg/l	1040	644 - 1450
COD Ratio, kg/kkg	34	29 - 42
Grease and Oil, mg/l	150	147 - 154
Grease and Oil Ratio, kg/kkg	5.6	4.3 - 6.9
Organic Nitrogen, mg/l	107	61 - 153
Organic Nitrogen Ratio, kg/kkg	3.6	2.7 - 4.4
Ammonia-N, mg/l	5.8	3.5 - 8.3
Ammonia-N Ratio, kg/kkg	0.2	0.16 - 0.24
pH[3]	7.0	6.8 - 7.2

1 day = 8 hrs
2 weight of raw product
3 laboratory pH

Table 6. Gulf Shrimp Canning Process Summary (4 plants)

Parameter	Mean	Standard Deviation	Coefficient of Variation (% of mean)	Range
Flow Rate, cu m/day[1]	788	927	12	695 - 905
(mgd)	(0.208)	(0.0245)	12	(0.184 - 0.239)
Flow Ratio, l/kkg[2]	46,900	9800	21	33,000 - 57,000
(gal/ton)	(11,000)	(2350)	21	(7900 - 14,000)
Settleable Solids, ml/l	13.9	5.3	38	5.4 - 31
Settleable Solids Ratio, l/kkg	520	470	90	184 - 978
Screened Solids, mg/l	--	--	--	-- - --
Screened Solids Ratio, kg/kkg	--	--	--	-- - --
Suspended Solids, mg/l	802	459	57	483 - 1100
Suspended Solids Ratio, kg/kkg	37.7	15.2	40	15.9 - 50.1
5 day BOD, mg/l[3]	1081	216	20	1008 - 1432
5 day BOD Ratio, kg/kkg	46	--	--	43 - 61
20 day BOD, mg/l	--	-	--	-- - --
20 day BOD Ratio, kg/kkg	--	--	--	-- - --
COD, mg/l	2296	653	28	1975 - 2658
COD Ratio, kg/kkg	109	20	18	86 - 122
Grease and Oil, mg/l	358	169	66	148 - 759
Grease and Oil Ratio, kg/kkg	11.0	9.8	88	5.4 - 36.4
Organic Nitrogen, mg/l	196	62	32	39 - 293
Organic Nitrogen Ratio, kg/kkg	7.6	7.7	102	1.9 - 13.4
Ammonia-N, mg/l	12	5.4	46	7 - 14
Ammonia-N Ratio, kg/kkg	0.51	0.12	24	0.22 - 0.47
pH[4]	6.7	--	--	6.5 - 7.0

1 day = 8 hrs
2 weight of raw product
3 based on one plant
4 laboratory pH

Table 7. Tuna Process Summary (9 plants)

Parameter	Mean	Standard Deviation	Coefficient of Variation (% of mean)	Range
Flow Rate, cu m/day[1]	3060	3370	11[illegible]	246 - 11,700
(mgd)	(0.808)	--	--	(0.065 - 3.1)
Flow Ratio, l/kkg[2]	18,290	9023	4[illegible]	5570 - 33,000
(gal/ton)	(4386)	--	--	(1336 - 7914)
Settleable Solids, ml/l	2.1	1.8	8[illegible]	0.2 - 5.9
Settleable Solids Ratio, l/kkg	29.0	15.5	5[illegible]	6.9 - 50.1
Screened Solids[3], mg/l[4]	63.5	--	--	-- - --
Screened Solids Ratio, kg/kkg	1.3	--	--	-- - --
Suspended Solids, mg/l	670	763.7	10[illegible]	357 - 1769
Suspended Solids Ratio, kg/kkg	10.1	4.5	4[illegible]	3.8 - 17.3
5 day BOD, mg/l	939	692	7[illegible]	421 - 2510
5 day BOD Ratio, kg/kkg	13.0	4.1	3[illegible]	6.8 - 19.9
20 day BOD, mg/l	--	--	--	-- - --
20 day BOD Ratio, kg/kkg	--	--	--	-- - --
COD, mg/l	2210	939.9	4[illegible]	1310 - 3940
COD Ratio, kg/kkg	35.[illegible]	15.3	5[illegible]	14.1 - 63.8
Grease and Oil, mg/l	364	207	5[illegible]	130 - 589
Grease and Oil Ratio, kg/kkg	5.78	3.40	5[illegible]	3.20 - 13.18
Organic Nitrogen, mg/l	56.5	25.10	44	30 - 93.8
Organic Nitrogen Ratio, kg/kkg	1.22	0.049	4[illegible]	0.75 - 2.17
Ammonia-N, mg/l	6.9	4.27	6[illegible]	2.2 - 13.[illegible]
Ammonia-N Ratio, kg/kkg	0.119	0.072	6[illegible]	0.02 - 0.23
pH[5]	6.7	0.408	6	6.2 - 7.2

nine plants

1 day = 8 hrs
2 weight of raw product
3 dry weight
4 two samples
5 laboratory pH

Control and Treatment Technology

Treatment control involves: minimizing use of water, recovery of dissolved protein and recovery of solid portions.

Protein Recovery: Several techniques are available for reclaiming protein from the portions of the products now being wasted. The protein can be recovered in the wet form and made into high quality frozen items or it can be recovered as a meal or flour, ranging from tasteless-odorless fish flour to fish meal for animal feed.

1. Conventional Reduction Processes

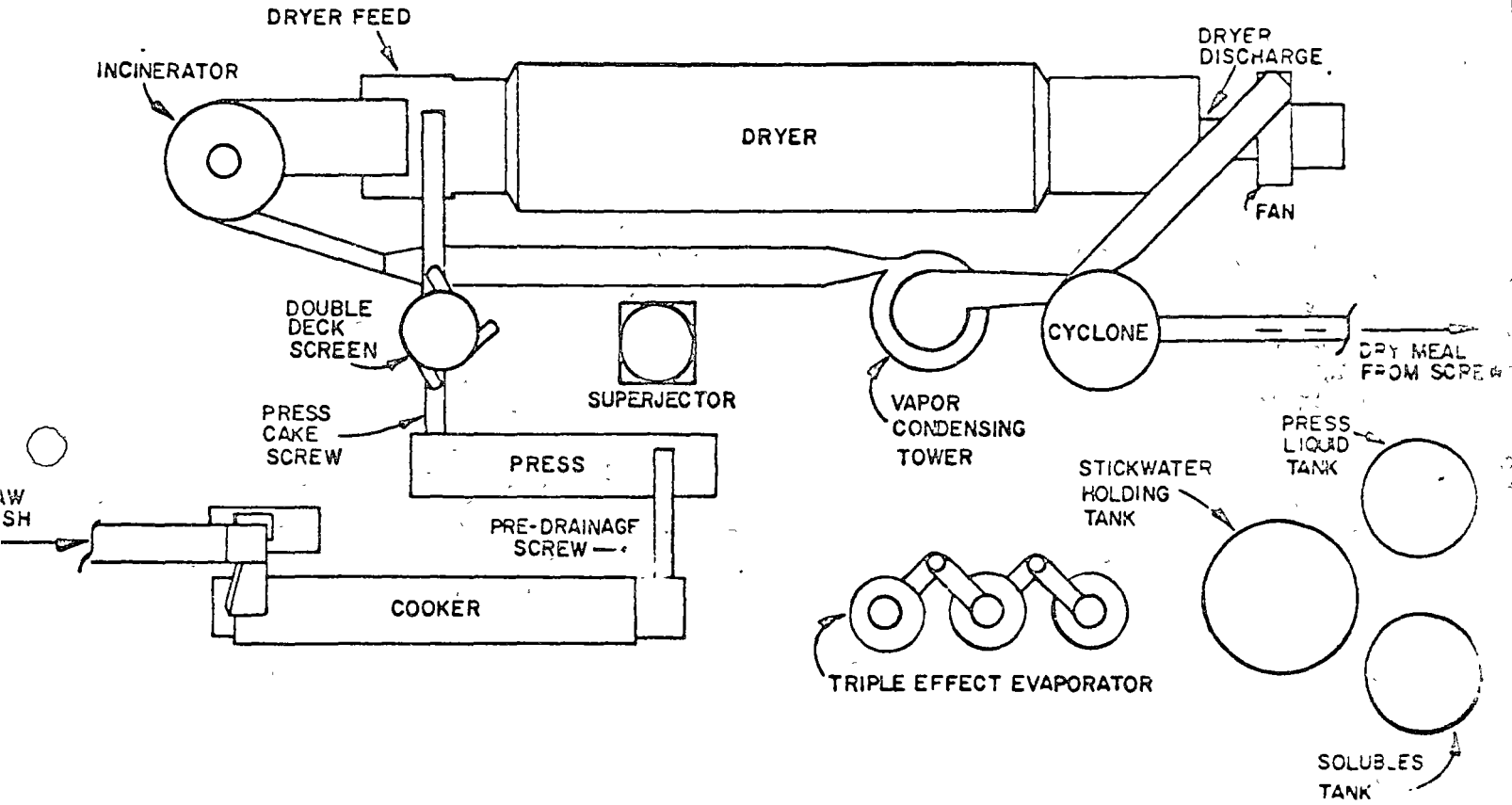
The conventional reduction process for converting whole fish or fish waste to fish meal for animal feed has been used for many years.

Since the batch process does not remove any oil from the fish, the process makes a rather undesirable product from oily fish. In this case the continuous or semi-continuous equipment should be used whereby the cooked fish is pressed to remove some of the oil. This approximately doubles the cost of a small plant.

Another drawback to a conventional meal plant is the odor caused by the drier. In areas where large processing plants are located, the odor problem has never been solved. Scrubbing has been the most sucessful technique, but is expensive. Air from the drier is frequently introduced into the furnace supplying heat to the dryer, where the temperature is approximately 760°C (1400°F), thus partially burning the malodorous materials left in the process air. This air is then exhausted but where there are many reduction plants the cumulative effect, even under the best control conditions, is quite obnoxious.

Of the catagories currently under consideration, only large tuna plants, such as those in Terminal Island, California and Puerto Rico have sufficient waste material to justify continuous meal plants with the required odor control and stickwater processing facilities (Figure 5) where operating costs can be as low as $66 to $88 per kkg ($60 to $80 per ton) since the small batch plants do not press the cooked fish to remove oil and the resulting product has an extremely high oil content. The oil content is the limiting factor in adding fish meal to an animal feed ration. The limit for conventional fish meal is 15% of the ration. More oily meals must be restricted to a lower level because the oil flavor is carried over into the flesh of the animal.

Figure 5. Continuous Fish Reduction Plant
With Soluble Recovery and Odor Control

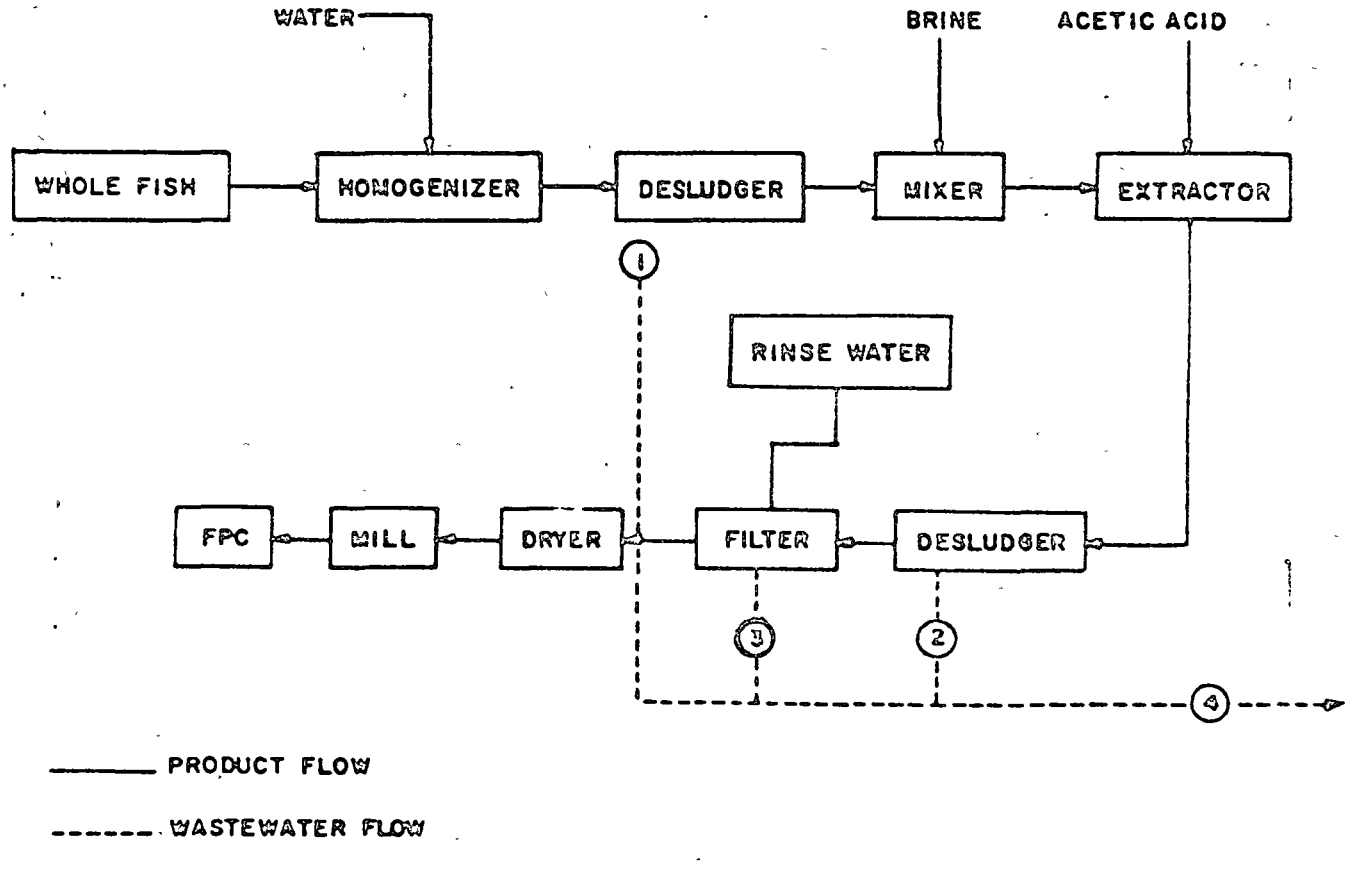


2. Aqueous Extraction

The only way that protein waste can be processed into a high grade flour for human consumption is to remove the oil from the product, thus preventing the development of rancid flavor and odor. A recent development has involved changing from an organic solvent to salt water or brine (Chu, 1974). The first phase of this process can be carried out in small as well as large processing plants with no highly skilled plant operators required. In order to be practical for commercialization, this process should be capable of handling any portion of fish scrap as well as whole industrial fish. This would make the process applicable to low grade fertilizer products, high grade animal feed and fish protein concentrate for human consumption. The process should also require only the low cost facilities avalilble to small companies. It should, furthermore, not require highly trained operating personnel and should not produce a waste that will contribute to the pollution problem.

Figure 6 shows the general brine-acid process used for treating the fish waste or raw fish which is presently being sutdied on a pilot plant scale. The material is ground and homogenized in various concentrations of water or brine and hydrochloric acid. The sodium chloride tends to decrease the solubility of various constituents and the acid minimizes the protein solubility. After varying incubation times the material is then centrifuged so that the lipid and water fractions separate from the solid residue. For animal feed this solid sresidue can then be dried and ground to the necessary particle size. Further washing and extracting is necessary if it is to be used for human consumption.

Figure 6. Brine Acid Extraction Process

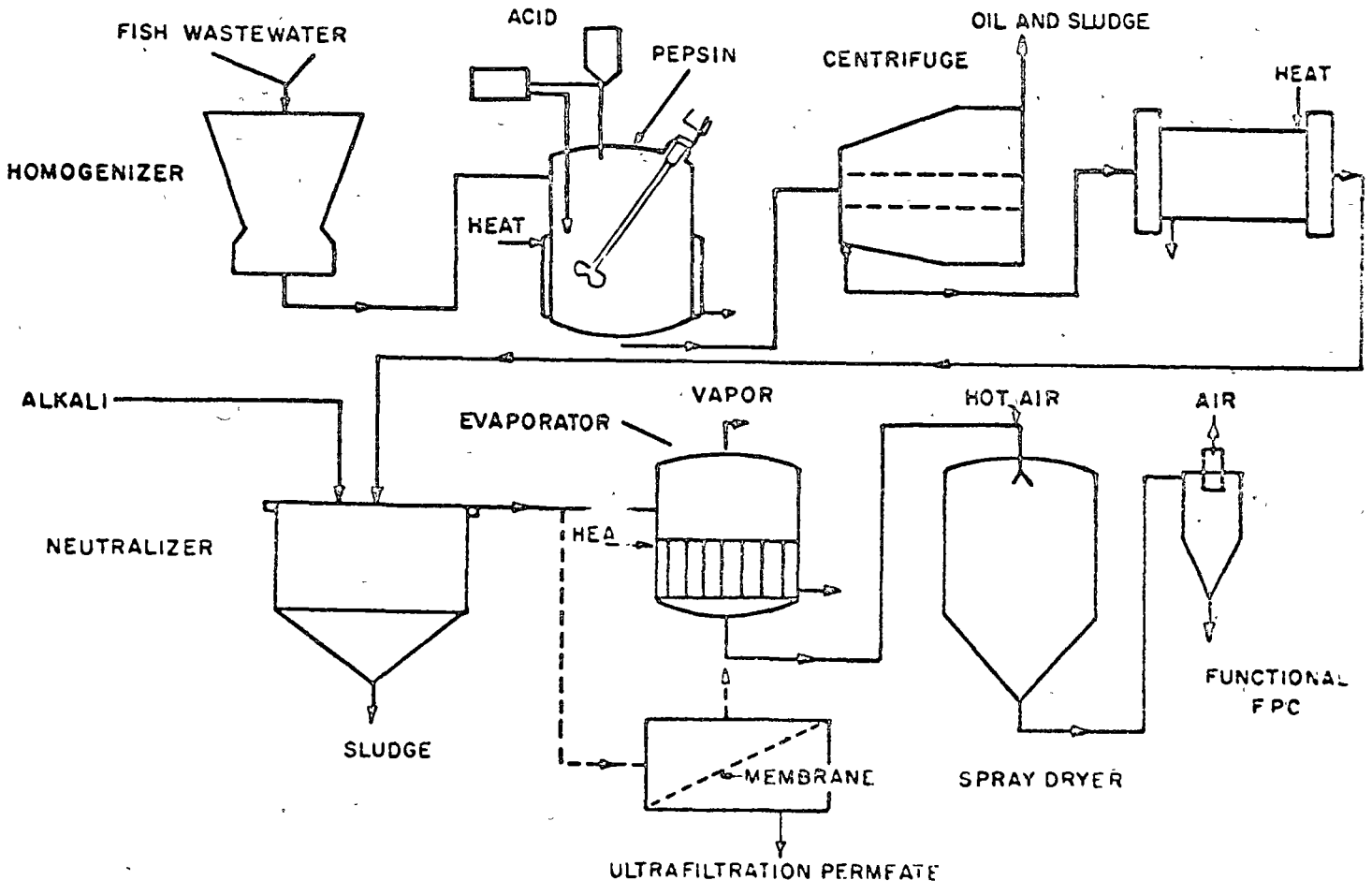


3. Enzymatic Hydrolysis Process

The use of enzymes to hydrolyze fish protein has been reported by several laboratories. Tryptic digestive enzymes, pepsin hydrolysis, papain, and many other enzymatic processes have been tried in an effort to produce a highly functional protein concentrate. In general, pepsin digestion with continuous pH control at 2.0 has proven to be one of the best procedures for producing a high quality bacteria-free product (Tarky and Pigott, 1973).

The basic procedure consists of adding pepsin to a homogenized fish waste substrate to which equal volumes of water have been added. The pH is lowered to 2.0 with hydrochloric acid and the mixture is then continuously stirred at 37°C (99°F). In general, this procedure yields about 12 percent product based on the raw material. The product has essentially no fat content and, when spray dried, is a highly functional powder which is low in only tryptophan. However, when added to vegetable proteins having sufficient tryptophan, the total protein is extremely high in quality. The material is cheaper to produce than milk [current estimate, 40 to 55 cents/kg (18 to 25 cents/lb)] and equal or better in protein value when added as a supplement. The process flow sheet is shown in Figure 7.

Figure 7. Enzymatic Hydrolysis of Solid Wastes



4. Protein Precipitation from Effluent Streams

Laboratory work has shown protein to be recoverable almost stoichiometrically by precipitation with sodium hexametaphosphate. The protein-phospate complex is highly nutritional and can be used as a high grade animal supplement.

5. Waste Treatment Techniques

Little of the technology which could be available to the seafood processing industry has been demonstrated at the operational level. Most of the processors have little if any significant wastewater treatment at the plant.

All of the subcategories produce large volumes of solids. Fish and shellfish solids in the waste streams have commercial value as by-products only if they can be collected prior to significant decomposition, economically transported to the subsequent processing location, and marketed. The importance of capturing such solids in dry form, in order to retard biochemical degradation, has been recognized by the processors and discussed in an earlier part of this section. Many end-of-pipe systems generate further waste solids ranging from dry ash to putrescible sludges containing 98 to 99.5 percent water.

Screening is practiced, in varying degrees, throughout the crab, shrimp, catfish, and tuna industries for solids recovery, where such solids have marketable value, and to prevent waste solids from entering receiving waters or municipal sewers. Vibratory screens are more commonly used in the seafood industry for processing operations rather than wastewater treatment. Tangential screens are finding increasing acceptance because of their inherent simplicity, reliability and effectiveness.

Disposal and wastewater treatment methods are not well established. Incineration of seafood solid wastes has not been tried in the catfish, crab, shrimp, or tuna industries. Where allowed and where land is available, private landfills may be a practical method of ultimate disposal. Deep sea disposal of fish wastes can be a means of recycling nutrients to the ocean. This method of disposal does not subject the marine environment to the potential hazards of toxicity and pathogens associated with the dumping of human sewage sludges, municipal refuse and many industrial wastes. The disposal of seafood wastes in deep water or in areas subject to strong tidal flushing can be a practical and possibly beneficial method of ultimate disposal. In some locations, the entire waste flow could be ground and pumped to a dispersal site in deep water without adverse effects. The U. S. Congress recognized the unique status of seafood wastes when, in 1972, they specifically exempted fish and shellfish processing wastes from the blanket moratorium on ocean dumping contained in the so-called "Ocean Dumping Act".

Wastewater treatment technology to treat practically any effluent to any degree of purity is available. The cost-effectiveness of a specific technology depends in part on the contaminants to be removed, the level of removal required, the scale of the operation, and (importantly) on local factors, including site availability and climate. Because these factors vary widely among individual plants in the catfish, crab, shrimp, and tuna industries, it is difficulty to attempt to identify a technology which may prove superior to all others, within an industrial subcategory.

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METAL FINISHING WASTES AND METAL PROCESSING WASTE TREATMENT

E. F. Gloyna

Wastes from plants manufacturing finished metal products may contain significant amounts of oil, other organic constituents and a variety of inorganic materials. Frequently the metals are relatively toxic to aquatic organisms.

Treatment Plant Design for any particular waste problem is based on the following considerations:

1. Volume of waste - including variations in flow.
2. Load of contaminants - including variation in concentrations.
3. Physical and chemical characteristics of the waste.
4. Regulatory agency requirements.
5. Factory layout and its effect on ease of collection of wastes.
6. Separation of industrial wastes from storm or cooling waters and from domestic sewage.
7. Dilution available from plant process and cooling waters following treatment and from receiving stream.
8. Possibility of pretreatment at source.
9. Wastes that can neutralize each other.
10. Cost and availability of chemicals.
11. Recoverable products for reuse.
12. Space available for treatment plant facilities.
13. Land requirements for sludge disposal.
14. Availability of equipment that can be used or modified for use.
15. Ventilation.
16. Maintenance costs.
17. Operating costs.

Selection of Batch or Continuous Treatment

Metal-finishing industry wastes may be treated on a continuous flow basis or collected in tanks and treated by batch operation. The selection of the method to be used in any plant requires consideration of the volumes of wastes to be handled, strength of the waste, type of treatment, and quality of the waste effluent desired as well as area restrictions within the plant.

Cyanide Plating Waste Treatment

Cyanide compounds are widely used in the metal finishing industry in the preparation of plating baths. Cyanide is commonly used in the preparation of zinc, copper, cadmium, gold, silver, bronze, and brass plating solutions, and often as a cleaning solution immediately prior to a plating process. A small quantity of this highly toxic solution will be dragged out of the plating bath as each part is removed and rinsed prior to the next plating operation. The rinse water will also contain cyanide. The problem is to safely dispose of cyanide without creating a water pollution hazard.

Under acidic conditions cyanide will hydrolyze to form the toxic HCN. The proportion of HCN present will depend on the hydrogen ion concentration according to the relationship:

$$\frac{CN^-}{HCN} = \frac{K_a}{H^+} = \frac{7.2 \times 10^{-10}}{H^+} \text{ at } 25^oC$$

Lagooning of cyanide waste will reduce the cyanide to ammonium formate and Asulmic acid

$$HCN + 2H_2O = HCOONH_4$$

Aerobic biological treatment processes can oxidize cyanide providing the concentration is below toxic limits and the system has been acclimated. The toxic effects of cyanide on various forms of biological life are summarized in Table 1.

Table 1

Toxic Effects of Cyanide

Subject	Toxic Concentration	Remarks
1. Sunfish	0.18	Conc. killing 50% of fish in 24 hrs
2. Daphinia	1.8	Conc. immobilizing 50% of organisms in 48 hrs
3. BOD	0.04	95% recovery
	0.4	60% recovery
4. Sludge Digestion	25	No adverse effect in 24 days
		3 ppm initial retarding effect for 6 days
	50	10% reduction in gas production

Collection: Sewers should be constructed so that only cyanide wastes are discharged to the treatment system. Treatment for other plating room chemicals are not usually compatible with the methods used for the destruction of cyanide wastes. Where large quantities of cyanide are used, it is usually necessary to

install separate sewers for dilute and concentrated cyanide wastes. A dual collection system will permit concentrated wastes to be collected and pumped at a controlled rate to the cyanide treatment system.

If separate collection system is not employed, the capacity of the chemical feed system will probably be exceeded during periods of slug charges.

Treatment: Cyanide wastes can be destroyed by oxidation processes to form carbon dioxide and nitrogen. Among the most widely recognized oxidation methods employed are (1) biological; (2) electrolytic; (3) incineration; (4) radiation; and (5) chemical.

Biological treatment--Cyanides can be destroyed in combination with domestic sewage through such biological means as the activated sludge or trickling filter processes. Sewage provides the required nutrients for the process, and a biological culture will be produced capable of approximately 99 per cent cyanide removal.

However, this process cannot tolerate the discharge of slug dosages of concentrated cyanides. Also, the biological population must receive necessary nutrients for growth as provided by domestic sewage. If sewage is not available, the required nutrients must be artificially added to sustain the biological population.

1. Electrolytic destruction: This method of cyanide destruction requires long periods of time--2 to 7 days--to reduce cyanide to a 1-ppm level. The anode used in this process can be copper, stainless steel or carbon steel. However, a current density from 30 to 80 amps/ft^2 must be maintained. The cathode employed can be made of carbon steel. Optimum operating temperature for this destruction process is approximately 200 F (93 C).

2. Incineration: Waste cyanide can be blended with an oil mixture and incinerated at approximately 2500 F.

3. Radiation: Cyanide solutions can be decomposed by radiation processes. Cyanide can be decomposed to within 90-95 per cent completion without excessive radiation dosages. However, to obtain further decomposition markedly higher radiation dosages are required. A solution containing 2 grams per liter of a zinc cyanide-sodium cyanide complex requires 83.6×10^6 rads for 95 per cent decomposition.

4. Chemical: The alkaline chlorination oxidation process is the most widely used process for the destruction of cyanide. The oxidation of cyanide by chlorination occurs by two separate and major chemical reactions. In the first stage cyanide is oxidized to cyanate; in the second stage cyanate is

oxidized to cyanate and nitrogen. The first stage of the oxidation can be illustrated by the following equations:

$$2Cl_2 + 2NaCN \longrightarrow 2CNCl + 2NaCl$$

$$2CNCl + 4NaOH \longrightarrow 2NaCNO + 2NaCl + 2H_2O$$

The first reaction is instantaneous and occurs at all pH levels, while the second is one of hydrolysis which converts cyanogen chloride to cyanate and is dependent upon pH. The hydrolysis reaction will not go to completion at pH levels of less than 7.5, but the hydrolysis rate will increase as the pH increases. At a pH of 9.0 the reaction will be completed in approximately 3 minutes. It is important that the hydrolysis of cyanogen chloride to cyanate be completed as rapidly as possible since cyanogen chloride is both volatile and toxic.

The second major stage of chemical destruction is the oxidation of the cyanate obtained in the first stage to carbon dioxide and nitrogen.

$$3Cl_2 + 4H_2O + 2NaCNO \longrightarrow$$

$$3Cl_2 + (NH_4)_2CO_3 + Na_2CO_3$$

$$3Cl_2 + 6NaOH + (NH_4)_2CO_3 + Na_2CO_3 \longrightarrow$$

$$2NaHCO_3 + N_2 + 6NaCl + 6H_2O$$

These reactions require an excess of chlorine and caustic. The rate of the reaction will increase as the pH of the solution decreases.

Because a pH level greater than 9.0 is required for the first stage oxidation (of cyanide to cyanate), and a pH of approximately 8.5 is required for the second stage oxidation of the cyanate, it is convenient to perform the oxidation in two separate processes. The prime difficulty in using a single chlorination step process is that a compromise pH condition must be selected and there will be a tendency to have both stages of the oxidation occurring simultaneously.

When solution pH is too low, there will be a tendency for carbon dioxide and nitrogen gases to be formed in the presence of cyanogen chloride, due to the incomplete hydrolysis to cyanate. Nitrogen gas will be swept out of solution, carrying cyanogen chloride with it, and creating a hazardous condition in the immediate work area.

If solution pH is too high, the oxidation of the cyanate will require excessively long detention periods and may never go to completion.

The alkaline chlorination process lends itself conveniently to automatic control. A system can be installed to maintain the required pH level conditions by controlling the addition of caustic. An ORP (Oxidation Reduction Potential) system can be used to control the addition of chlorine. With a properly designed and operated plant it is possible to maintain about a 10-ppm excess chlorine residual in the final effluent.

Treatment System: The configuration and size of a treatment system will, of course, be dictated by local conditions. Figure 1 shows a schematic diagram for a typical batch type treatment process; Fig. 2 shows a flow-through type treatment process.

Even though Fig. 1 shows only one treatment tank in the batch type system, a well designed treatment plant will normally contain three tanks. One tank will be filling, the second tank treating influent contaminants, and the third tank discharging. A treatment plant designed in this manner allows maximum flexibility for nearly all situations which could arise.

The treatment plant should also provide for a means for the effluent to be discharged into a solids removal system. Final effluent of the treatment plant will normally contain toxic heavy metals employed in the plating processes which normally must be removed to comply with state and local regulations.

Example of Alkaline Chlorination Process:

1. Chemical Reactions: Alkaline Chlorination Process

   a. CN^- oxidized to CN^+:

   $$CN^- + Cl_2 \longrightarrow CNCl + Cl^-$$
   $$26 \quad 71 \quad 61.5$$

   b. Formation of Cyanate

   $$CNCl + 2NaOH \xrightarrow[30\ min.]{pH\ 8.5} Na\,CNO + H_2O + NaCl$$
   $$61.5 \quad 80 \quad 65$$

   c. Oxidation of Cyanate

   $$2Na\,CNO + 3Cl_2 + 4NaOH \longrightarrow 6NaCl + 2CO_2 + N_2 + 2H_2O$$
   $$130 \quad 213 \quad 160$$

   d. Oxidation of Fe^{++}

   $$2Fe^{++} + Cl_2 \longrightarrow 2Fe^{+++} + 2Cl^-$$
   $$111.2 \quad 71$$

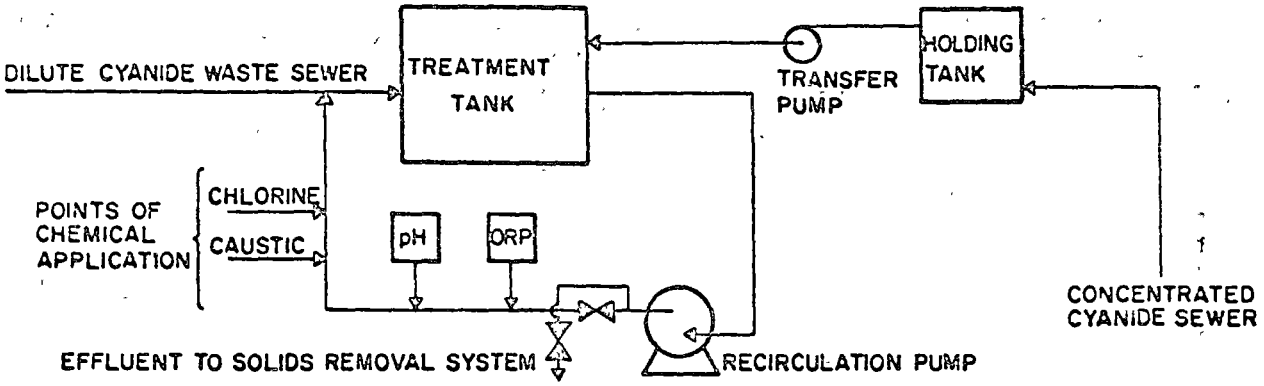

FIG. 1. SHOWN IS A TYPICAL SCHEMATIC DIAGRAM FOR A BATCH TYPE TREATMENT PROCESS FOR DESTROYING CYANIDE WASTES.

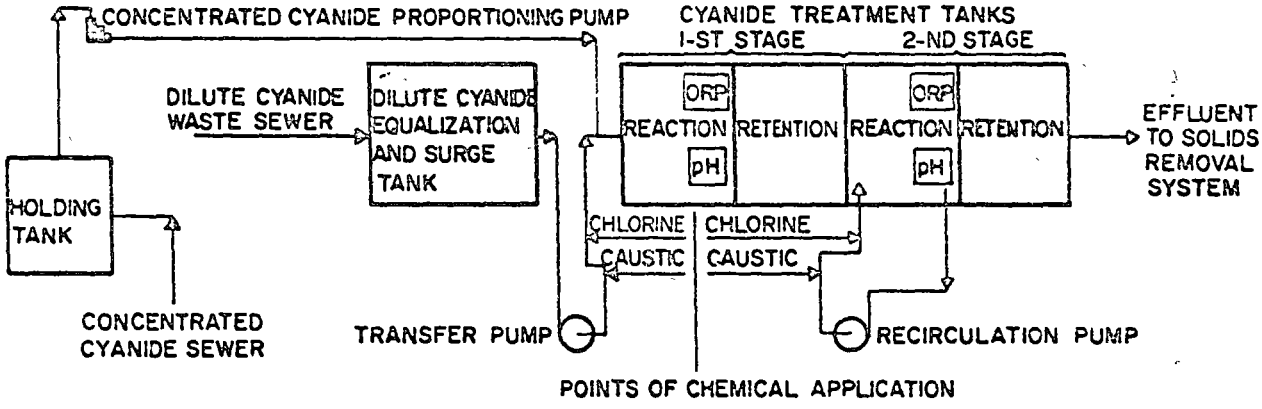

FIG. 2. CYANIDE WASTES CAN ALSO BE TREATED BY THE FLOW THRU TYPE PROCESS AS SHOWN IN THE SCHEMATIC DIAGRAM.

e. Precipitation of Iron

$$Fe^{+++} + 3NaOH \longrightarrow Fe(OH)_3 + 3Na^+$$

55.6 120 106.6

f. Precipitation of Cu

$$Cu^{++} + 2NaOH \longrightarrow Cu(OH)_2 + 2Na^+$$

63.5 80 97.5

2. Calc. Solubility of $Cu(OH)_2$ & $Fe(OH)_3$.

a. $Cu(OH)_2$ Ph = 8.5

$k_{sp} = 5.6 \times 10^{-20} = [Cu^{++}] \cdot [OH^-]^2$

$\log_{10} k_{sp} = \log [Cu^{++}] + 2 \log [OH^-]$

$pk_{sp} = - \log k_{sp} = 19.25$

$\log k_{sp} = -19.25$

pH = 8.5 pOH = 5.5 = -log $[OH^-]$

$\log [OH^-] = -5.5$

$\log [Cu^{++}] = -2 \log [OH^-] + \log k_{sp}$

$= -2 (-5.5) + (-19.25)$

$\log [Cu^{++}] = 11.00 - 19.25 = -8.25$

$\log [Cu^{++}] = 0.75 - 9$

$[Cu^{++}] = 5.6 \times 10^{-9} \frac{\text{moles}}{1}$

$$\text{Solubility} = \frac{5.6 \times 10^{-9} \text{ moles}}{1} \cdot \frac{63.54 \text{ g}}{\text{mole}} \cdot \frac{1000 \text{ mg}}{\text{g}}$$

Solubility = $3.5 \times 10^{-4} \frac{\text{mg}}{1}$ @ pH 8.5

Very Insoluble

b. $Fe(OH)_3$

$k_{sp} = 4 \times 10^{-38}$ $pk_{sp} = 37.4$

$\log k_{sp} = \text{Log} [Fe^{+++}] + 3 \log [OH^-]$

$\log [Fe^{+++}] = 3(5.5) - 37.4 = 20.9$

$\log [Fe^{+++}] = 0.10 - 21$

$[Fe^{+++}] = 1.26 \times 10^{-21} \frac{\text{moles}}{1}$

$$\text{Solubility} = \frac{1.26 \times 10^{-21} \text{ moles}}{1} \quad \frac{55.6 \text{ g}}{\text{mole}} \quad \frac{1000 \text{ g}}{\text{mg}}$$

Solubility = 7×10^{-17} $\frac{mg}{l}$ @ pH 8.5

Very Insoluble

3. Chemicals Required Flow = 15 $\frac{Gal}{min}$ $\frac{60\ min}{hr}$ $\frac{16\ hr}{day}$ = 14,400 $\frac{gal}{day}$

Chlorine

CN^- : 1 mg CN^- requires 7.35 mg Cl_2 ($\frac{Ind.\ Waste}{Trmt.,\ p.\ 132}$)

$\frac{20\ mg\ CN^-}{l}$ $\frac{7.35\ mg\ Cl_2}{mg\ CN}$ = $\frac{147\ mg\ Cl_2}{1\ of\ Flow}$

Fe^{++}: 2 moles Fe^{++} requires 1 mole Cl_2

$\frac{10 mg\ Fe^{++}}{l}$ $\frac{35.5\ mg\ Cl_2}{55.6\ mg\ Fe^{++}}$ = $\frac{6.5\ mg\ Cl}{1\ of\ Flow}$

Daily Dose = $\frac{154\ mg}{l}$ $\frac{0.0144\ MGal}{day}$ $\frac{8.34\ Lb.}{MGal\text{-}mg/l}$ = 18Lb. Cl_2

Available Chlorine 25 Cl_2

Sodium Hydroxide

CN^-: 1 mole CN^- requires 2 Moles NaOH

$\frac{20\ mg\ CN^-}{l}$ $\frac{2(40)\ mg\ NaOH}{26\ mg\ CN^-}$ = $\frac{62\ mg\ NaOH}{1\ of\ Flow}$

Fe^{+++}: 1 Mole Fe^{+++} requires 3 Moles NaOH

$\frac{10\ mg\ Fe^{+++}}{l}$ $\frac{3(40)\ mg\ NaOH}{55.6\ mg\ Fe^{+++}}$ = $\frac{22\ mg\ NaOH}{1\ of\ Flow}$

Cu^{++}: 1 Mole Cu^{++} requires 2 Moles NaOH

$\frac{8\ mg\ Cu^{++}}{l}$ $\frac{2(40)\ mg\ NaOH}{63.5\ mg\ Cu^{++}}$ = $\frac{10\ mg\ NaOH}{1\ of\ Flow}$

Daily Dose = $\frac{(62 + 22 + 10)\ mg}{l}$ $\frac{0.0144\ MGal}{Day}$ $\frac{8.34\ Lb}{MGal\text{-}mg/l}$

Daily Dose = 11 Lb. of NaOH (100%)

4. Sludge Produced

Weight

$Fe(OH)_3$: $\frac{10\ mg\ Fe^{+++}}{l}$ $\frac{106.6\ mg\ Fe(OH)_3}{55.6\ mg\ Fe^{+++}}$ $\frac{0.0144\ MGal}{Day}$ $\frac{8.34\ Lb.}{MGal\text{-}mg/l}$ =

2.3 Lb./Day (Dry Wgt)

$Cu(OH)_2$: $\frac{8\ mg Cu^{++}}{l}$ $\frac{97.5\ mg\ Cu(OH)_2}{63.5\ mg\ Cu^{++}}$ $\frac{0.0177\ MGal}{Day}$ $\frac{8.34}{MGal\text{-}mg/l}$ =

1.5 Lb./Day (Dry Wgt.)

Volume

Assume sludge concentrates to 1% on bottom of tank.

$$\text{Daily accumulation} = \frac{3.8 \text{ Lb. Solids}}{\text{Day}} \quad \frac{100 \text{ Lb. Sludge}}{1 \text{ Lb. Solids}} =$$

$$380 \frac{\text{Lb Sludge}}{\text{Day}}$$

Assume sludge unit wgt. = 8.34 Lb./Gal

$$\text{Daily Volume} = \frac{380 \text{ Lb/Day}}{8.34 \text{ Lb/Gal}} = 46 \text{ Gal./Day}$$

5. System Components

a. Treatment Tank

(1) $\text{Volume} = 14{,}400 \frac{\text{Gal}}{\text{Day}} \times 1 \text{ Day} = 14{,}400 \text{ Gal.}$

$$\text{Volume} = \frac{14{,}400 \text{ Gal}}{7.48 \text{ Gal/CF}} = 1920 \text{ Ft}^3$$

Set water depth = 10' Surface Area = 192 Ft^2

For square tank Side length = 16'

USE 2 Treatment Tanks, each 16' x 16' x 10'

(2) Mixing, Assume 0.5 HP/1000 Gal. required

HP Required = 14.4 10^3 Gal x 0.5 HP/10^3 Gal = 7.2HP

USE 1 - 7.5 HP Mixer in each Tank

Chromium Treatment by Reduction and Precipitation

Reduction and precipitation is a process whereby a soluble metallic ion is reduced through an oxidation-reduction reaction and then precipitated by conversion to an insoluble metallic hydroxide. The process finds principal application in the treatment of plating wastes containing chromium salts.

Chromium is found in wastes from metal plating and finishing operations. It is present in rinse waters from chromic acid baths and in spent baths from electroplating and anodizing processes. These baths are made up of CrO_3 and $H2SO_4$ or $Na_2Cr_2O_7 \cdot 2H_2O$ and H_2SO_4. They have a pH of 0.5 and a Cr^{+6} concentration of 20,000 ppm (approx.). The acidity in chrome waste waters is proportional to the chromium concentration.

The reducing agents commonly used are ferrous sulfate, sodium metabisulfite or sulfur dioxide.

Ferrous sulfate and sodium metabisulfite may be dry or solution fed while SO_2 is diffused into the system directly from gas cylinders. Since the reduction of chromium is most effective at acidic pH values, a reducing agent with acidic properties is desirable. When ferrous sulfate is used as the reducing agent, the Fe^{++} is oxidized to Fe^{+++} while in the case of metabisulfite or sulfur dioxide the negative radical $SO_3^{=}$ is converted to $SO_4^{=}$.

Ferrous ion reacts with hexavalent chromium in an oxidation reduction reaction, reducing the chromium to a trivalent state and oxidizing the ferrous ion to the ferric state. This reaction occurs rapidly at pH levels less than 3.0. The acidic properties of ferrous sulfate are low at high dilution so that acid must be added for pH adjustment. The use of ferrous sulfate as a reducing agent has the disadvantage that a contaminating sludge of $Fe(OH)_3$ is formed on the addition of an alkali. In order to obtain a complete reaction, an excess dosage of two and one half times the theoretical addition of ferrous sulfate must be made. The reactions are:

$$2\ CrO_3 + H_2O = H_2Cr_2O_7$$

$$2\ H_2CrO_4 + FeSO_4 + 6H_2SO_4 = Cr_2(SO_4)_3 + 3Fe_2(SO_4)_3 + 8H_2O \qquad (1)$$

$$Na_2Cr_2O_7 + 6FeSO_4 + 7H_2SO_4 = Cr_2(SO_4)_3 + 3Fe_2(SO_4)_3 + 7H_2O + Na_2SO_4 \qquad (2)$$

$$Cr_2(SO_4)_3 + 3Ca(OH)_2 = 2Cr(OH)_3 + 3CaSO_4 \qquad (3)$$

$$Fe_2(SO_4)_3 + 3Ca(OH)_2 = 2Fe(OH)_3 + 3CaSO_4 \qquad (4)$$

The oxidation-reduction which occurs is:

$$6Fe^{++} = 6Fe^{+++} + 6e$$

$$Cr_2O_7^{=} + 6e = 2Cr^{+++} + 7H_2O$$

The theoretical quantities of chemical required are:

1 ppm Cr requires	16.03 ppm	$FeSO_4 \cdot 7H_2O$
	6.01 ppm	H_2SO_4
	9.48 ppm	90% lime

The quantity of sludge produced in the reaction is:

1 ppm $FeSO_4 \cdot 7H_2O$ produces	0.38 ppm $Fe(OH)_3$
Lime	1.84 ppm $CaSO_4$
Cr	1.98 ppm $Cr(OH)_3$

Sulfur Dioxide and Metabisulfite

Reduction of chromium can be accomplished using either sodium metabisulfite or SO_2. In either case reduction is accomplished by the H_2SO_3 produced in the reaction.

The H_2SO_3 ionizes according to the reaction:

$$1.72 \times 10^{-2} = \frac{(H^+)\ (HSO3^-)}{H_2SO_3} \qquad (5)$$

above pH 4.0 only 1% of sulfite is present as H_2SO_3 and the reaction is very slow.

When Metabisulfite is used the salt hydrolyzes to sodium bisulfite:

$$Na_2S_2O_5 + H_2O = 2NaHSO_3 \qquad (6)$$

which in turn dissociates:

$$Na^+ + HSO_3^- + H_2O = H_2SO_3 + NaOH \qquad (7)$$

This reaction requires acid to neutralize the NaOH formed during the reaction. The reaction is highly dependent on both pH and temperature. Due to the dependency of ionization of H_2SO_3 on pH excess SO_2 is required. At pH levels below 2.0 the reaction is practically instantaneous at close to the theoretical requirements. Depending on the pH of the reaction, the basicity of the chrome salt produced will vary. At pH values less than 2.0, $Cr_2(SO_4)$ is formed; at pH 3 - 4 $Cr_4(OH)_6(SO_4)_3$ is formed; at pH > 6.5 $Cr(OH)_3$ is formed. At close to theoretical requirements, the reaction time has been reported as follows:

Time for 99% completion min.	pH
0.1	1.0
0.5	1.5
5.0	2.0
30.0	3.0
60.0	4.0
200.0	5.0

The reaction with SO_2 is:

$$2H_2CrO_4 + 3H_2SO_3 = Cr_2(SO_4)_3 + 5H_2O \qquad (8)$$

and the reaction with bisulfite:

$$2H_2CrO_4 + 3NaHSO_3 + 3H_2SO_4 = Cr_2(SO_4)_3 + 3NaHSO_4 + 5H_2O \quad (9)$$

In both cases the precipitation reaction is the same as equation (3). The theoretical quantity of chemicals required is:

1 ppm Cr requires:

2.81 ppm $Na_2S_2O_5$ (97.5%)

1.52 ppm H_2SO_4

2.38 ppm lime (90%)

1.85 ppm SO_2

At pH levels > 3, when a basic chrome sulfate is produced, the quantities of lime required for subsequent neutralization are reduced.

At pH 8.0 - 9.0 $Cr(OH)_3$ is virtually insoluble. Experimental investigations have shown that the sludge produced will compact to 1-2% by weight.

Since dissolved oxygen is usually present in rinse waters, an excess of SO_2 must be added to account for the oxidation of the SO_3 to SO_4.

$$H_2SO_3 + 1/2\ O_2 = H_2SO_4$$

An excess dosage of 35 ppm SO_2 will usually be sufficient for reaction with dissolved oxygen present.

Acid Requirements

The acid requirements for the reduction of Cr^{+6} depend upon the acidity of the original waste, the pH of the reduction reaction, and the type of reducing agent used (e.g. SO_2 produces an acid while metabisulfite does not). Since it is difficult, if not impossible, to predict these requirements, it is usually necessary to titrate a sample to the desired pH end point with standardized acid.

An ingeneous system has been developed by Lancy in which the reduction and precipitation process is integrated into the plating lime. In this process the first tank at the end of the plating lime continuously received SO_2 such that an excess is maintained at all times. The contents of the unit is continuously recirculated through a storage reservoir. The second tank recirculates through a lime mixing tank in which the reduced chrome is precipitated. The precipitate is removed through a diatomite filter and the clarified liquid recirculated through the second treatment tank. A third tank containing a clear water rinse is provided to rinse any residues from the plated parts. This process is schematically shown in Figure 3.

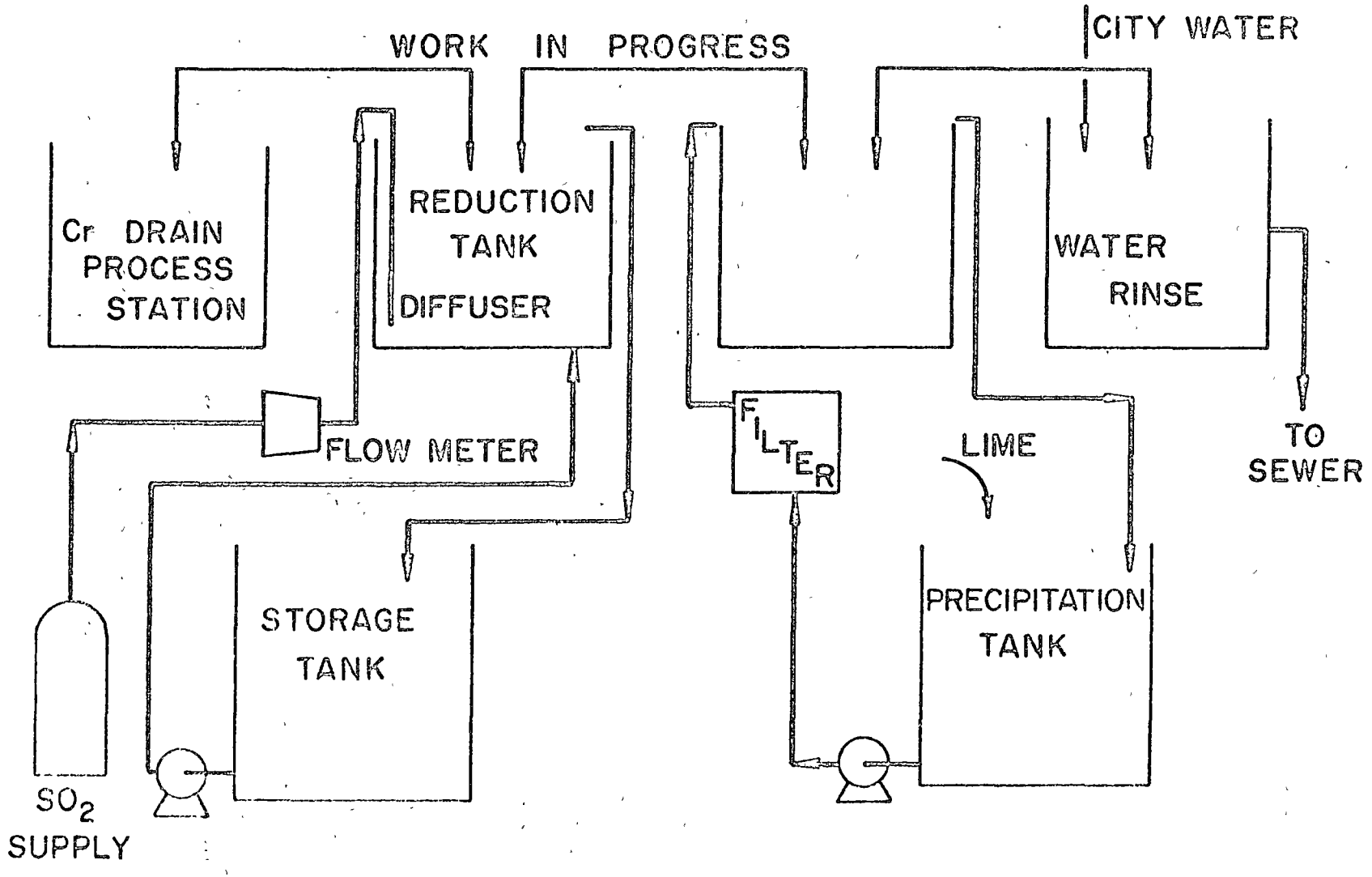

FIG.3. LANCY INTEGRATED SYSTEM.

Figure 4 shows processes which are applicable to mixed chromium and cyanide rinse waters.

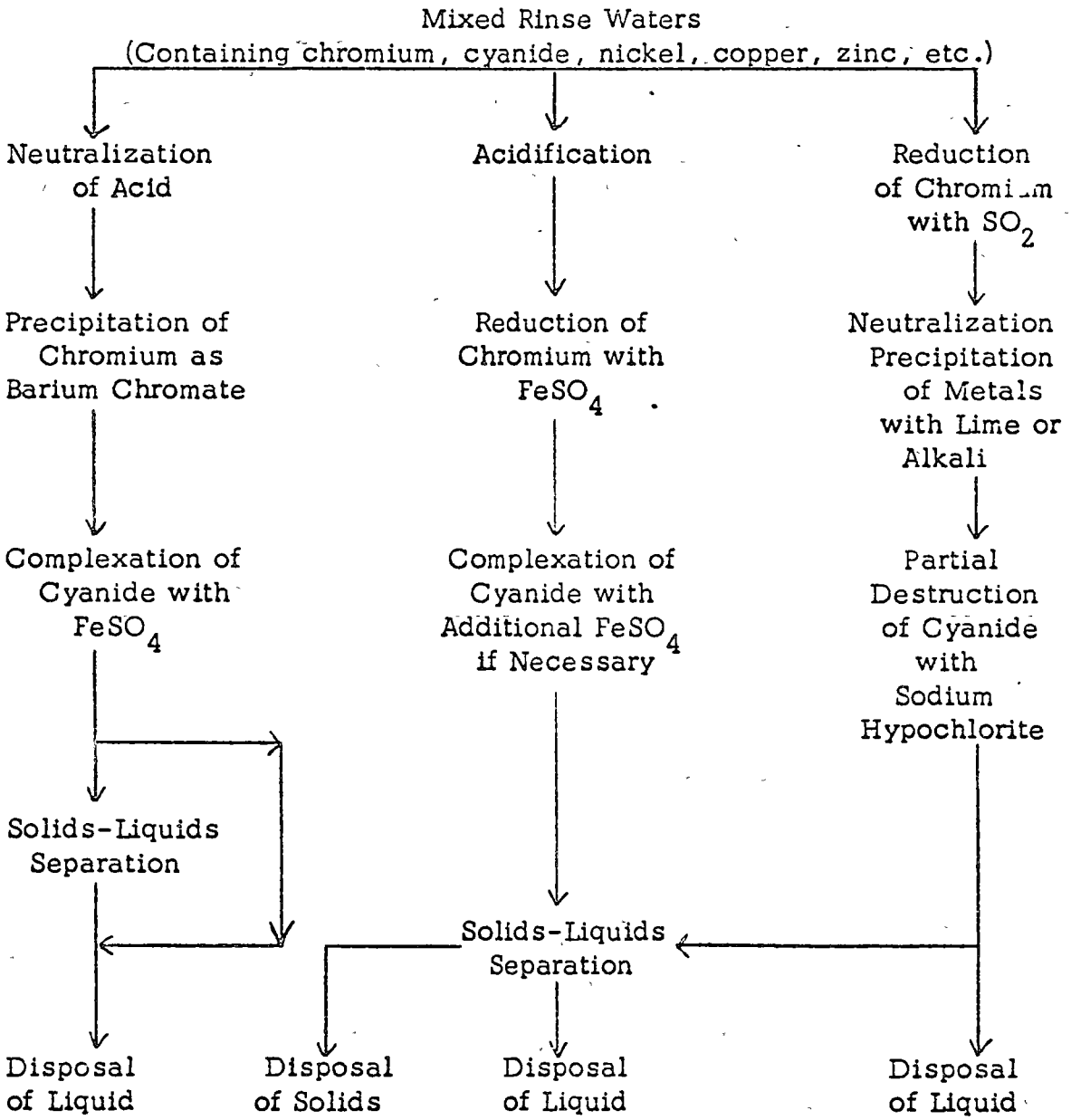

FIG. 4. PROCESSES APPLICABLE TO MIXED CHROMIUM AND CYANIDE RINSE WATERS

In some cases it is easier to remove metal ions, including chromium, through the use of special ion exchange media. Figure 5 shows a flow diagram.

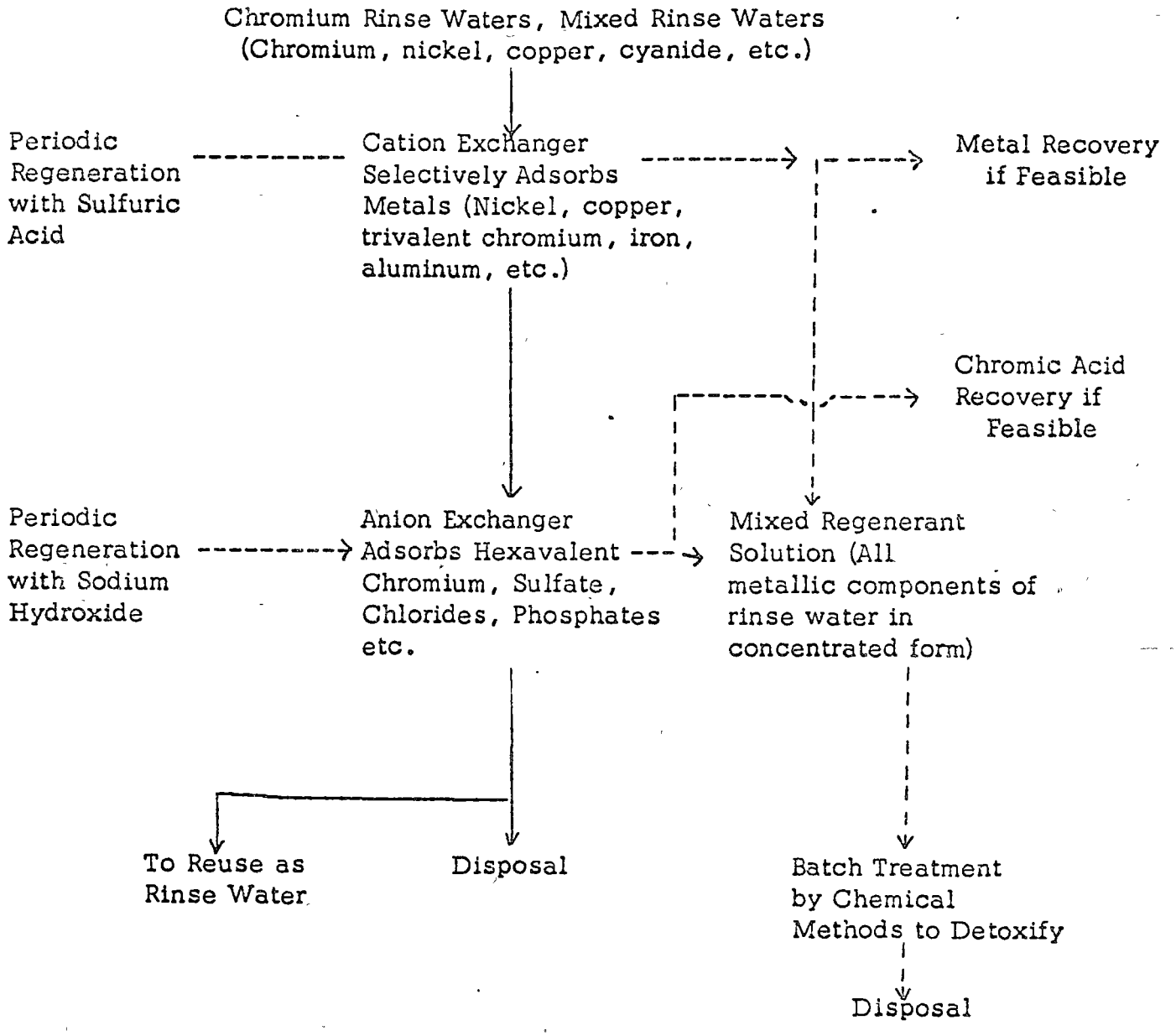

FIG. 5. ION EXCHANGE METHOD OF TREATING CHROMIUM RINSE WATERS OR MIXED RINSE WATERS

A typical cation-anion exchange calculation is as follows:

1. Cation Exchange

Operating Capacity = $1.5 \frac{\text{equiv.}}{1} = 1.5\ (28.3 \frac{1}{CF}) = 42 \frac{\text{eq.}}{CF}$

Regenerant - 5% H_2SO_4, Dosage = 12 lB/Ft^3

Operation:

Cations Removed = (75 gpm) $(\frac{960 \text{ min}}{\text{day}})$ $(\frac{3.781}{\text{gal}})$.

$$(10 \frac{\text{mg Cu}}{1.} \frac{\text{meg.}}{63.54 \text{ mg}} + 8 \frac{\text{mg Ni}}{1.} \frac{\text{meg}}{58.7 \text{ mg Ni}}) \cdot (\frac{\quad}{103 \text{ meg}}) =$$

80 equivalents per day

Note that 80 eq. is only 10% of the 800 eq. cation capacity required for the daily H_2CrO_4 recovery. Therefore the recovery operation dictates the capacity of the cation exchanger. Design cat. ex. for 880 equiv./day with once daily regeneration.

Bed. Vol. = $\frac{880 \text{ eq.}}{\text{day}} \frac{Ft^3}{42 \text{ eq.}} = 21\ Ft^3$

Check Flow Rate: $\frac{75 \text{ GPM}}{21\ Ft^3} = 3.6$ GPM/CF OK

Set Depth = 30" (Diam. Calc. same an Anion Ex.)

USE 2 Beds, 30" Deep x 2.5 ft. Diam.

Regeneration:

Daily dose of H_2SO_4 = (21 Ft^3) $(12 \frac{\text{Lb}}{Ft^3}$ = 252 Lb. $(^{100\%}_{H_2SO_4})$

Regen. Tank Vol. = $\frac{252}{0.05} \times \frac{1}{(1.0383)8.34} = 582$ Gal.

Regen. Time @ 1.0 GPM/CF = 10 min.

Rinse Vol. @ 120 Gal/CF = (21 CF (120) = 2500 Gal.

Rinse Rate 1.5 GPM/CF . Time = $\frac{120 \text{ Gal/CF}}{1.5 \text{ GPM/CF}} = 80$ min.

2. Anion Exchange

Operating Capacity - 3.8 Lb.CrO_3 per Ft^3

Regenerant - 10% NaOH, Dosage 4.8 Lb NaOH/Ft^3

Operation:

75 mg/l as Cr = $75 \frac{52 + 3(16)}{52} = 144 \frac{\text{mg}}{1}$ as CrO_3

Daily CrO_2 Input = $144 \frac{mg}{l} (75 \text{ gpm})(\frac{960 \text{ min}}{\text{day}})$

$$\frac{8.34}{10^{-6}} = \frac{86.5 \text{ Lb}}{\text{day}}$$

For daily regeneration: Bed Vol. $= \frac{86.5 \text{ Lb}}{3.8 \text{ Lb/CF}} = 23 \text{ Ft}^3$

Check Flow Rate: $\frac{75 \text{ gpm}}{24 \text{ CF}} = 3.3 \frac{\text{gpm}}{\text{Ft}^3}$ OK

Set resin depth = 30 in.

Surface area $= \frac{23 \text{ Ft.}^3}{2.5 \text{ Ft}} = 9.2 \text{ Ft}^2$

Try 2 Beds, Ea. with $4.6 \text{ Ft}^2 = \frac{D^2}{4}$

$D = (4 \ 4.6)^{\frac{1}{2}} = (5.9)^{\frac{1}{2}} = 2.43$ Ft.

USE 2 Beds, 30" Deep x 2.5 Ft. Diam.

Regeneration:

Daily Dose of NaOH = $(23 \text{ Ft}^3)(4.8 \frac{\text{Lb NaOH}}{\text{Ft}^3}) = \frac{100 \text{ Lb.}}{(100\% \text{ NaOH})}$

Regenerant Tank Vol. $= \frac{100 \text{ Lb}}{\text{day}} \frac{10 \text{ Lb Brine}}{1 \text{ Lb NaOH}} \frac{\text{Gal. Brine}}{9.6 \text{ Lb Brine}} =$

Regenerant Tank Vol. = 104 Gallons

Regeneration Time @ $1.0 \frac{\text{GPM}}{\text{CF}} = \frac{11.5 \text{ CF}}{1.0} = 12$ minutes

Rinse Volume = $(23 \text{ CF})(100 \frac{\text{Gal}}{\text{CF}}) = 2300$ Gal.

Chromic Acid Recovery: Re-cycle 70% of acid regenerants to cation ex.

Cation Exchg. Equiv. Reg'd = $0.7 \frac{100 \text{ Lb NaOH}}{40 \text{ g/eq.}} \cdot \frac{453 \text{ g}}{\text{Lb}} = 800$ equiv.

Case History

1. Steel Mill cold finishing facility. Figure 6 shows the facilities and Figure 7 illustrates the waste treatment facilities. Tables 2 and 3 respectively provide the oil and chemical usage, and the amount of contaminated wastewater flow. Table 4 shows the design criteria.

Fig. 6 Typical steel mill cold finishing facilities

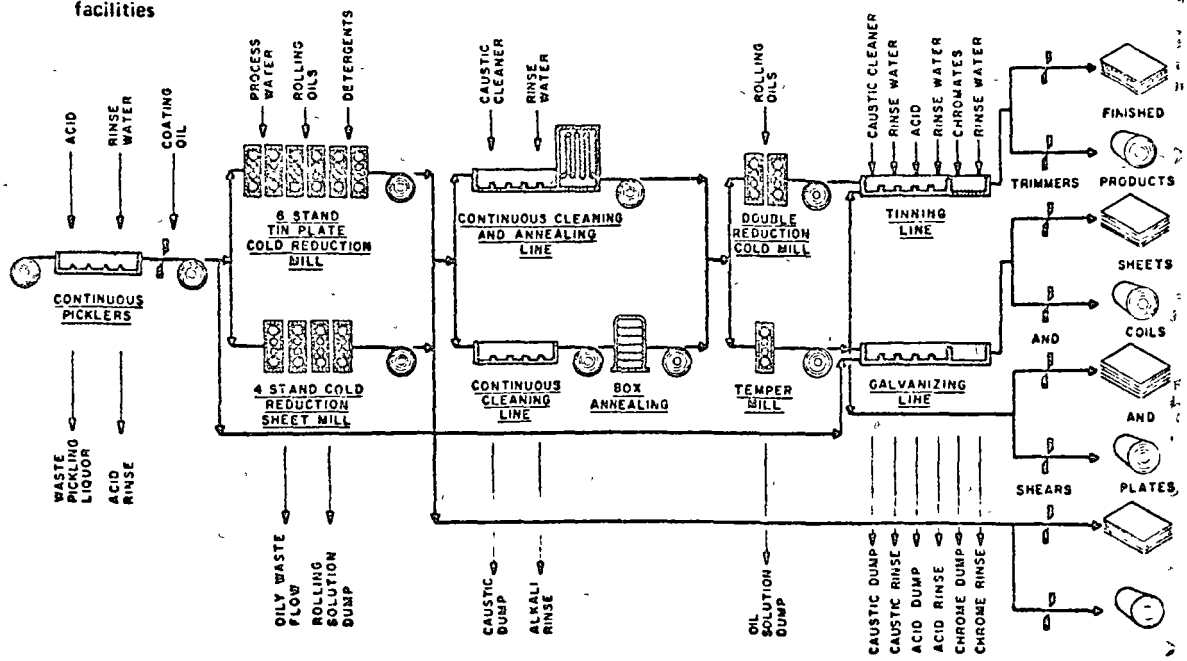

Fig. 7 Typical wastewater treatment facilities

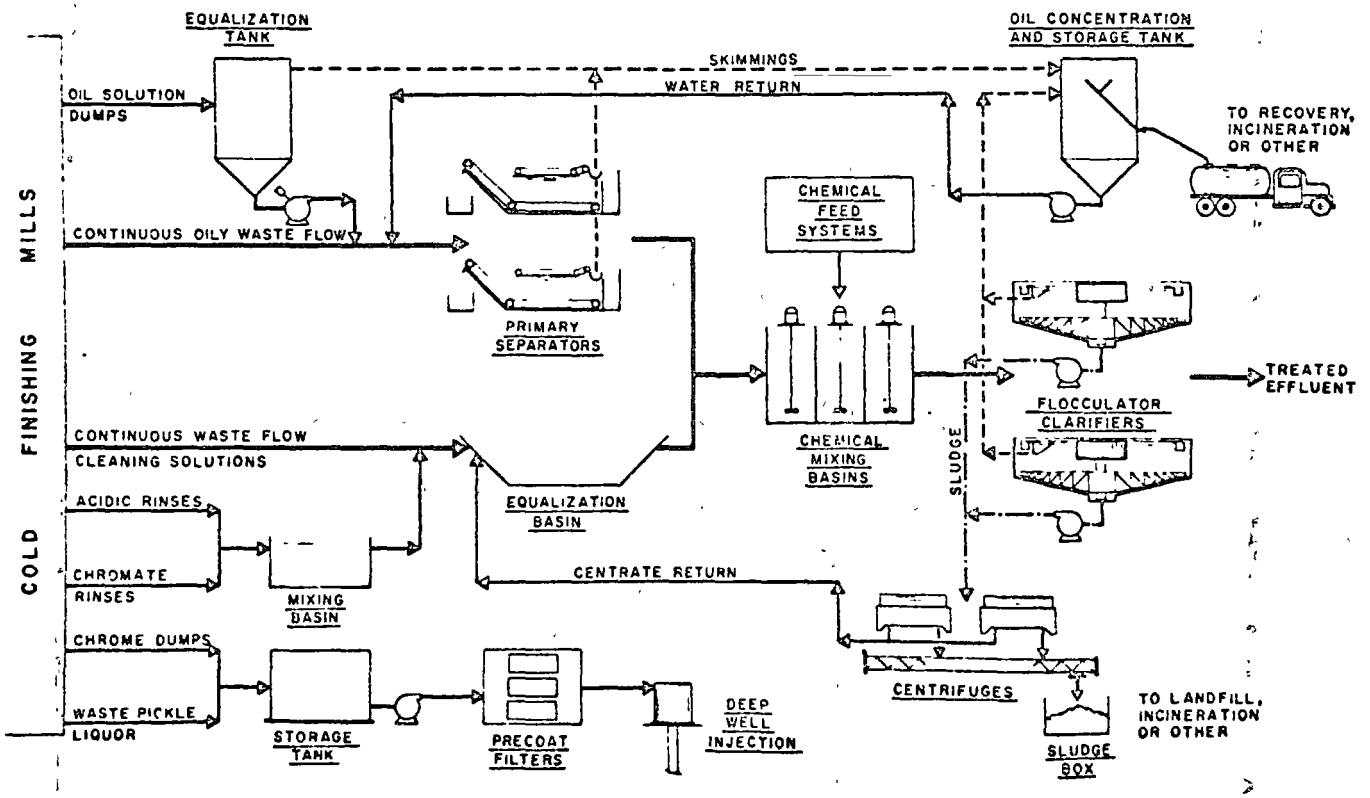

TABLE 2-OIL AND CHEMICAL USAGE

Unit	Dosage (lb per ton)
Continuous pickler	
Acid	40 to 70
Coating oil	1.5 to 3.0
Cold reduction mills	
Rolling oils	3 to 6
Cleaning lines	
Cleaner	2 to 4
Tinning lines	
Cleaner	1.5 to 2
Acid	15 to 25
Chromates	0.7 to 1.5
Galvanizing lines	
Cleaners	1.5 to 2
Acid	15 to 20
Chromates	0.3 to 1
Miscellaneous oils and lubricants	0.3 to 0.7

TABLE 3-CONTAMINATED WASTEWATER FLOWS AND DUMPS

	Continuous flows (gpm)
Pickling line	
Pickle liquor	30 to 100
Rinse water	150 to 350
Cold reduction mill	300 to 10,000
Cleaning line	100 to 300
Tinning line	300 to 1500
Galvanizing line	200 to 600
Miscellaneous shops	to 2000
	Schedule dumps (g/wk)
Pickling acids	5000 to 15,000
Acid	2 to 8%
Ferrous iron	3 to 10%
Rolling solutions	10,000 to 30,000
Oil	2 to 8%
Cleaning solutions	5000 to 30,000 g/wk/line
Caustic	3%
PO_4	0.5%
Oils	1.0%
Chromate solutions	1000 to 15,000 g/wk/bath
Cr^{+6}	1 to 12%

TABLE 4-TREATMENT FACILITIES DESIGN CRITERIA

Unit	Criteria
Oil dump equalization tank	12 to 48 hr
Acid-chromate rinse mixing tank	5 to 20 min
Waste acid storage tank	1 to 2 days
Precoat filters	1 to 1.5 gpm/sf
Deep well injection rate	100 to 500 gpm
Primary separators	10 to 30 min
	2 to 5 gpm/sf
Equalization basins	8 to 24 hr
Mixing basins	5 to 25 min
Flocculator-clarifier	
Flocculation	10 to 30 min
Settling	1 to 3 hr
Sludge storage	12 to 48 hr
Oil skimmings tank	
Oil storage	up to 1 wk (oil)
Separation zone	up to 1 day (skimmings)

CASE HISTORY, NONFERROUS METALS, MINING & SMELTING INDUSTRY

Process Waste Water Treatment at Bunker Hill Company

G. M. Baker* and A. H. Larson**

August 1973

ABSTRACT

At the Bunker Hill Company mining and metallurgical complex in Northern Idaho all metallurgical waste waters that cannot be recycled without treatment are combined with milling effluent and acid mine drainage in one large impoundment pond. The overflow from this pond is currently discharged directly into the South Fork Coeur d'Alene River. A new treatment plant utilizing a lime neutralization process is being installed to treat this discharge in order to minimize discharge of dissolved heavy metals. A bench-scale pilot plant was operated to provide an experimental basis for establishing treatment effectiveness. Based on these tests, a full scale plant was designed and is now under construction. Capital and operating costs for this plant have been projected.

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INTRODUCTION

The Bunker Hill Company is a wholly-owned subsidiary of Gulf Resources and Chemical Company, Houston, Texas. All of the Bunker Hill Company's operations are located in the Coeur d'Alene Mining District of Northern Idaho, approximately 75 miles south of the Canadian border. The Coeur d'Alene mining district embraces an area 23 miles long by 9 miles wide, and produces approximately 47% of the nation's silver, 11% of its lead, and 8% of its zinc.

The Bunker Hill Company mining operations are performed at three majc subsurface mines. Also included is a large metallurgical complex for smelting and refining primary lead and zinc metals. Related by-products, including silver, gold, copper, cadmium and antimony are recovered from processed concentrates. Three sulfuric acid plants are operated to recover sulfur dioxide from the smelting processes.

In addition to the mining and metallurgical operations, Bunker Hill, in a joint venture with Stauffer Chemical Company, produces phosphoric acid and ammonium phosphate fertilizers at Kellogg.

SOURCES AND NATURE OF WASTE WATER

Liquid effluents are discharged from the Bunker Hill Mine and all of the surface plants, with the exception of the lead smelter, into a 160 acre central impoundment pond for separation and retention of suspended solids. The clarified effluent is presently decanted from this area into the South Fork Coeur d'Alene River. The sources and nature of waste water influents and effluents from the central impoundment pond are shown in Table I.

At the Zinc Plant and Phosphoric Acid Plant operations, facilities have been installed to recycle a majority of the water discharged from cooling processes. The remainder of the effluent, which is from metallurgical processing and air pollution control equipment, is not amenable to recycle without treatment. It is transported along with slurried gypsum from the phosphoric acid plant in a one-mile long 12 inch diameter PVC pipeline and discharged into the Central Impoundment Pond for clarification. This combined discharge is low in pH. It contains dissolved zinc, cadmium, mercury, fluoride, sulfate, phosphate, and includes gypsum as a suspended solid.

Mine drainage is the major volume of waste water. It is acidic in nature and originates from surface and ground waters which seep into the extensive workings of the mine. Combination of air and water along with complex bacterial action in contact with pyrite, creates sulfuric acid lowering the pH of the water and dissolving heavy metals from mineralized areas. The dissolved metals are then carried to the surface in mine drainage water. As noted in Table I, this waste stream contains dissolved iron, lead, zinc, sulfate, and considerable suspended solids.

TABLE I. Characteristics of Waste Water Influents and Central Impoundment Pond Effluent (CIP)

Dissolved Elements	Influent				Effluent
	Zinc Plant	Phosphoric Acid Plant	Bunker Hill Mine	Mill	CIP (mg/L)
Fe	-	-	X	-	20 - 30
Pb	-	-	X	X	2 - 8
Zn	X	-	X	X	90 - 170
Cd	X	-	-	-	0.5 - 0.9
Hg	X	-	-	-	0.003 - 0.02
F	-	X	-	-	190 - 250
PO_4	-	X	-	-	90 - 120
SO_4	X	-	X	-	1200 - 1500
pH	Low	Low	Low	High	2.5 - 3.0
Suspended Solids (mg/L)	28,000		6,000 - 13,000	130,000	20 - 40

X = present in significant concentrations
- = not present in significant concentrations

At the mill, waste products from wet grinding and flotation operations are cycloned before discharge into the impoundment pond and the coarse fraction is pumped back into the mine to refill mined-out areas. During this "sand-fill operation", fines drain into the mine drainage system from underground cycloning systems and from the areas being filled with sand slurry. These fines return to the surface as suspended solids contained in the acid mine drainage. The mill effluent is characteristically high in pH containing dissolved zinc and lead, and suspended solids.

The central impoundment pond is equipped with a decant for discharging clarified overflow from the center of the pond. The overflow is low in suspended solids but contains the dissolved elements shown in Table I. The concentrations of dissolved heavy metals must be reduced to meet currently proposed State and Federal requirements.

CONSIDERATIONS FOR SELECTION OF A TREATMENT SYSTEM

In the selection of a system for waste water treatment there were four interrelated requirements: acceptable effluent quality, minimum sludge production, maximum system reliability, and acceptable capital and operating costs. On the basis of previous experience at Bunker Hill and a state-of-the-art technology study by Envirotech Systems, Incorporated* with acid mine water and other heavy-metal-containing waste waters, lime treatment was selected as the only practical system for meeting these criteria.

The initial investigations using lime neutralization were conducted on individual waste water discharges from the Zinc Plant and Mine. These investigations assumed treatment of the discharges at their sources. Although lime additions to pH 9.0 to 10.5 produced treated effluents which would meet the proposed regulations for dissolved heavy metals, the volume of low-density sludge presented impossible storage and disposal problems.

Laboratory tests using lime neutralization of Zinc Plant waste water produced a sludge containing 6% solids by weight (77,000 pounds per day of dry solids). Comparable tests with the Mine effluent produced a sludge containing 0.4% solids by weight (29,000 pounds per day dry solids). The total volume of sludge produced from the two systems represented 1135 acre-feet per year; 160 from the Zinc Plant waste water and 975 from the Acid Mine drainage.

Chemical analyses of the sludges indicated that Zinc Plant sludge was predominantly calcium sulfate (due to the high sulfate concentration of the waste water) and zinc hydroxide, while the Mine sludge was predominantly hydroxides of zinc and iron.

In order to reduce the sludge volume, three simultaneous approaches were used:

1. Reduction of the sulfate concentration by recycling within the Zinc Plant,

2. Combination of the remaining Zinc Plant effluent with the Mine drainage to reduce sulfate concentration to a level where precipitation of calcium sulfate would not occur during lime neutralization, and

3. Utilization of a thickener underflow sludge recycle system whereby the sludge concentration can be increased by including recycled underflow solids with incoming plant feed.**

The potential sludge volume reduction incorporating the approaches listed above is shown in Table 2.

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* Envirotech Systems, Inc., Menlo Park, California, was retained as a consultant during the initial investigation period.

** J. Smith III, "The Advantage of a Crowd for Acid Waste Liquors", paper presented at the 1972 AIME Annual Meeting in San Francisco.

TABLE 2. Comparison of Sludges from Individually Treated Zinc Plant and Mine Effluents and Treatment of Combined Effluents

	Zinc Plant	Mine	Combination *
Sulfate, ppm	4500 (est)	1000 - 1200	1200 - 1500
Thickener Underflow Solids, pounds per day	77,000	29,000	35,000
Solids, % by Weight	6	0.4	8
Sludge Volume, acre ft/year	160	975	55

* Suspended solids in untreated water are not included.

On the basis of this projected combination advantage, a combined Zinc-Mine effluent treatment plant was considered mandatory since the problem of disposing of the volume of sludge generated by individual treatment was of major concern in the mountainous terrain of the Kellogg area. While developing this rationale and considering the location of other effluent sources and previous installations, it became apparent that this combined plant should include treatment for all the waste water presently being discharged from the central impoundment pond. The advantages of such an overall approach are as follows:

1. The total sludge volume will be minimized,
2. The central impoundment pond will serve as a clarifier for the removal of high concentrations of suspended solids prior to lime treatment, thus removing a heavy burden from the treatment plant - especially important when utilizing a solids recycle system,
3. The high pH Mill effluent will help neutralize acid Mine drainage,
4. A central plant is more economical than several individual plants from both capital and operating standpoints,
5. The central impoundment pond will provide surge holding capacity during treatment plant upsets or breakdowns, thereby protecting the quality of the river course at all times,
6. Processing facilities for possible future recovery of metals from waste sludge will be centralized.

EVALUATION OF A LIME-TREATMENT SYSTEM

The dissolved metal constituents of major concern in the central impoundment pond effluent are zinc, iron, lead, cadmium, and mercury. The major dissolved non-metal constituents are sulfate, phosphate, and fluoride. The results of beaker-scale lime treatment of one sample of this effluent water are shown in Figure 1. With the exception of sulfate, all the dissolved constituents showed increased precipitation with increased pH levels up to a pH of 9 to 10. It should be mentioned, however, that lead above a pH of 9 and zinc above a pH of 10.5 exhibited amphoteric behavior; hence, these precipitated metals re-dissolved. Lime requirements to change the pH are shown in Figure 2. Over a period of time with different samples the $Ca(OH)_2$ consumption varied from 0.8 to 1.7 mg/L to reach a pH of 10.

In order to evaluate the lime treatment system a bench-scale pilot plant (miniplant) of the proposed system was set up and operated. This bench-scale circuit is shown schematically in Figure 3. Since iron is present in the waste water mainly as ferrous iron, it was decided that oxidation to ferric iron by aeration would be necessary to achieve more complete precipitation of iron and better sludge densification. Typical ranges of results obtained by operation of the bench-scale pilot plant at feed rates of 10 - 15 gph and sludge recycle rates of 10 to 40 are shown in Table 3. These tests as well as laboratory tests by Envirotech Systems, Inc. on the effect of sludge recycle proved general applicability of the proposed system for Bunker Hill's use. Although these tests included the waste water from the Phosphoric Acid Plant, it was decided that this plant waste water should be removed from the inflow to the central treatment plant and handled separately by a closed loop recycle system developed by the Stauffer Chemical Company. In addition to reducing fluoride emissions, this closed loop system was more economical. The 160 acre impoundment pond has, therefore, been diked-off into two areas with one area of 43 acres serving as a settling-cooling basin for recycled water to be returned to the Phosphoric Acid Plant process.

Time was not available to operate a large scale pilot plant nor was additional verification considered mandatory. Bunker Hill, therefore, decided to proceed with construction of the full scale operational plant.

TABLE 3 Bench-Scale Pilot Plant Results

Dissolved Element	Thickener Overflow (ppm)	Thickener Underflow* (Wt. %)
Cd	0.04 - 0.06	0.1
Cu	0.02 - 0.13	0.1
Fe	0.05 - 0.6	3 - 6
Hg	0.001 - 0.004	-
Pb	0.3 - 0.6	0.2 - 0.3
Zn	0.05 - 0.6	8 - 14
CaO	700 - 900	17 - 23
SO_4/S	500 - 700	1 - 2
PO_4/P	0.1 - 1.3	1 - 2
F	25 - 35	7
Suspended Solids	15 - 70 ppm (5 - 15 JTU)	-
pH	9.7 - 10.5	-

* Underflow sludge varied from 2 - 8% solids by weight

DESCRIPTION OF OPERATIONAL TREATMENT PLANT

Treatment facilities are divided into two parts: the Central Treatment Plant and Offsite facilities. The Central Treatment Plant is shown schematically in Figure 4.

1. Central Treatment Plant

The Central Treatment Plant consists of lime neutralization, aeration, flocculation, sedimentation, thickener underflow solids recycle, and acidification. A 200 ton lime storage bin and 8000 lb/hr lime slaker unit will provide lime slurry for neutralization. This slurry will be combined with thickener underflow in a 15,000 gallon mixing tank. The decanted effluent from the Central Impoundment Pond will be combined with the output of the mixing tank in a 60' x 50' x 10' neutralization-aeration basin and controlled at a pH of 10. The overflow from this basin will be conditioned in a 32' x 32' x 11' flocculation tank. Chemical flocculants will be used as required.

The flow from the flocculation basin will enter a 236 ft. diameter thickener for solids settling and clarification. The majority of the thickener underflow will be recycled through the mixing tank to increase the density of the sludge. The sludge bleed from the thickner will be blended with the Mill tailings and distributed around the perimeter of the Central Impoundment Pond.

The clarified thickener overflow will be acidified with sulfuric acid as it flows to the Mill water supply reservoir. The Mill will recycle part of this water for process requirements. The excess treated effluent will be discharged into the South Fork Coeur d'Alene River.

2. Offsite Facilities

Offsite facilities include recycle within the Zinc Plant to reduce sulfate discharge and a pipeline for transporting Zinc Plant effluent to the Central Impoundment Pond.

As part of these facilities, the Phosphoric Acid Plant effluent recycle system is included and will utilize a 43 acre portion of the Central Impoundment Pond for settling and cooling. After settling and cooling, the effluent will be recycled directly back to the Phosphoric Acid Plant. Required make-up water will be supplied from the Lead Smelter water recycle system. The Lead Smelter effluent will normally be recycled within the Smelter. Provisions will be incorporated to discharge all or any portion of this Lead Smelter effluent to the Central Impoundment Pond for treatment in the Central Treatment Plant during periods of process upset within the Lead Smelter.

Projected Capital and Operating costs for the treatment system are shown in Table 4.

The Central Treatment Plant being constructed is shown diagrammatically in Figure 5. Construction is now about 60% complete with startup scheduled to begin in late 1973.

TABLE 4. Projected Capital and Operating Costs

Capital Costs:	
Central Treatment Plant: (6000 gpm Design Flow)	$ 550,000
*Offsite Facilities Costs: (Including pipelines to impounding areas, decants, and various plant effluent recycle systems)	730,000
Total Capital Costs:	$1,280,000
Annual Operating Costs:	
Direct Operating Cost: (at Design Flow)	$ 592,000
Indirect Operating Cost: (including depreciation, taxes, and insurance)	110,000
Total Annual Operating Costs:	$ 703,000

* Not included is $995,000 spent previously for water treatment facilities which were necessary for the proper operation of this facility.

ACKNOWLEDGEMENTS

The authors would like to acknowledge the consulting services of Envirotech Systems, Inc. during the initial stage of this investigation. Dr. E. Weisberg, formerly Manager of Systems Technology, Envirotech Systems, previously presented a paper on this subject at the 1972 AIME Annual meeting in San Francisco.

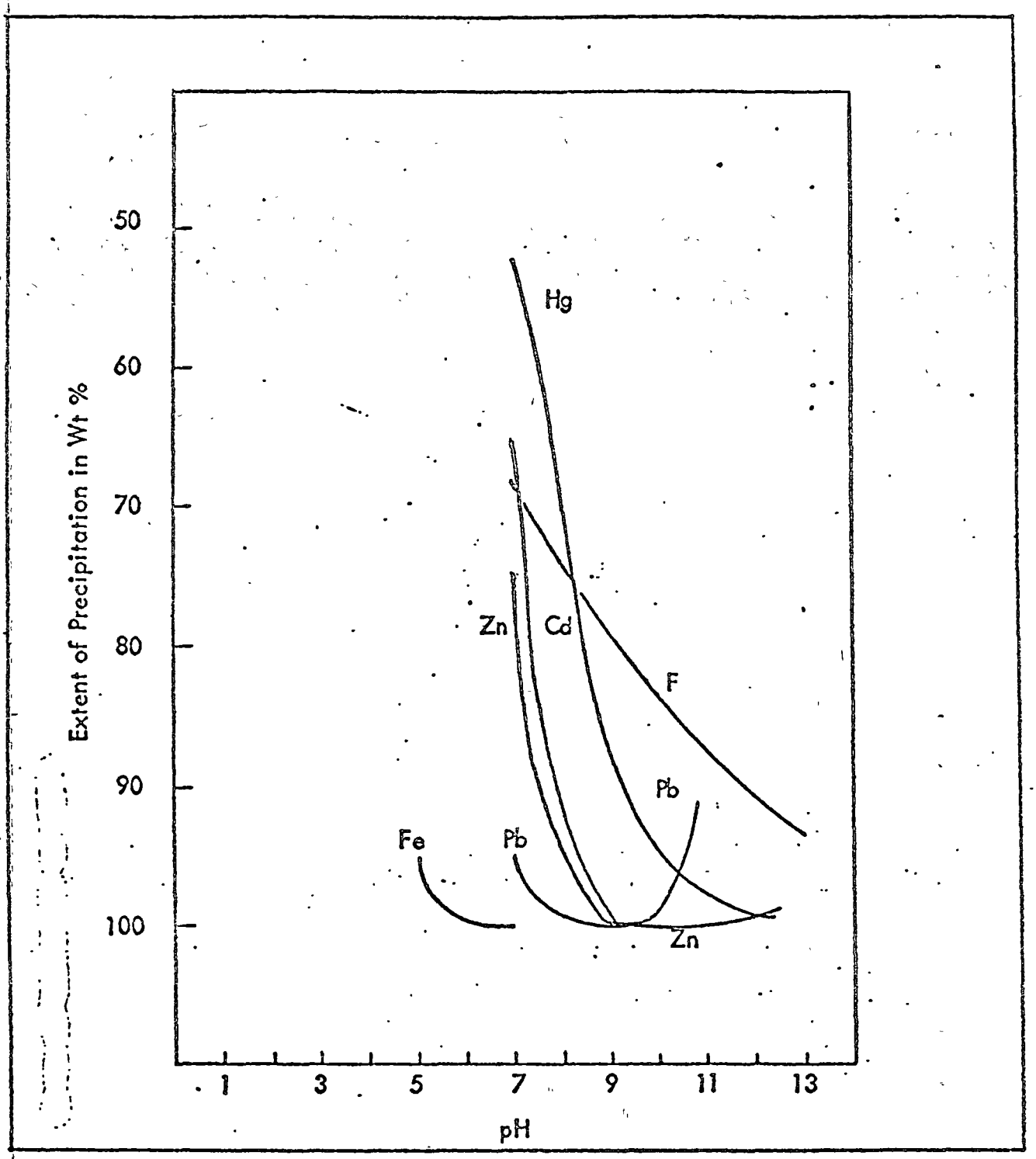


FIGURE 1 HEAVY METAL PRECIPITATION vs pH for CENTRAL IMPOUNDMENT POND EFFLUENT - pH ADJUSTMENTS BY LIME ADDITIONS

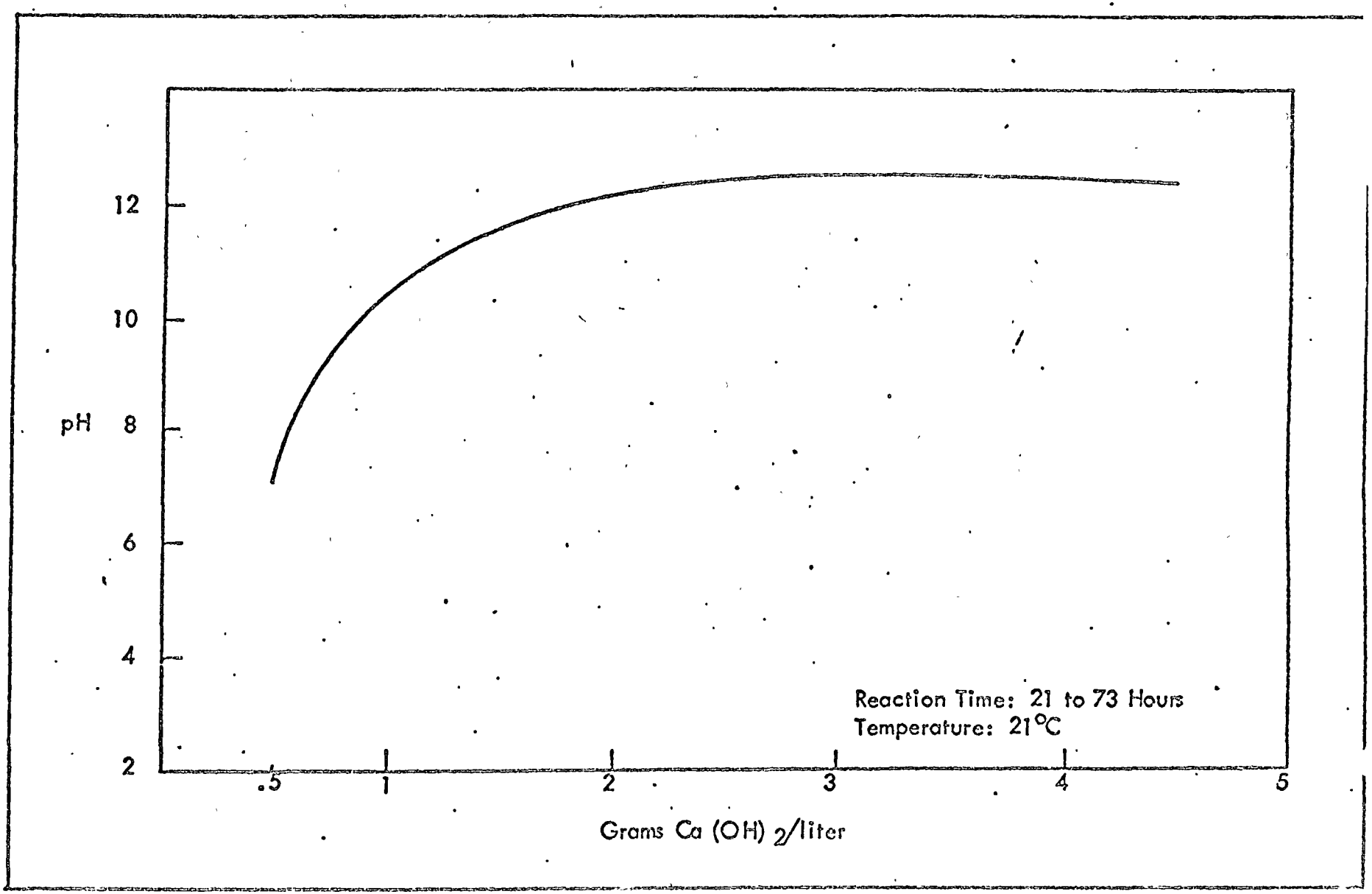


FIGURE 2 LIME CONSUMPTION vs pH for CENTRAL IMPOUNDMENT POND EFFLUENT

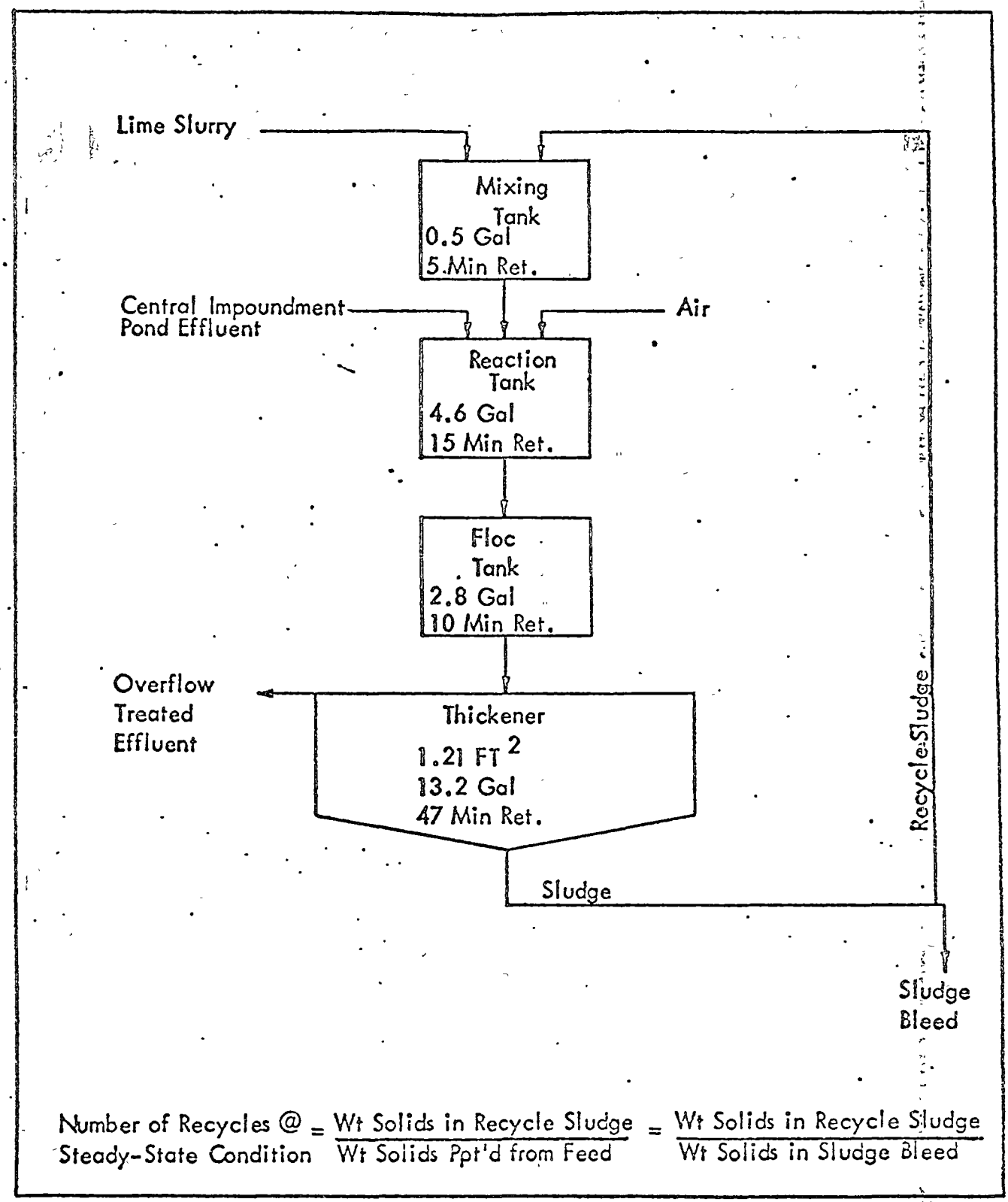


FIGURE 3 LAB SCALE SIMULATION OF CIP EFFLUENT TREATMENT FLOW DIAGRAM

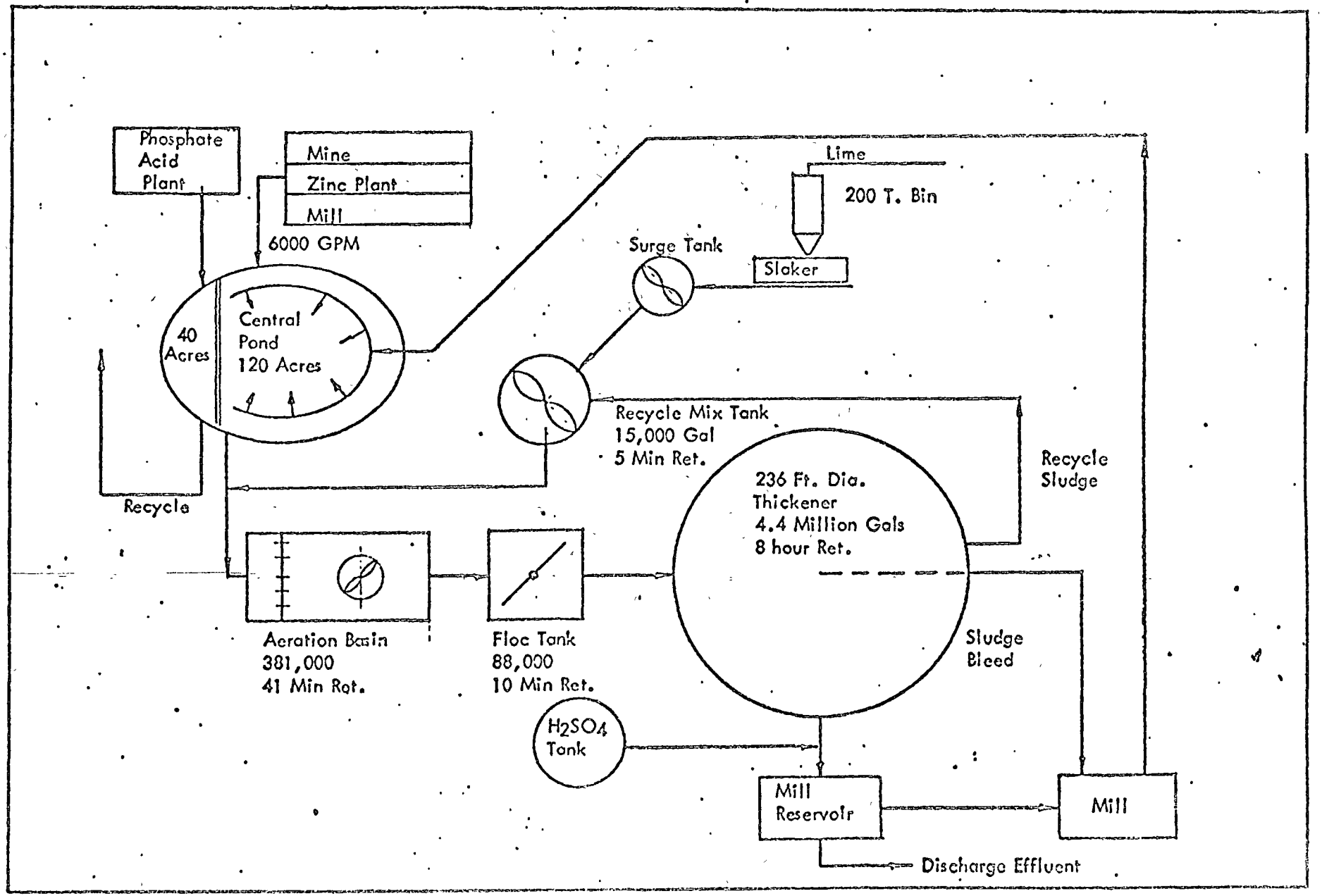


FIGURE 4 CENTRAL TREATMENT PLANT - FLOW SHEET

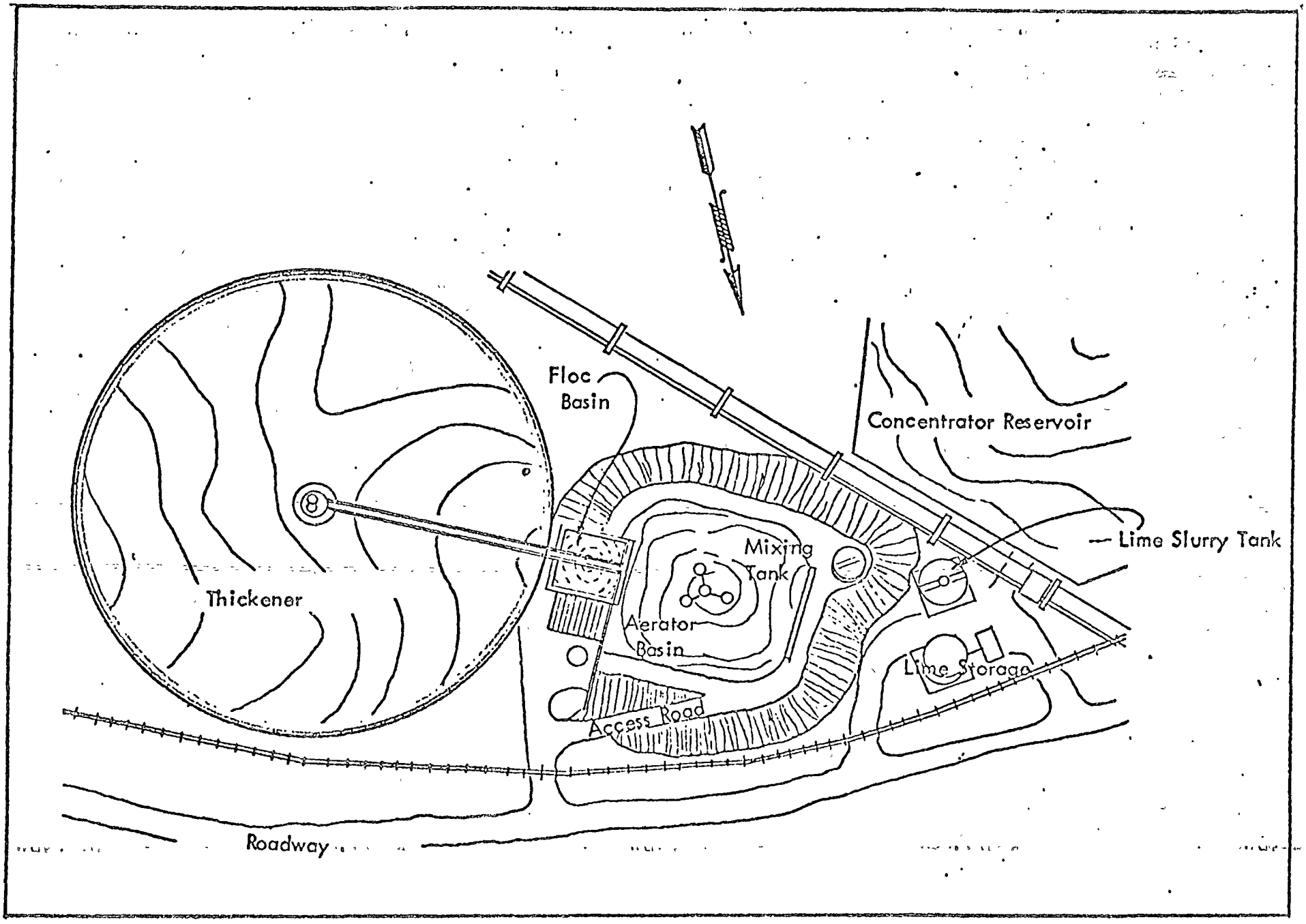


FIGURE 5 SKETCH OF CENTRAL TREATMENT PLANT

STEEL MAKING

E. F. Gloyna

Reference is made to Development Document for Effluent Limitations Guidelines and New Source Performance Standards for the Steel Making Industry, EPA-440/1-74-024-a, June 1974.

For the purpose of establishing effluent guidelines and standards of performance for the raw steel making operations of the iron and steel industry, the industry was divided into subcategories as follows:

I By-Product Coke Subcategory

II Beehive Coke Subcategory

III Sintering Subcategory

IV Blast Furnace (Iron) Subcategory

V Blast Furnace (Ferromanganese) Subcategory

VI Basic Oxygen Furnace (Semiwet Air Pollution Control Methods) Subcategory

VII Basic Oxygen Furnace (Wet Air Pollution Control Methods) Subcategory

VIII Open Hearth Furnace Subcategory

IX Electric Arc Furnace (Semiwet Air Pollution Control Methods) Subcategory

X Electric Arc Furnace (Wet Air Pollution Control Methods) Subcategory

XI Vacuum Degassing Subcategory

XII Continuous Casting Subcategory

The selection of these subcategories was based upon distinct differences in type of products produced, production processes, raw materials used, waste waters generated and control and treatment technologies employed. Subsequent waste characterizations of individual plants substantiated the validity of this subcategorization.

The effluent limitations guidelines for the iron and steel industry representing the effluent quality obtainable by existing point sources through the application of the best practicable control technology currently available (BPCTCA or Level I) for each industry subcategory, are as follows:

I. By-Product Coke Subcategory

BPCTCA Effluent Limitations
Units: kg pollutant per kkg of product
or: lb pollutant per 1,000 lb of product

Pollutant Parameter	Maximum for any One Day Period Shall Not Exceed	Maximum Average of Daily Values for any Period of 30 Consecutive Days
Cyanide	0.0657	0.0219
Phenol	0.0045	0.0015
Ammonia	0.2736	0.0912
Oil & Grease	0.0327	0.0109
Suspended Solids	0.1095	0.0365
pH	6.0 to 9.0	

II. Beehive Coke Subcategory

BPCTCA Effluent Limitations
Units: kg pollutant per kkg of product
or: lb pollutant per 1,000 lb of product

Pollutant Parameter	Maximum for any One Day Period Shall Not Exceed	Maximum Average of Daily Values for any Period of 30 Consecutive Days
Cyanide	No discharge of process waste water pollutants to navigable waters	
Phenol		
Ammonia		
Sulfide		
Oil & Grease		
Suspended Solids		
pH		

III. Sintering Subcategory

BPCTCA Effluent Limitations
Units: kg pollutant per kkg of product
or: lb pollutant per 1,000 lb of product

Pollutant Parameter	Maximum for any One Day Period Shall Not Exceed	Maximum Average of Daily Values for any Period of 30 Consecutive Days
Suspended Solids	0.0312	0.0104
Oil & Grease	0.0063	0.0021
pH	6.0 to 9.0	

IV. Blast Furnace (Iron) Subcategory

BPCTCA Effluent Limitations
Units: kg pollutant per kkg of product
or: lb pollutant per 1,000 lb of product

Pollutant Parameter	Maximum for any One Day Period Shall Not Exceed	Maximum Average of Daily Values for any Period of 30 Consecutive Days
Suspended Solids	0.0780	0.0260
Cyanide	0.0234	0.0078
Phenol	0.0063	0.0021
Ammonia	0.1953	0.0651
pH	6.0 to 9.0	

V. Blast Furnace (Ferromanganese) Subcategory

BPCTCA Effluent Limitations
Units: kg pollutant per kkg of product
or: lb pollutant per 1,000 lb of product

Pollutant Parameter	Maximum for any One Day Period Shall Not Exceed	Maximum Average of Daily Values for any Period of 30 Consecutive Days
Suspended Solids	0.3129	0.1043
Cyanide	0.4689	0.1563
Phenol	0.0624	0.0208
Ammonia	1.5636	0.5212
pH	6.0 to 9.0	

VI. Basic Oxygen Furnace (Semiwet Air Pollution Control Methods) Subcategory

BPCTCA Effluent Limitations
Units: kg pollutant per kkg of product
or: lb pollutant per 1,000 lb of product

Pollutant Parameter	Maximum for any One Day Period Shall Not Exceed	Maximum Average of Daily Values for any Period of 30 Consecutive Days
Suspended Solids	No discharge of process waste water pollutants to navigable waters	
pH		

VII. Basic Oxygen Furnace (Wet Air Pollution Control Methods) Subcategory

BPCTCA Effluent Limitations
Units: kg pollutant per kkg of product
or: lb pollutant per 1,000 lb of product

Pollutant Parameter	Maximum for any One Day Period Shall Not Exceed	Maximum Average of Daily Values for any Period of 30 Consecutive Days
Suspended Solids	0.0312	0.0104
pH	6.0 to 9.0	

VIII. Open Hearth Furnace Subcategory

BPCTCA Effluent Limitations
Units: kg pollutant per kkg of product
or: lb pollutant per 1,000 lb of product

Pollutant Parameter	Maximum for any One Day Period Shall Not Exceed	Maximum Average of Daily Values for any Period of 30 Consecutive Days
Suspended Solids	0.0312	0.0104
pH	6.0 to 9.0	

IX. Electric Arc Furnace (Semiwet Air Pollution Control Methods) Subcategory

BPCTCA Effluent Limitations
Units: kg pollutant per kkg of product
or: lb pollutant per 1,000 lb of product

Pollutant Parameter	Maximum for any One Day Period Shall Not Exceed	Maximum Average of Daily Values for any Period of 30 Consecutive Days
Suspended Solids	No discharge of process waste water pollutants to navigable waters	
pH		

X. Electric Arc Furnace (Wet Air Pollution Control Methods) Subcategory

BPCTCA Effluent Limitations
Units: kg pollutant per kkg of product
or: lb pollutant per 1,000 lb of product

Pollutant Parameter	Maximum for any One Day Period Shall Not Exceed	Maximum Average of Daily Values for any Period of 30 Consecutive Days
Suspended Solids	0.0312	0.0104
pH	6.0 to 9.0	

XI. Vacuum Degassing Subcategory

BPCTCA Effluent Limitations
Units: kg pollutant per kkg of product
or: lb pollutant per 1,000 lb of product

Pollutant Parameter	Maximum for any One Day Period Shall Not Exceed	Maximum Average of Daily Values for any Period of 30 Consecutive Days
Suspended Solids	0.0156	0.0052
pH	6.0 to 9.0	

XII. Continuous Casting Subcategory

BCPTCA Effluent Limitations
Units: kg pollutant per kkg of product
or: lb pollutant per 1,000 lb of product

Pollutant Parameter	Maximum for any One Day Period Shall Not Exceed	Maximum Average of Daily Values for any Period of 30 Consecutive Days
Suspended Solids	0.0780	0.0260
Oil & Grease	0.0234	0.0078
pH	6.0 to 9.0	

The effluent guidelines representing the effluent quality obtainable by existing point sources through the application of the best available technology economically achievable (BATEA or Level II) for each industry subcategory are as follows:

I. By-Product Coke Subcategory

BATEA Effluent Limitations
Units: kg pollutant per kkg of product
or: lb pollutant per 1,000 lb of product

Pollutant Parameter	Maximum for any One Day Period Shall Not Exceed	Maximum Average of Daily Values for any Period of 30 Consecutive Days
*Cyanide (A)	0.0003	0.0001
Phenol	0.0006	0.0002
Ammonia	0.0126	0.0042
Sulfide	0.0003	0.0001
Oil & Grease	0.0126	0.0042
Suspended solids	0.0312	0.0104
pH	6.0 to 9.0	

II. Beehive Coke Subcategory

BATEA Effluent Limitations
Units: kg pollutant per kkg of product
or: lb pollutant per 1,000 lb of product

Pollutant Parameter	Maximum for any One Day Period Shall No Exceed	Maximum Average of Daily Values for any Period of 30 Consecutive Days
*Cyanide (A) Phenol Ammonia Sulfide Oil & Grease Suspended Solids pH	No discharge of process waste water pollutants to navigable waters	

*Cyanide (A): Cyanide amenable to chlorination. Reference ASTM D 2036-72.

III. Sintering Subcategory

BATEA Effluent Limitations
Units: kg pollutant per kkg of product
or: lb pollutant per 1,000 lb of product

Pollutant Parameter	Maximum for any One Day Period Shall Not Exceed	Maximum Average of Daily Values for any Period of 30 Consecutive Days
Suspended Solids	0.0156	0.0052
Oil & Grease	0.0063	0.0021
Sulfide	0.00018	0.00006
Fluoride	0.0126	0.0042
pH	6.0 to 9.0	

IV. Blast Furnace (Iron) Subcategory

BATEA Effluent Limitations
Units: kg pollutant per kkg of product
or: lb pollutant per 1,000 lb of product

Pollutant Parameter	Maximum for any One Day Period Shall Not Exceed	Maximum Average of Daily Values for any Period of 30 Consecutive Days
Suspended Solids	0.0390	0.0130
*Cyanide (A)	0.0004	0.00013
Phenol	0.0008	0.00026
Ammonia	0.0156	0.0052
Sulfide	0.0005	0.00016
Fluoride	0.0312	0.0104
pH	6.0 to 9.0	

*Cyanide (A): Cyanides amenable to chlorination. Reference ASTM D 2036-72.

V. Blast Furnace (Ferromanganese) Subcategory

BATEA Effluent Limitations
Units: kg pollutant per kkg of product
or: lb pollutant per 1,000 lb of product

Pollutant Parameter	Maximum for any One Day Period Shall Not Exceed	Maximum Average of Daily Values for any Period of 30 Consecutive Days
Suspended Solids	0.0780	0.0206
*Cyanide (A)	0.0008	0.00026
Phenol	0.0016	0.00052
Ammonia	0.0312	0.0104
Sulfide	0.0009	0.0003
Manganese	0.0156	0.0052
pH	6.0 to 9.0	

*Cyanide (A): Cyanides amenable to chlorination. Reference ASTM D 2036-72.

VI. Basic Oxygen Furnace (Semiwet Air Pollution Control Methods) Subcategory

BATEA Effluent Limitations
Units: kg pollutant per kkg of product
or: lb pollutant per 1,000 lb of product

Pollutant Parameter	Maximum for any One Day Period Shall Not Exceed	Maximum Average of Daily Values for any Period of 30 Consecutive Days
Suspended Solids	No discharge of process waste water pollutants to navigable waters	
Fluoride		
pH		

VII. Basic Oxygen Furnace (Wet Air Pollution Control Methods) Subcategory

BATEA Effluent Limitations
Units: kg pollutant per kkg of product
or: lb pollutant per 1,000 lb of product

Pollutant Parameter	Maximum for any One Day Period Shall Not Exceed	Maximum Average of Daily Values for any Period of 30 Consecutive Days
Suspended Solids	0.0156	0.0052
Fluoride	0.0126	0.0042
pH	6.0 to 9.0	

VIII. Open Hearth Furnace Subcategory

BATEA Effluent Limitations
Units: kg pollutant per kkg of product
or: lb pollutant per 1,000 lb of product

Pollutant Parameter	Maximum for any One Day Period Shall Not Exceed	Maximum Average of Daily Values for any Period of 30 Consecutive Days
Suspended Solids	0.0156	0.0052
Fluoride	0.0126	0.0042
Nitrate (as NO_3)	0.0282	0.0094
Zinc	0.0030	0.0010
pH	6.0 to 9.0	

IX. Electric Arc Furnace (Semiwet Air Pollution Control Methods) Subcategory

BATEA Effluent Limitations
Units: kg pollutant per kkg of product
or: lb pollutant per 1,000 lb of product

Pollutant Parameter	Maximum for any One Day Period Shall Not Exceed	Maximum Average of Daily Values for any Period of 30 Consecutive Days
Suspended Solids	No discharge of process waste water pollutants to navigable waters	
Zinc		
Fluoride		
pH		

X. Electric Arc Furnace (Wet Air Pollution Control Methods) Subcategory

BATEA Effluent Limitations
Units: kg pollutant per kkg of product
or: lb pollutant per 1,000 lb of product

Pollutant Parameter	Maximum for any One Day Period Shall Not Exceed	Maximum Average of Daily Values for any Period of 30 Consecutive Days
Suspended Solids	0.0156	0.0052
Fluoride	0.0126	0.0042
Zinc	0.0030	0.0010
pH	6.0 to 9.0	

XI. Vacuum Degassing Subcategory

BATEA Effluent Limitations
Units: kg pollutant per kkg of product
or: lb pollutant per 1,000 lb of product

Pollutant Parameter	Maximum for any One Day Period Shall Not Exceed	Maximum Average of Daily Values for any Period of 30 Consecutive Days
Suspended Solids	0.0078	0.0026
Zinc	0.0015	0.0005
Manganese	0.0015	0.0005
Lead	0.00015	0.00005
Nitrate (as NO_3)	0.0141	0.0047
pH	6.0 to 9.0	

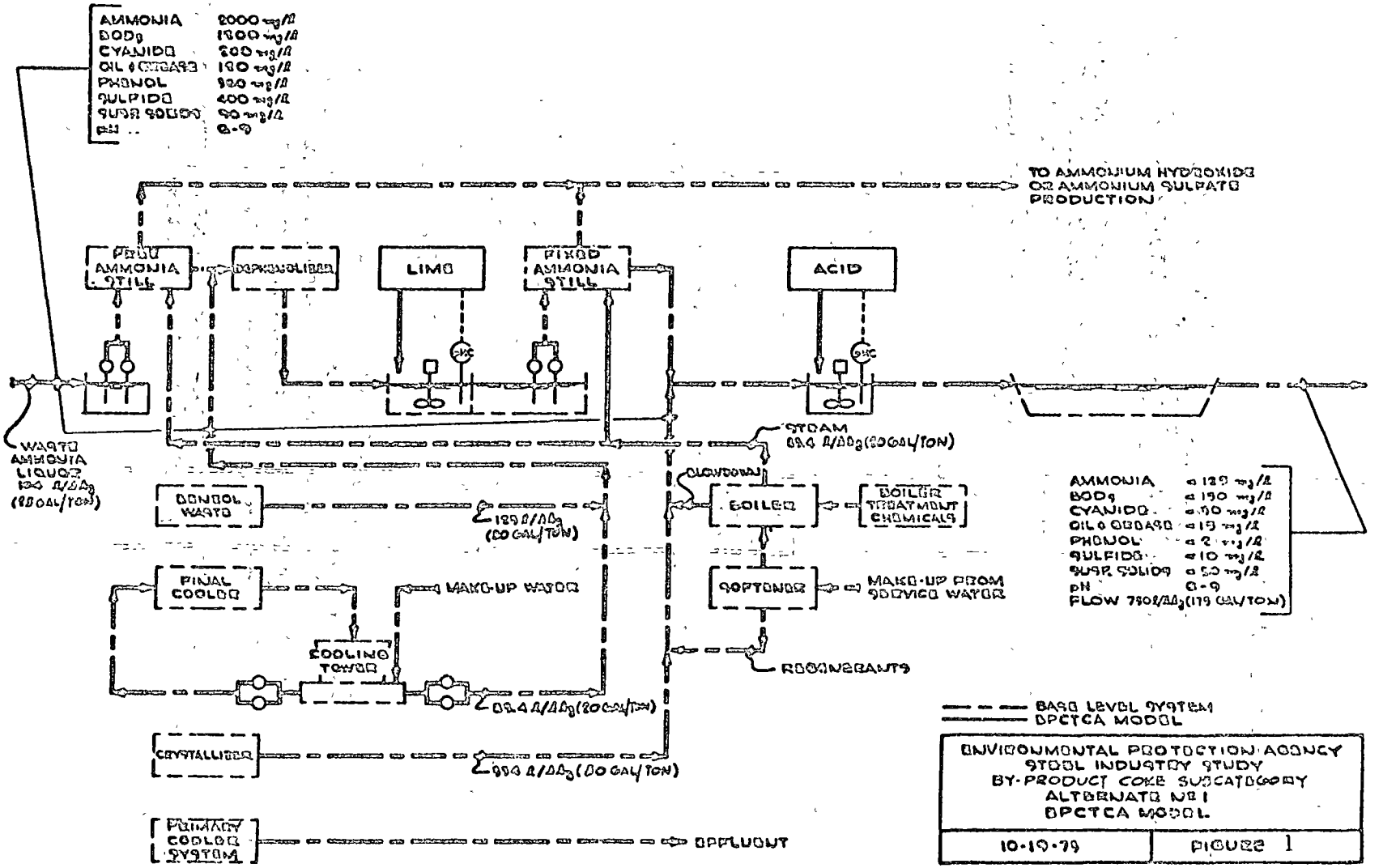
XII. Continuous Casting Subcategory

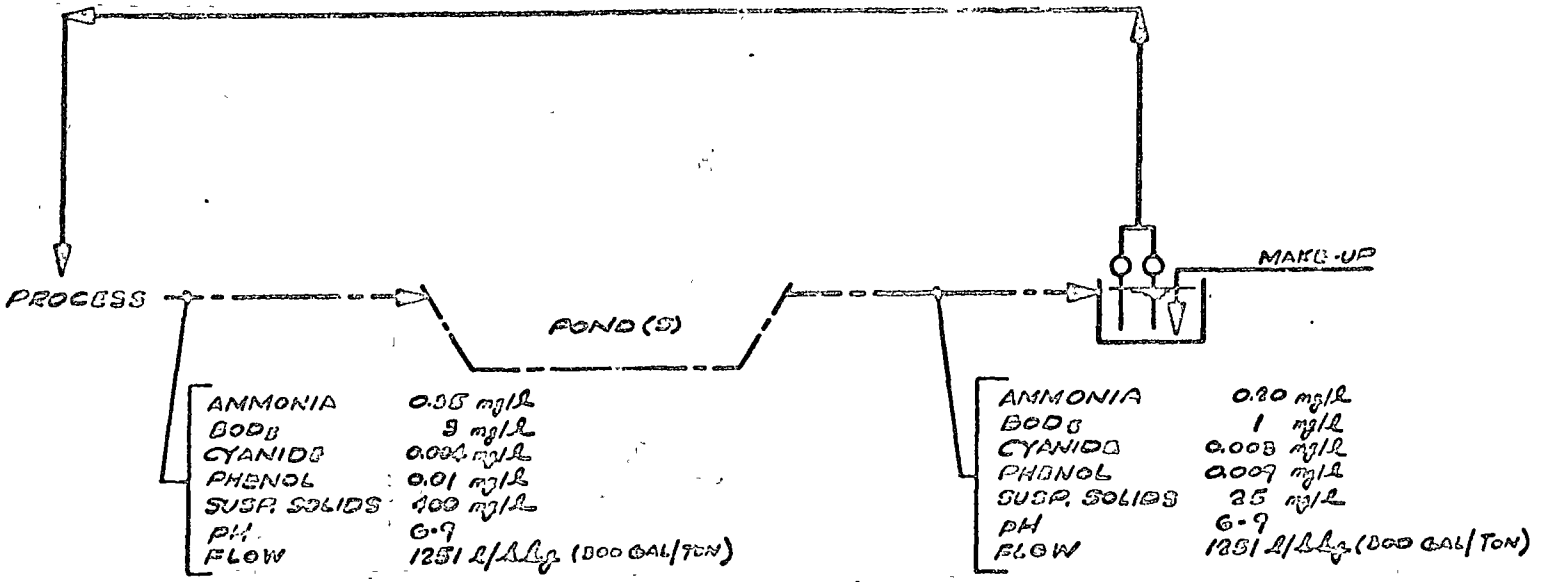
BATEA Effluent Limitations
Units: kg pollutant per kkg of product
or: lb pollutant per 1,000 lb of product

Pollutant Parameter	Maximum for any One Day Period Shall Not Exceed	Maximum Average of Daily Values for any Period of 30 Consecutive Days
Suspended Solids	0.0156	0.0052
Oil & Grease	0.0156	0.0052
pH	6.0 to 9.0	

The effluent guidelines representing the effluent quality attainable by new sources (NSPS or Level III) through the application of the best available demonstrated control technology, (BADCT) processes, operating methods or other alternatives for each industry sub-category are as follows:

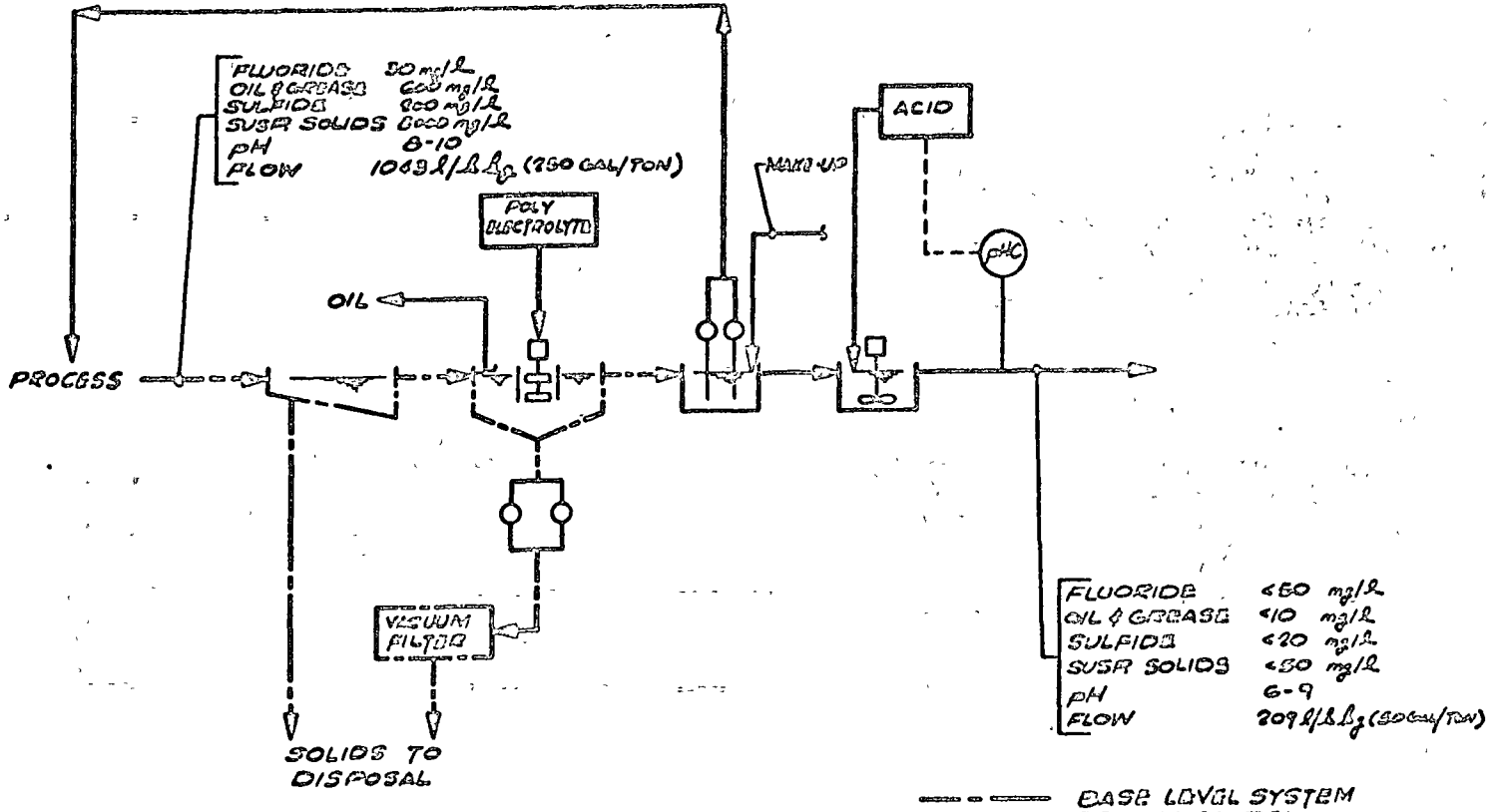
Same as BATEA for all categories except that the nitrate limitations on the open hearth and vacuum degassing subcategories shall not apply.


AMMONIA 2000 mg/l
BOD5 1900 mg/l
CYANIDE 200 mg/l
OIL & GREASE 100 mg/l
PHENOL 300 mg/l
SULFIDE 400 mg/l
SUSP SOLIDS 50 mg/l
pH 8-9
TO AMMONIUM HYDROXIDE OR AMMONIUM SULFATE PRODUCTION
FREE AMMONIA STILL
DEPHENOLIZER
LIME
FIXED AMMONIA STILL
ACID
WASTE AMBONIA LIQUOR 134 l/ΔΔg (32 GAL/TON)
STEAM 834 l/ΔΔg (200 GAL/TON)
BLOWDOWN
BENZOL WASTE
189 l/ΔΔg (45 GAL/TON)
BOILER
BOILER TREATMENT CHEMICALS
PINAL COOLER
MAKE-UP WATER
DEAERATOR
MAKE-UP FROM POTABLE WATER
COOLING TOWER
RECIRCULATE
834 l/ΔΔg (200 GAL/TON)
CRYSTALLIZER
834 l/ΔΔg (200 GAL/TON)
PRIMARY COOLER SYSTEM
EFFLUENT
AMMONIA ≤ 129 mg/l
BOD5 ≤ 190 mg/l
CYANIDE ≤ 20 mg/l
OIL & GREASE ≤ 15 mg/l
PHENOL ≤ 2 mg/l
SULFIDE ≤ 10 mg/l
SUSP SOLIDS ≤ 50 mg/l
pH 8-9
FLOW 7502/ΔΔg (179 GAL/TON)
BASE LEVEL SYSTEM
BPCTCA MODEL
ENVIRONMENTAL PROTECTION AGENCY
STEEL INDUSTRY STUDY
BY-PRODUCT COKE SUBCATEGORY
ALTERNATE NO 1
BPCTCA MODEL
10-19-79
FIGURE 1



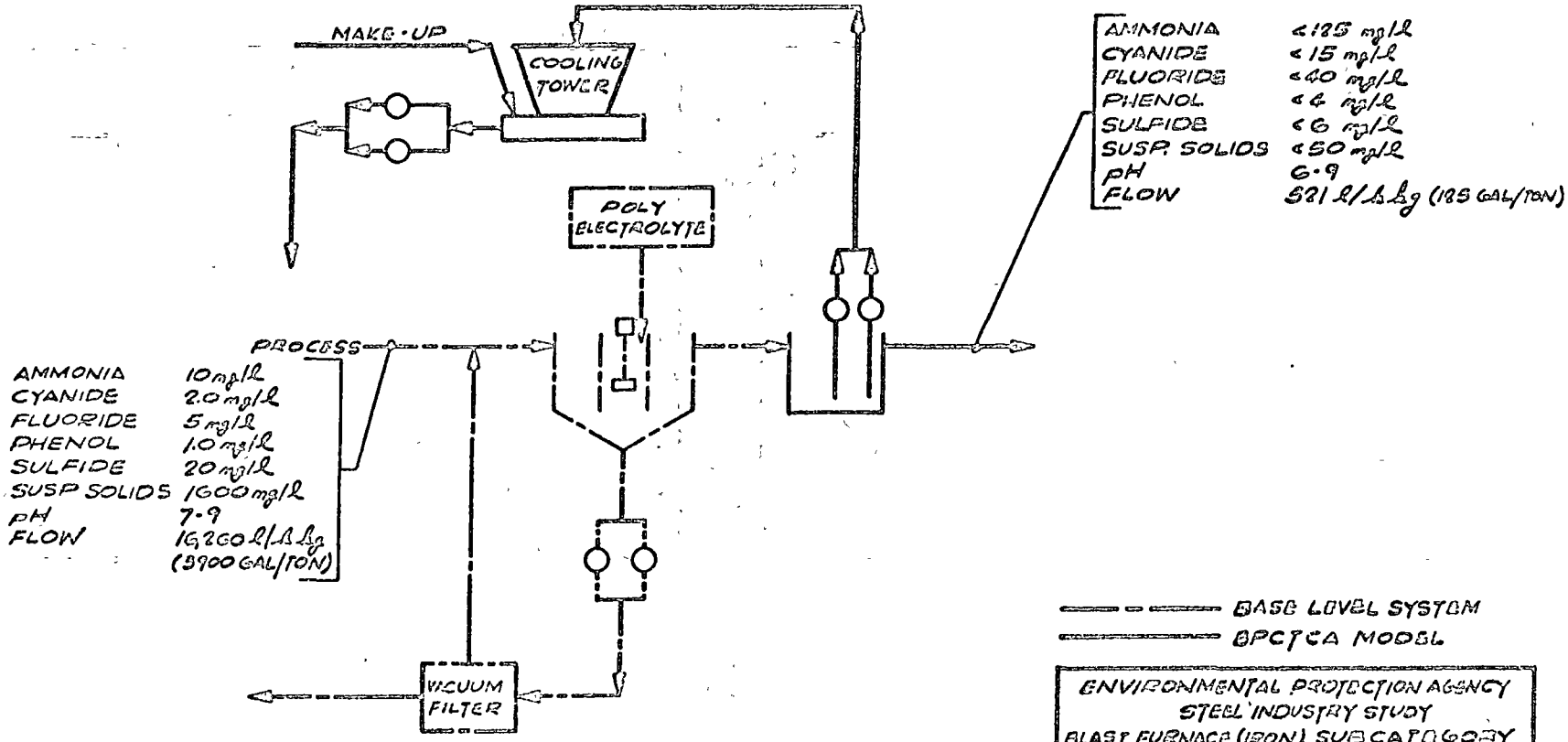
BASE LEVEL SYSTEM
BPCTCA / BATEA MODEL

ENVIRONMENTAL PROTECTION AGENCY STEEL INDUSTRY STUDY BEEHIVE COKE SUBCATEGORY BPCTCA MODEL	
11-19-73	FIGURE 2



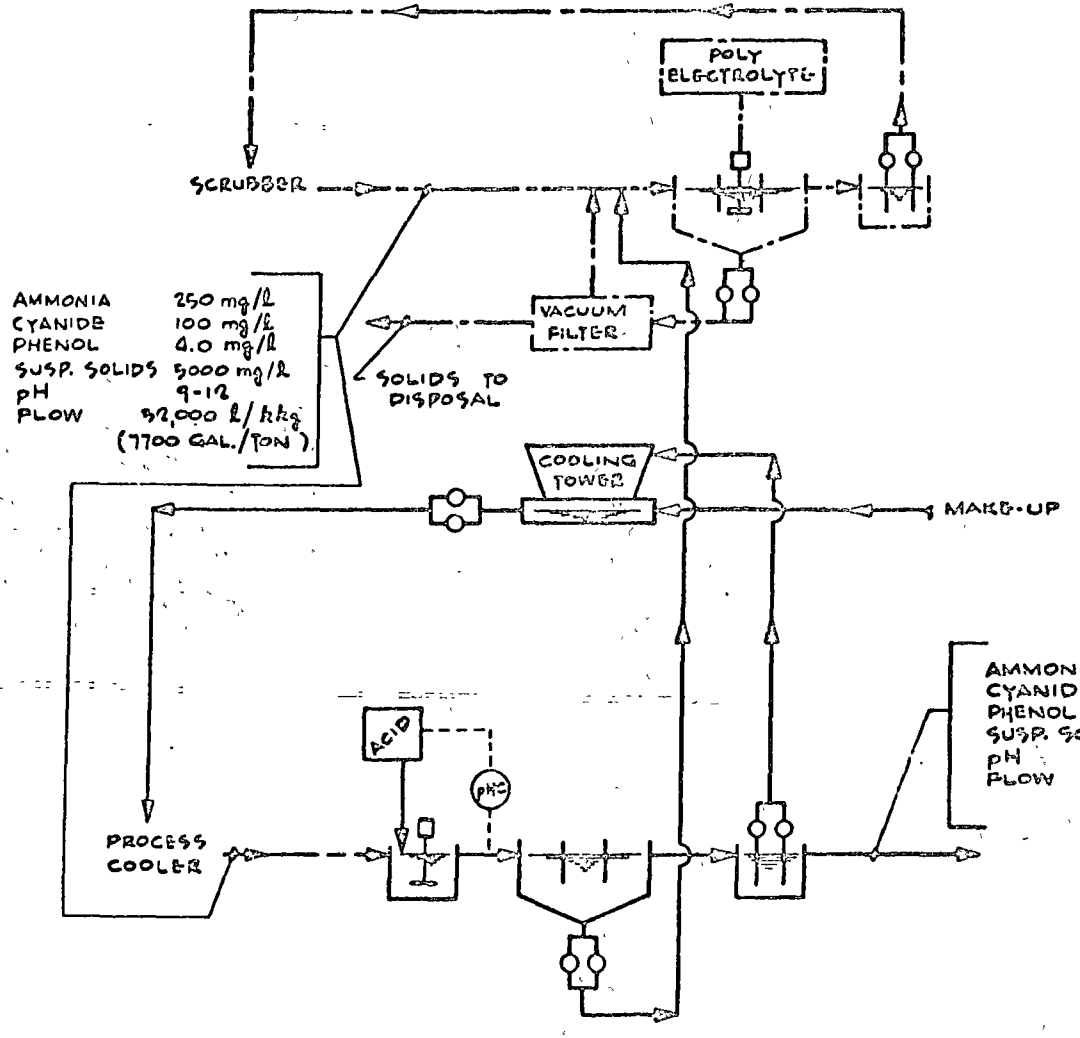
ENVIRONMENTAL PROTECTION AGENCY
STEEL INDUSTRY STUDY
SINTERING SUBCATEGORY
DPCTCA MODEL

11-14-73	FIGURE 3



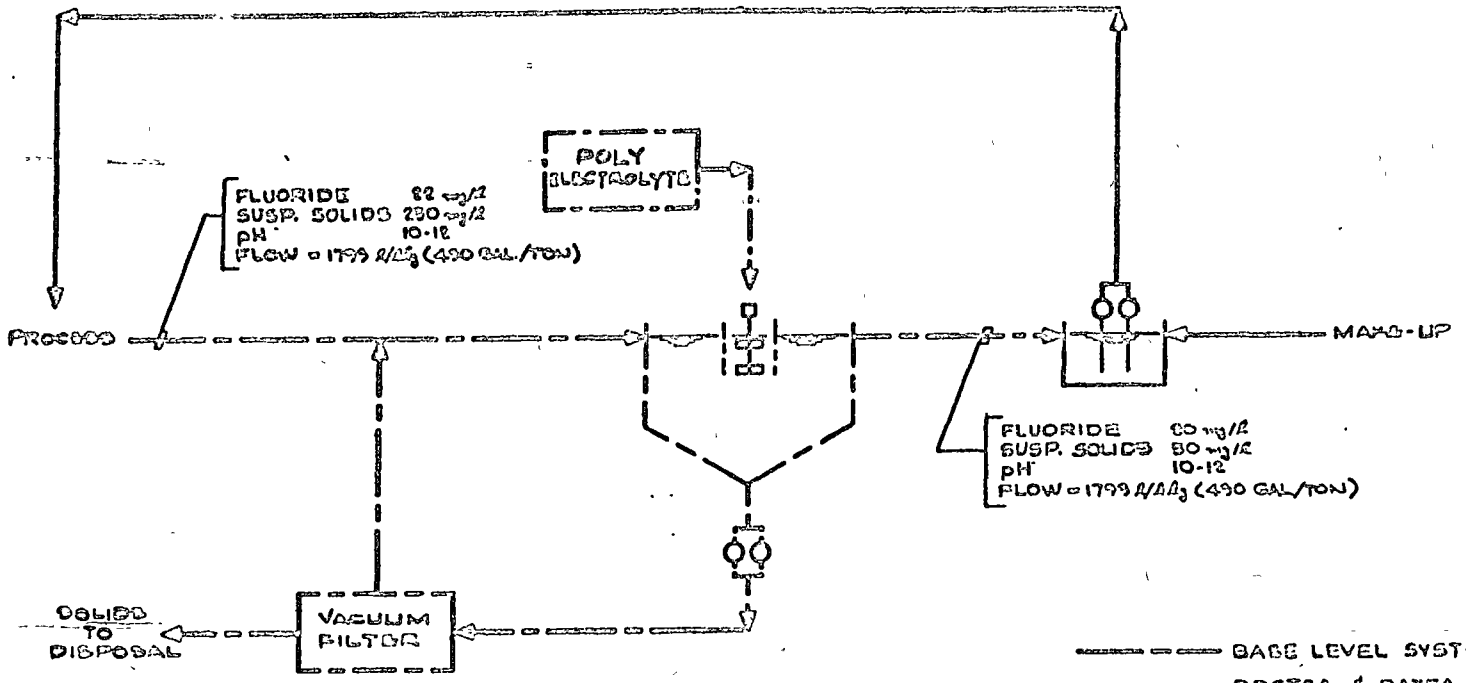
ENVIRONMENTAL PROTECTION AGENCY
STEEL INDUSTRY STUDY
BLAST FURNACE (IRON) SUBCATEGORY
BPCTCA MODEL

11-13-73	FIGURE 4



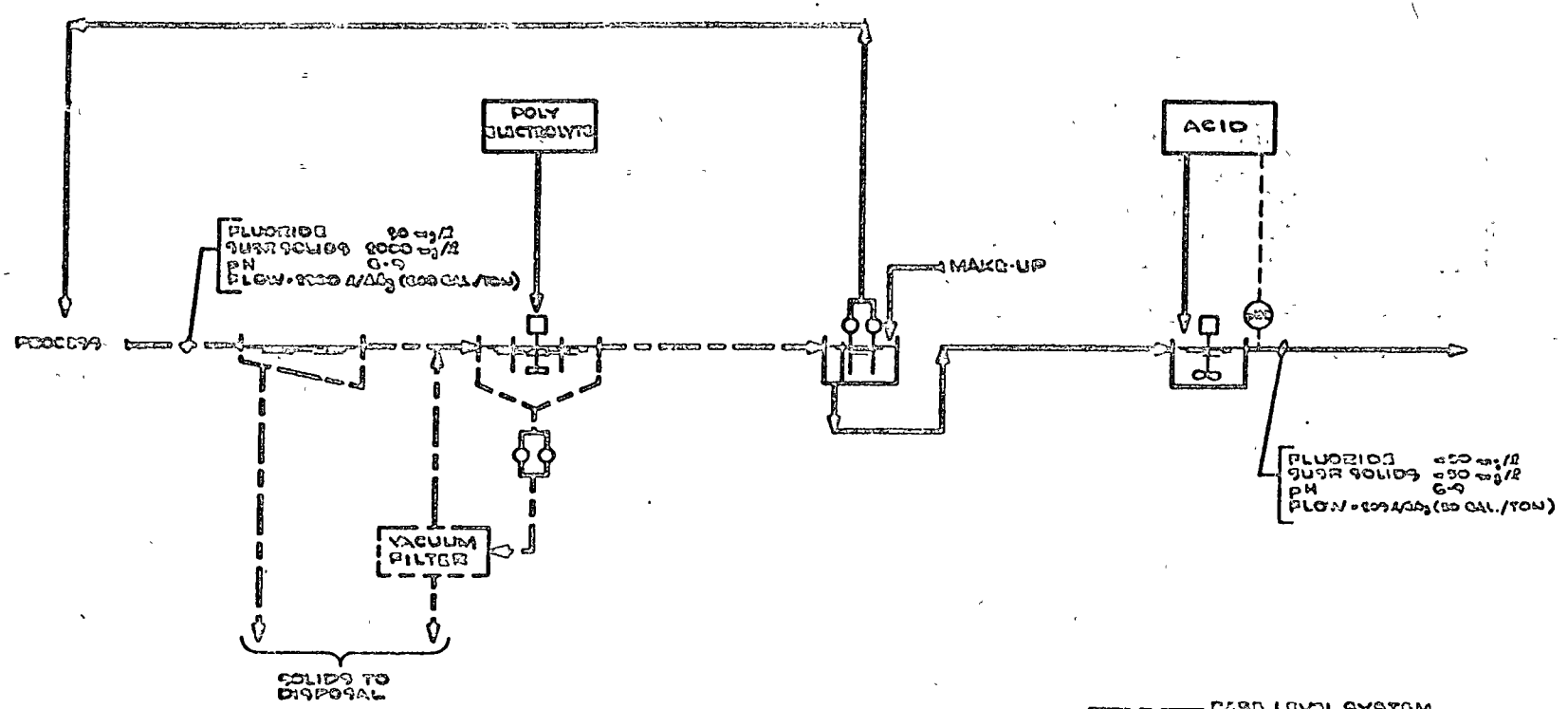
BASE LEVEL SYSTEM
BPCTCA MODEL

ENVIRONMENTAL PROTECTION AGENCY STEEL INDUSTRY STUDY BLAST FURNACE-FERROMANGANESE SUBCATEGORY BPCTCA MODEL	
11-13-79	FIGURE 5



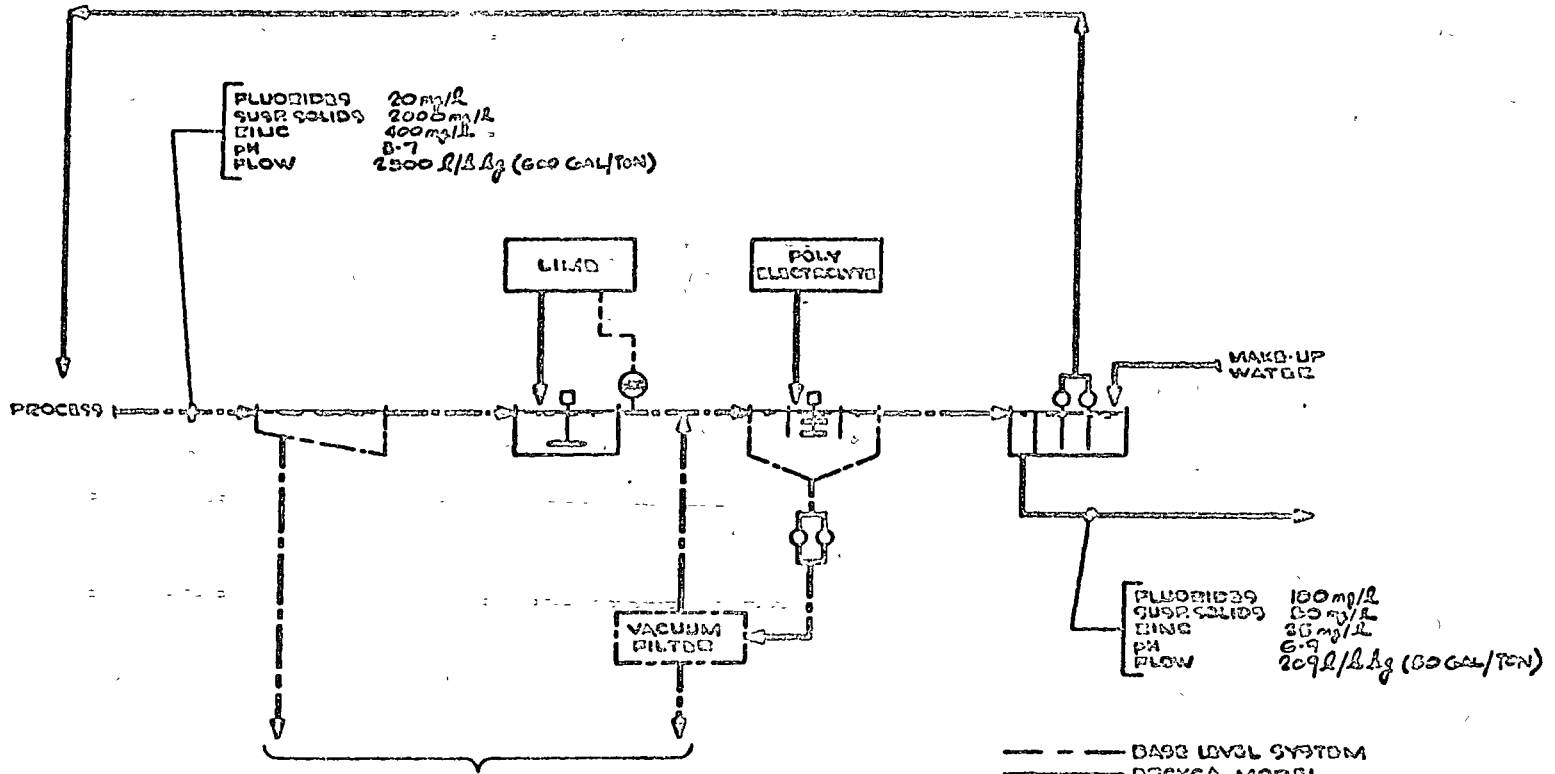
ENVIRONMENTAL PROTECTION AGENCY
STEEL INDUSTRY STUDY
BASIC OXYGEN FURNACE (SEMI-WET)
SUBCATEGORY
BPCTCA MODEL

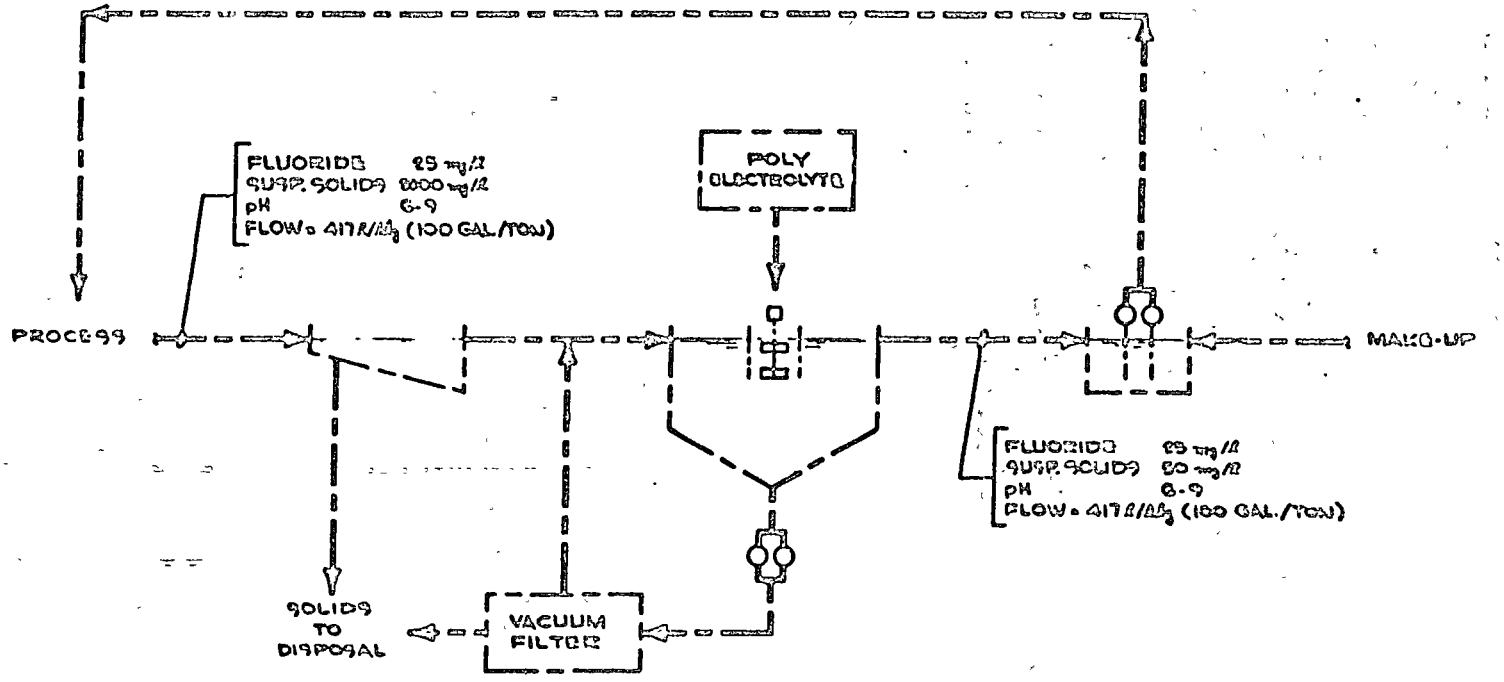
11-13-73	FIGURE 6



CASE LEVEL SYSTEM
DPCTCA MODEL

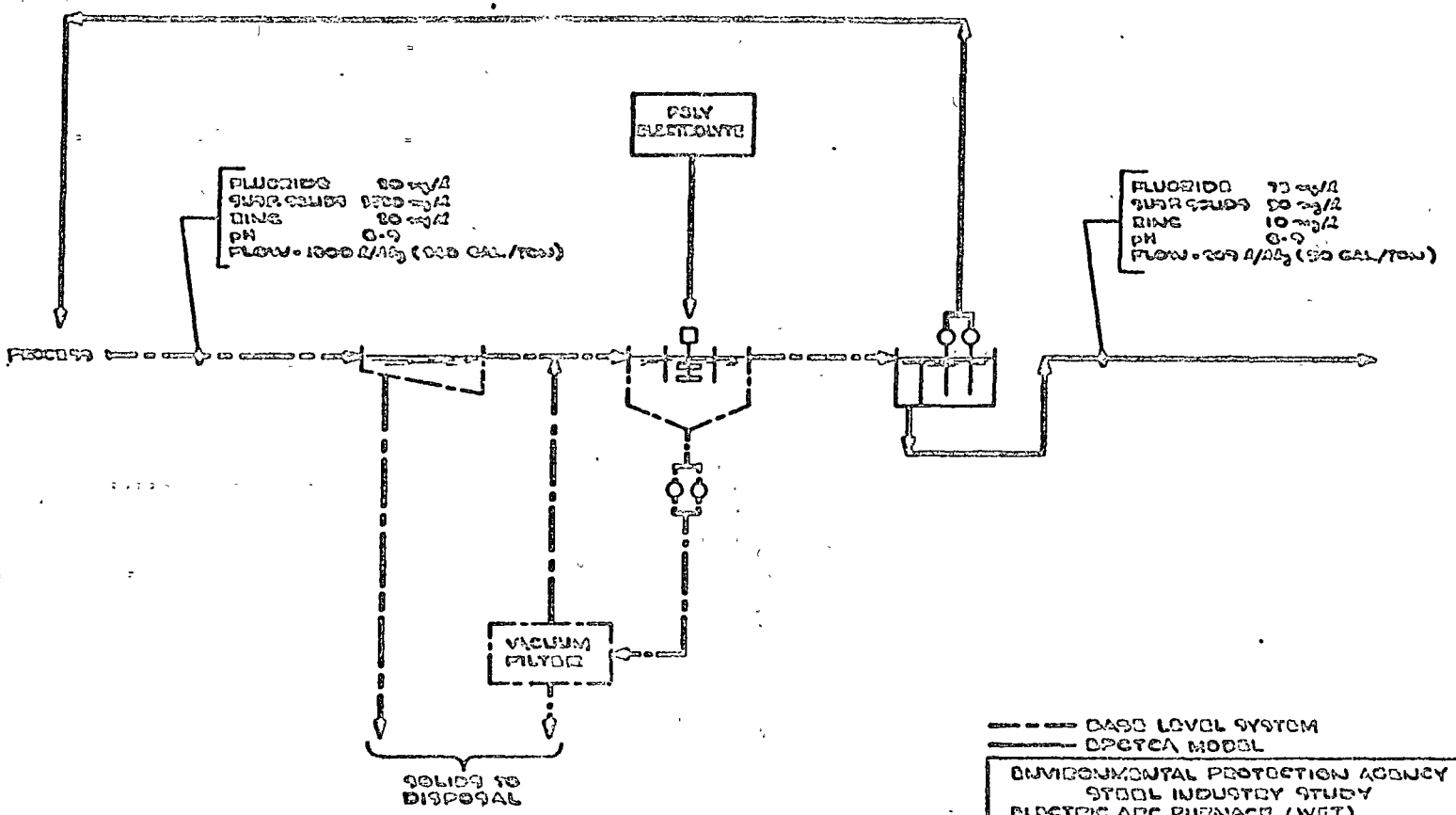
ENVIRONMENTAL PROTECTION AGENCY STEEL INDUSTRY STUDY BASIC OXYGEN FURNACE (WET) SUBCATEGORY DPCTCA MODEL	
11-16-79	FIGURE 7


FLUORIDES 20 mg/L
SUSP SOLIDS 2000 mg/L
ZINC 400 mg/L
PH 8-7
FLOW 2500 L/kg (600 GAL/TON)
LIME
POLY ELECTROLYTE
MAKE-UP WATER
PROCESS
VACUUM FILTER
SOLIDS TO DISPOSAL
FLUORIDES 100 mg/L
SUSP SOLIDS 50 mg/L
ZINC 20 mg/L
PH 6-9
FLOW 2090 L/kg (500 GAL/TON)
BASE LEVEL SYSTEM
OPCYCA MODEL
ENVIRONMENTAL PROTECTION AGENCY
STEEL INDUSTRY STUDY
OPEN HEARTH FURNACE SUBCATEGORY
OPCYCA MODEL
11-13-79
FIGURE 8

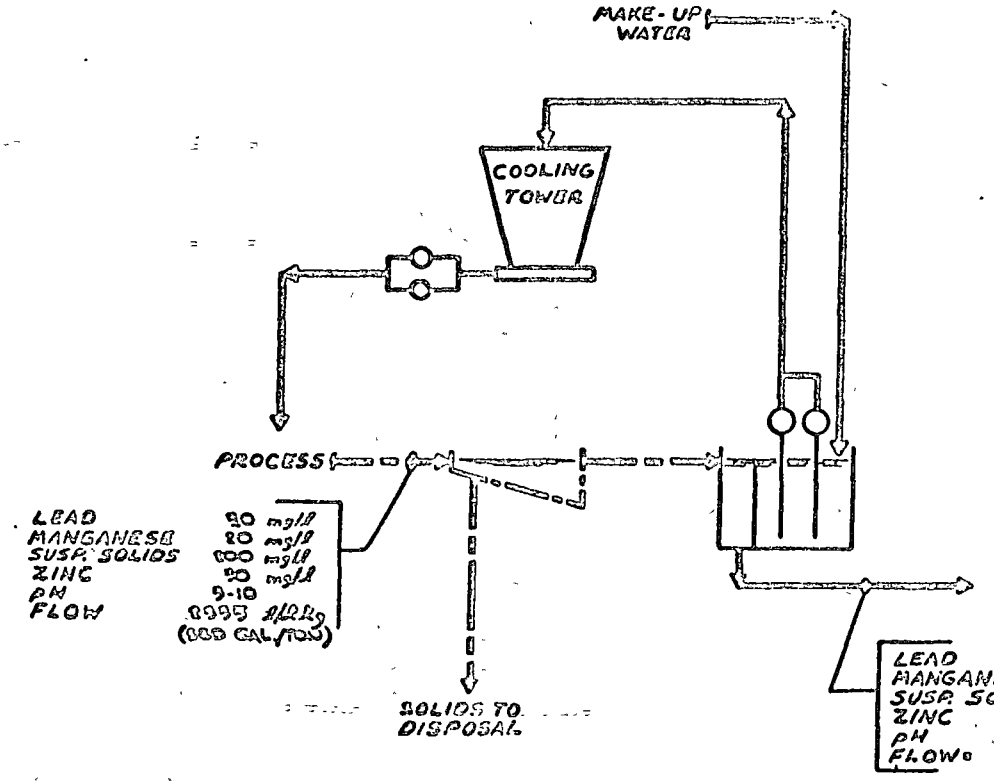


— — — BASE LEVEL @ BPCTCA MODEL

ENVIRONMENTAL PROTECTION AGENCY STEEL INDUSTRY STUDY ELECTRIC ARC FURNACE (SEMI-WET) SUBCATEGORY BPCTCA MODEL	
11-19-79	FIGURE 9



ENVIRONMENTAL PROTECTION AGENCY STEEL INDUSTRY STUDY ELECTRIC ARC FURNACE (WET) SUBCATEGORY DPETCA MODEL	
11-13-79	FIGURE 10

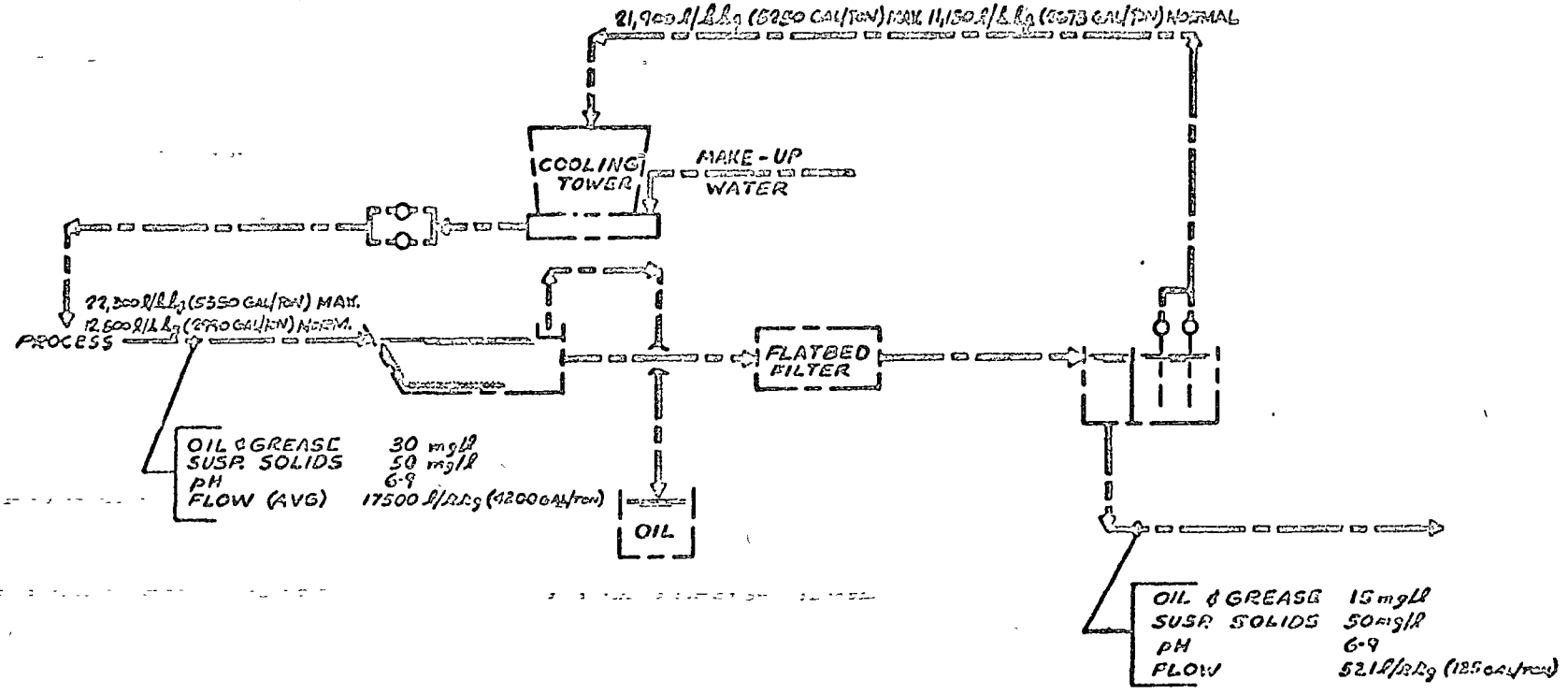


BASE LEVEL SYSTEM

BPCTCA MODEL

ENVIRONMENTAL PROTECTION AGENCY
STEEL INDUSTRY STUDY
VACUUM DEGASSING OPERATION
BPCTCA MODEL

11-14-73 | FIGURE 11



ENVIRONMENTAL PROTECTION AGENCY
STEEL INDUSTRY STUDY
CONTINUOUS CASTING SUBCATEGORY
BPCTCA MODEL

11-19-79 | FIGURE 12

In this process dirt, salt, blood, manure, and nonfibrous proteins are removed from the hides. There is considerable variation in the quantity of such waste material, depending on the time of year and the source of the hides.

Depending on the type of leather produced, additional washes (rinses) may also occur at several other points in the tanning process, including after liming and dehairing, after bating, after tanning, and prior to and following coloring.

Unhairing -- Hair is removed by chemical loosening followed by either machine pulling or chemically dissolving the hair. Machine removal is practiced where it is desired to recover the hair. The dissolving process is referred to as "pulping" or "burning."

For either type of unhairing, the hides are placed in vats (with or without paddles), drums, or hide processors with a lime slurry to which sharpeners such as sodium sulfide and sodium sulfhydrate are added. When the hair is to be saved, the strength of the solution and the time in contact with the hide is limited to that necessary to loosen the hair sufficiently for mechanical pulling. If the hair is to be pulped, stronger solutions and/or longer time cycles are used and the hair may be totally dissolved.

Sometimes hides are relimed to make the hide swell for easier splitting. In a save hair operation, flesh and hair removal is sometimes followed by a "scudding" step to ensure removal of hair roots and fine hairs.

The liming and unhairing process is one of the principal contributors to the waste effluent. In a save hair operation with good recovery of hair, the contribution to the effluent is substantially lower than in the pulp hair operation.

2. Tanhouse

(a) Bating -- Bating is the first step in preparing the stock for the tanning process. It may be done in either vats (with or without paddles), drums, or

hide processors. The hides are placed in the processing equipment which contains a solution of ammonium salts and enzymes. The purpose of this operation is to:

1) De-lime skins

2) Reduce swelling

3) Peptize fibers

4) Remove protein degradation products

(b) Pickling -- The pickling follows the bating step and is normally done in the same equipment. A brine and acid solution is used to bring the hides to an acid condition in preparation for subsequent tanning sub-process. In addition to conditioning the hide for receiving the tanning agent, it prevents precipitation of chromium salts.

Pickling is always done before the chrome tanning process and may be done before vegetable tanning.

(c) Tanning -- Nearly all cattlehides in this country are either chrome or vegetable tanned; very little is tanned with alum or other tanning materials.

Vegetable tanning is the older process, and is performed in a solution containing plant extracts such as vegetable tannins. This method is usually used for the heavy leathers such as sole leather, mechanical leathers, and saddle leathers. Shoe upper leathers and other lighter leathers are usually chrome tanned by immersion in a bath containing proprietary mixtures of basic chromium sulfate.

Vegetable tanning is usually done in vats, principally due to longer process times, while chrome tanning takes place in drums or hide processors.

In some cases, depending on type of leather being produced, hides are tanned in the tanhouse and later retanned as a part of the retan, color, fatliquor process. Where different tanning agents are used in the initial and retan steps, it is referred to as combination tanning.

Waste effluents from the tanning process are substantial. Recycle of vegetable tan solutions is becoming more common in the industry; that which cannot be recycled may

be used for retanning or evaporated and recovered. Recycle and recovery of chrome tanning solutions is also practiced at a few locations.

(d) Splitting -- The tanned hide is split to produce a grainside piece of essentially constant thickness and a flesh side layer. The flesh side layer or split can be processed separately or sold to split tanners.

3. Retan, Color, Fatliquor

(a) Retan -- Retanning is done to impart different characteristics in the finished leather; using chrome, vegetable, or synthetic tanning agents.

(b) Bleaching -- Bleaching hides with sodium bicarbonate and sulfuric acid after tanning is commonly practiced in the sole leather industry.

(c) Coloring -- Coloring is done in the same drums as retanning, and may be done either before or after fatliquoring.

(d) Fatliquoring -- This operation adds oils replacing the natural oils lost in the beamhouse and tanhouse processes and to make the leather pliable.

Liquid wastes from the retan, color, and fatliquor process may be high volume-low strength compared with the other processes.

4. Finishing

Finishing operations such as drying, wet-in coating, staking or tacking, and plating which follow the wet processes provide only minor contributions to the liquid waste primarily from cleanup of the paster drying plates and from paint spray booth water baths.

Trimmings are disposed as solid waste, and dust collected may be disposed in either wet or dry form.

Sheepskin Tannery Processes: In this process, like pigskin tanning, there is no beamhouse process and degreasing is required. The three major processes are: (1) tanhouse; (2) retan, color, and fatliquor; and (3) finishing.

2. Tanhouse

(a) Receiving -- Skins are salted, cured, and tied in bundles of one dozen skins. These skins have had the wool removed at the packer or wool pullery and processed to the pickled condition. The wool pulling represents a beamhouse process.

Skins tanned with the wool intact are referred to as shearlings. Tanning of these skins does not involve a beamhouse process.

Pickled skins have been preserved for shipment and storage by immersion in a solution of brine and acid. Shearling skins are cured in a salt brine only. Excess solution is drained prior to bundling.

(b) Storage -- Pickled skins held for extended periods should be kept below 30°C (86°F) to avoid deterioration.

(c) Fleshing -- Fleshings and trimmings are normally collected and disposed of as a solid waste.

(d) Degreasing -- Grease is recovered as a by-product from those skins which have had the wool removed. When solvent degreasing is used, the solvent is recovered and reused.

Skins with the wool on (shearlings) require substantially more water in the washing (scouring) operations and grease recovery is not normally practiced.

There is a waste effluent from this process and a small amount of vapor, including solvent exhausted to the atmosphere.

(e) Tanning -- Sheepskins may be either chrome or vegetable tanned, although the majority are chrome tanned.

(f) Refleshing -- In some cases, there is a refleshing operation following tanning, which produces a small amount of solid waste.

2. Color and Fatliquor

(a) Coloring -- Skins to be colored are immersed in a dye solution in drums. Generally, synthetic dyes are used.

Some bleaching may be done prior to coloring of shearlings.

(b) Fatliquoring -- This operation is performed in the same drum used for coloring. Skins are immersed in a solution containing various oils to replace the natural oils of the skin lost in the tanning process.

3. Finishing

This is an essentially dry process, and the only liquid waste contributed is from cleanup operations.

Solid wastes from the finishing operation include trimmings and skivings. Dust from the sanding and buffing operations may be collected dry and disposed of as a solid waste or wet and carried into the waste water system.

Pigskin Tannery Processes: In this operation there is essentially no beamhouse process. Hair is removed at the packing house. The tanhouse, color and fatliquor and finishing processes are generally similar to those mentioned previously.

Waste Constituents

Wastes in tanneries are derived from the following:

Hair	Lime	Sugars
Hide scraps	Soluble protein	Starches
Flesh	Sulfides	Oils, fats
Blood	Amines	Detergents
Manure	Chromium salts	Acids
Dirt	Tannin	Dyes
Salt	Soda ash	Solvents

The BOD contribution from a typical cattlehide tannery may be as follows:

Soak	20%
Unhair	52%
Re-lime	2%
De-lime and Bate	13%
Pickle	4%
Chrome Tan	6%
Color and Fatliquor	2%

Figure 4 shows potential pollution sources in terms of BOD, flow and SS. The beamhouse produces the largest load. However, the wastewater flow for various production units is highly variable, Fig. 5.

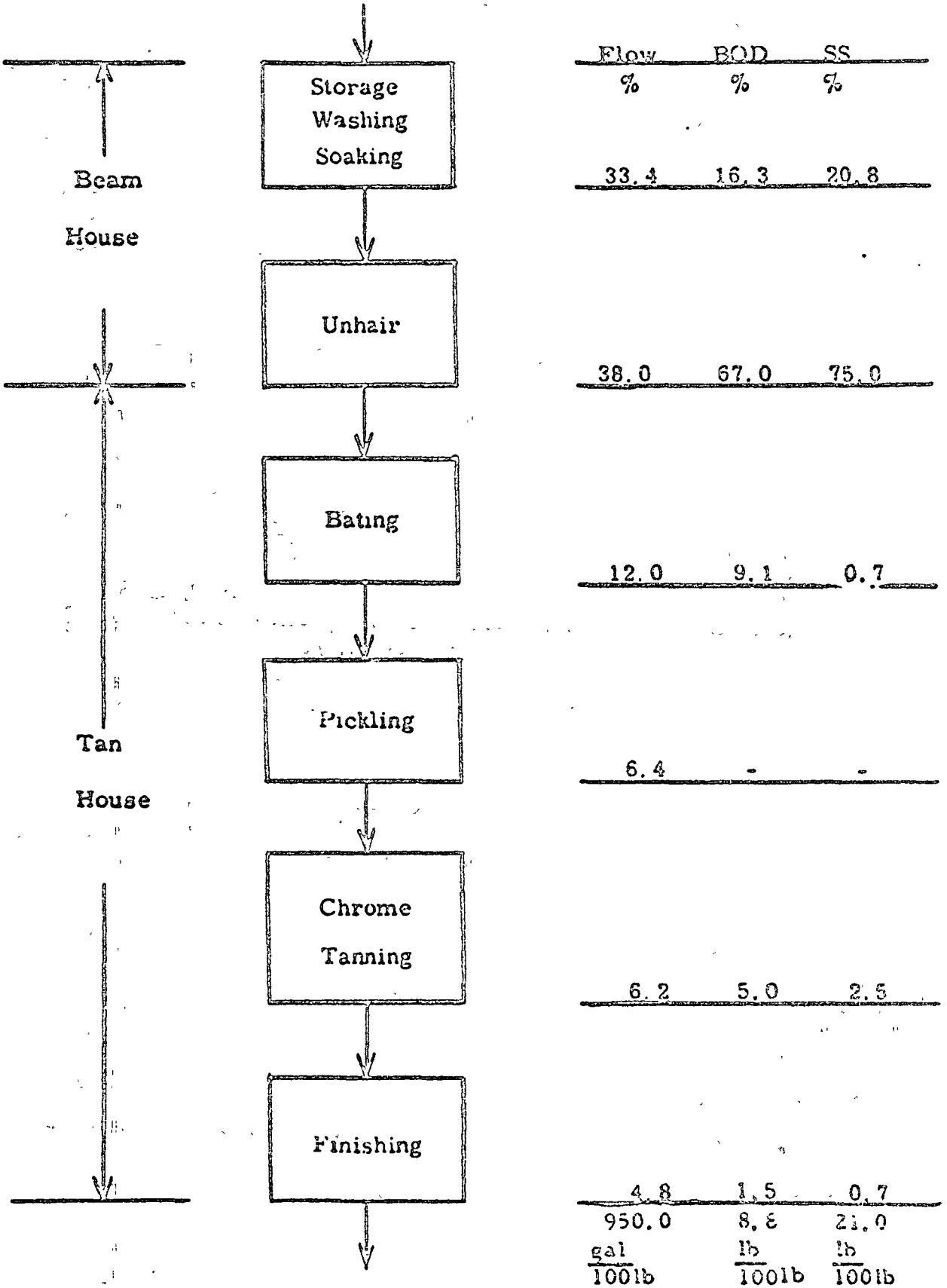


Fig. 4 Potential Pollution Sources - Tannery

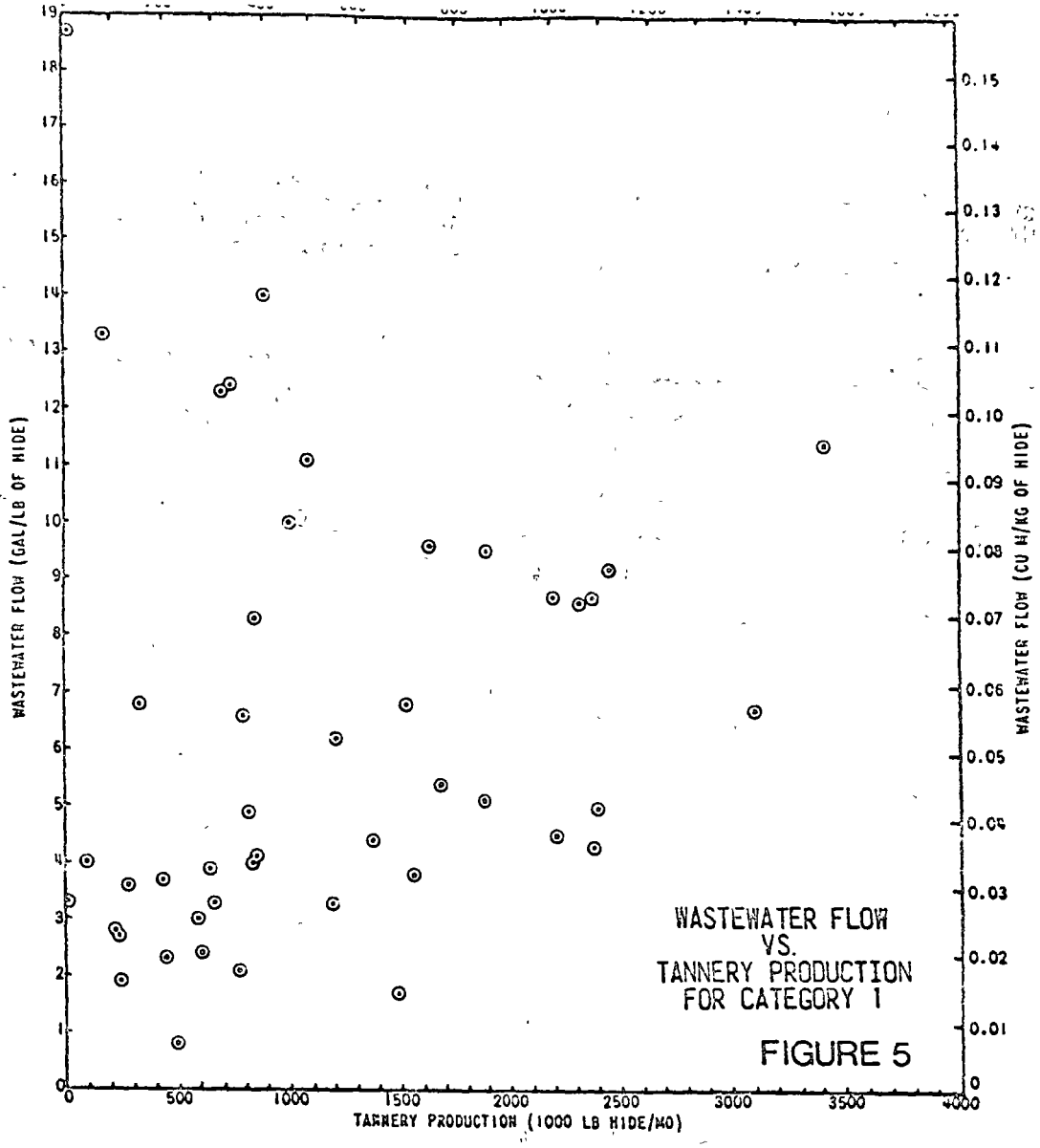


FIGURE 5

Typical characterization of waste from a hide curing operation is as shown in Table 1.

Table 1. Hide Curing

Waste Characteristics	Concentration (mg/l)	kg/1,000 kg Hide (lb/1,000 lb Hide)
BOD_5	15,610	3.9
COD	29,610	7.4
Total Solids	280,500	70.1
Suspended Solids	10,400	2.6
Oil and Grease	40,200	10.0
Water Use, l/kg (gal/lb)	0.24 (0.03)	

Wastewater Treatment

The following unit processes appear necessary to meet the present water pollution control standards.

1. Equalization
2. Primary sedimentation
3. Carbonation and sedimentation
4. Addition of municipal sewage
5. Activated sludge treatment
6. Sludge dewatering by centrifuge
7. Effluent chlorination

Equalization, carbonation with flue gasses, and sedimentation are desirable. Equalization is an important unit process for minimizing variations in discharge flows and waste strength. Based on the quantity and quality of the tannery discharge, a minimum of 4 hours is probably required.

Primary sedimentation basins designed with an overflow rate of 32.9 cu m/day/sq m (700 gpd/sq ft) should produce a sludge with 8 percent solids. Heavy duty sludge removal equipment will be required due to the volume and density of the sludge produced.

Pilot tests indicate that carbonation after equalization provides a rapid absorption of carbon dioxide (CO_2) gas. A contact time of 20 minutes was sufficient for flue gas carbonation. The resulting calcium carbonate precipitate is expected to aid in the removal of other suspended solids by sedimentation prior to secondary treatment.

A volumetric loading of about 973 kg BOD 5/day/1,000 cu m (60 lb BOD5/day/1,000 cu ft) for the aeration basin with aeration capacity of 123 kw (165 hp) is proposed for combined treatment. Tests indicate foaming may be an operational problem. The fullscale design should include provisions for surface sprays and chemical addition.

The biological floc produced in the pilot aeration basin was found to be very light and settled with difficulty. An overflow rate not to exceed 23.5 cu m/day/sq m (500 gpd/sq ft) is proposed for secondary sedimentation. Upon resettling of the waste secondary sludge in the primary clarifier, a mixture resulted which dewatered readily on drying beds. Since large

volumes of sludge are produced, excessive amounts of land would be required for drying beds. Sludge is, therefore, proposed to be dewatered in a solid bowl centrifuge with the resulting cake containing 20 to 30 percent solids hauled to a sanitary landfill.

A two-stage biological treatment plant, 1,514 cu m/day (0.4 mgd), receiving combined municipal and tannery sewerage has been used successfully (Nemerow). The treatment system consisted of the following processes:

1. Primary sedimentation
2. Roughing filter
3. Activated sludge
4. Secondary sedimentation

The primary sedimentation unit with overflows between 15.5 and 23.0 cu m/day/sq m (330 and 490 gpd/sq ft) produced removal efficiencies of 48 percent for BOD5 and 24 percent for suspended solids. Comparable values with polymers were 75 percent and 39 percent, respectively (24). The organic load on the filter ranged from 1,135 to 3,242 kg BOD5/day/1,000 cu m (70 to 200 lb BOD5/day/1,000 cu ft) with BOD5 removals of 37 and 30 percent, respectively (24). The activated sludge unit produced the highest organic removal efficiency (85 percent) at food to active mass (F/M) ratio of 0.2. The mixed liquor suspended solids (MLSS) concentrations in the parallel basins were maintained at 2,000-3,500 mg/l. Flotation thickeners without polymers were loaded at 5.9 to 17.1 kg/sq m/hr (1.2 to 3.5 lb/sq ft/hr) and consistently produced sludge concentrations of 5 percent. Total system BOD5 removals ranged between 80 to 90 percent.

In general, combined treatment is viable if proper design considerations assessing the effects of tannery waste waters are considered.

The present U. S. Guidelines utilize the best practical effluent limitations, Table 2 and best available effluent limitations, Table 3.

Table 2. Best Practicable Effluent Limitations

Maximum Thirty Day Average
(July 1, 1977)

PARAMETER (1)	SUBCATEGORY kg/1000 kg hide (lb/1000 lb hide)					
	1	2	3	4	5	6
BOD5	4.0	4.6	3.8	1.6	4.8	2.8
TOTAL CHROMIUM	0.10	0.12	0.05	0.10	0.06	0.10
OIL & GREASE	0.75	0.90	0.75	0.25	0.90	0.35
TSS	5.0	5.8	4.8	2.0	6.0	3.4

(1) For all subcategories pH should range between 6.0 and 9.0 at any time.

Table 3. Best Available Effluent Limitations
(July 1, 1983)

PARAMETER(1)	SUBCATEGORY kg/1000 kg hide (lb/1000 lb hide)					
	1	2	3	4	5	6
BOD5	1.40	1.60	1.30	0.50	1.60	0.70
TOTAL CHROMIUM	0.05	0.06	0.05	0.02	0.06	0.03
OIL & GREASE	0.53	0.63	0.50	0.24	0.63	0.34
SULFIDE	0.005	0.006	0.005	0.002	0.006	0.003
TSS	1.5	1.8	1.4	0.6	1.8	0.8
TKN	0.27	0.32	0.25	0.10	0.31	0.14

(1) For all subcategories pH should range between 6.0 and 9.0 at any time

For all subcategories Most Probable Number (MPN) of Fecal Coliforms should not exceed 400 counts per 100 ml

Table 4. Chemical Characteristics of Alum Tanning Process Wastes at The Caldwell Lace Leather Company*

Parameter	Washing and Soaking	Lime Pit Discharge	Lime Washout	Bate and Delime Washout	Spent Alum Tanning Liquor	Spent Dye Solution
Conductivity, micromhos/cm	13,800 -	27,000 -	2,600 -	4,400 -	60,000 -	- -
pH	7.2 6.8-7.4	12.1 11.9-12.3	11.1 10.9-11.3	8.8 8.7-8.9	3.3 3.2-3.6	3.4 -
Phenolphthalein Alkalinity, mg/l as $CaCO_3$	- -	4,980 3,810-6,150	180 130-225	160 130-190	- -	- -
Total Alkalinity, mg/l as $CaCO_3$	215 140-295	6,240 4,970-7,500	380 335-430	460 430-480	- -	- -
Mineral Acidity, mg/l as $CaCO_3$	- -	- -	- -	- -	13,400 9,000-20,200	9,600 -
Total Acidity, mg/l as $CaCO_3$	25 0-40	- -	- -	- -	22,100 20,000-27,400	17,200 -
Chlorides, mg/l as Cl^-	5,100 2,590-8,250	11,980 8,350-15,600	580 530-630	940 710-1180	33,160 24300-38700	25,480 25250-25700
Total Hardness, mg/l as $CaCO_3$	210 -	6,480	280 -	540 -	- -	- -

*Values tabulated are averages with range underneath

Because of the difficulty of determining the final quantity or the precise effect of the dye waste on the treated final effluent, an agreement was reached with the state pollution control authorities whereby color removal facilities would not be initially installed so long as they can be added later if found to be necessary. This has not been found necessary.

4. Screening and Equalization - Screening of the waste is mandatory to remove hair, flesh particles, and bits of leather from the waste stream. Preliminary studies were conducted using a vibrating screen, but during construction, a sloping slotted screen was substituted. This type of screen had just appeared on the market and was especially recommended for applications such as this.

5. Equalization Basin - Because of the variations in waste flow and characteristics and the necessity of operating the biological process on weekends when the plant is not in operation, some type of equalization basin was necessary.

For an average weekly flow of approximately 160,000 gallons it was proposed to feed the waste to the treatment plant as follows:

Weekdays - 1500 gallons per hour from 7 am to 5 pm
750 gallons per hour from 5 pm to 7 am

Weekends - 750 gallons per hour

This pumping schedule results in a daily design flow of 25,500 gallons per day for weekdays and a weekly flow of 163,500 gallons. Design of sedimentation basins and other facilities with short detention times was based on the daytime flowrate of 1500 gallons per hour or 25 gallons per minute. The average weekday flowrate of 25,500 gallons per day is 17.7 gallons per minute.

If an equalization basin of 50,000 gallons or less had been constructed, it would have been necessary to schedule the pumping rates to the treatment units so that the basin was essentially empty on Monday morning. This would have resulted in unequalized, undiluted waste being pumped directly to the treatment units on Monday morning. To prevent this, a basin of 62,500 gallons capacity was provided so that a buffer volume of 12,000 to 15,000 gallons of waste remains in the tank at the start of operations on Monday morning.

A 10-hp mechanical mixer is mounted on beams above the tank, and has turbine blades located near the bottom of the tank. An air compressor provides about 10 cfm of air, released below the turbine blades, to prevent anaerobic conditions.

6. Primary Clarifier - A surface loading of 635 gallons per day per square foot and a detention of 1.5 hours was provided for the primary clarifier at the design flow of 1500 gallons per hour. A conical hopper bottom with a 60-degree slope provides for storage and some compaction of sludge. A chamber was provided on the outside of the tank to provide a two-minute reaction time with the coagulant aid prior to entering the settling basin.

7. Aeration Basin - The report recommended a loading of about 0.70 pounds COD per day per pound of mixed liquor volatile suspended solids. A basin with capacity of one day's average flow of 25,500 gallons was provided.

The design load is 3,000 pounds of COD per week, and 50% of this load was assumed to be removed in the primary clarifier, thus leaving 1,500 pounds of COD to reach the biological process. At the proposed treatment rates the plant will handle 25,500 gallons per day for five days, or a daily flow of 15.6% of the weekly flow. Thus, the design daily COD load to the biological process was 234 pounds and the maximum day of 36,000 gallons would provide 330 pounds of COD.

The design for the maximum day COD required 330/.70 = 472 pounds of MLVSS. At the average day flow, the loading would be 0.50 pounds of COD per day per pound of MLVSS. In a basin of 25,500 gallons capacity this would result in a MLVSS concentration of 2,220 mg/l and a total MLSS concentration of 3,470 mg/l, which is the approximate concentration at which the pilot tests were run.

Oxygenation is provided by a 5-hp mechanical surface aerator. Calculations indicated that a 3-hp unit would have been sufficient, but a 5-hp unit was provided to give a slight margin of safety.

8. Final Clarifier - A circular center-feed clarifier with a 45-degree conical bottom was provided following the aeration basin. The surface loading at the design flow of 1500 gallons per hour is 653 gal/day-sq ft, and the detention time is two hours. Settled sludge is pumped continuously from the point of the cone.

9. Sludge Concentration and Storage Tank - The laboratory data showed that after one hour of settling the sludge volume is about 25 percent of the original and that after 14 hours of settling the volume of sludge is reduced to about one-half of the one-hour volume. On the basis of 25,500 gallons flow per day, this would result in a 3,190 gallons of primary sludge per day. Waste activated sludge was projected at about 1,000 gallons per day at 1 percent solids concentration. Thus, the expected solids volume was 4,190 gallons per day. A circular tank with a conical bottom was constructed to provide 12,570 gallons of sludge storage, or about three days production.

This capacity was considered to be conservative, since this sludge volume was based on the total flow from the plant, whereas the sludge volume measurements were made on the composite alum tanning process waste alone. Additional storage time in the sludge storage basin was expected to result in an increase in the solids concentration and, thus, in a lesser quantity of sludge to be hauled away.

Piping was provided from the sludge storage tank to the suction of the raw waste pumps and an alternate pump discharge line was provided for filling the tank truck.

10. Lime Waste Storage - Lime waste is discharged from the beam house vats every other work day, making four days one week and three days the next week. The volume of the solution added to the vats is approximately 2,200 gallons. It is desirable to distribute this flow somewhat evenly into the equalization basin, so a new 2500-gallon storage tank for this purpose was provided.

11. Nutrient Requirements - The laboratory studies found that the industrial waste does not contain sufficient phosphorus to support the biological life in the system. The phosphorus required is one pound per 100 pounds of BOD applied to the secondary system. The average weekly BOD load is 916 pounds, so 9.16 pounds of phosphorus per week would be required.

The most economical source of phosphorus is Triple Super Phosphate fertilizer which contains 42 percent P_2O_5 and costs approximately $5.00 per 100 pounds. About 50 pounds of Triple Super Phosphate is required per week so, ten pounds of the fertilizer was originally added to the qualization basin each working day of the week.

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COAGULATION AND PRECIPATION IN THE REMOVAL OF ORGANICS FROM INDUSTRIAL WASTEWATER[1]

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Jim M. Eller, P.E.[3]

INTRODUCTION

Pretreatment is usually required to remove suspended matter, but the removal of soluble organics during pretreatment should not be overlooked. The objective of this paper is to establish the importance of lime pretreatment for removal of organics. Specifically, case histories are provided to illustrate the role of pretreatment for the removal of (a) insoluble hydrocarbons, (b) soluble and insoluble hydrocarbons plus inorganic particulates, (c) soluble hydrocarbons and co-precipitated hydrocarbons, and (d) organic particulates and precipitated inorganics. The scope of this paper is to include discussion on: (a) neutralization, (b) coagulation, (c) flocculation, and (d) gravity separation.

The design of industrial wastewater treatment plants, usually entails three major efforts: (a) a detailed wastewater characterization; (b) evaluation of appropriate treatment processes; and (c) designing an efficient facility that may be operated easily and one in which expansion and process changes can be made with minimum difficulty. As industrial operations continue to grow in complexity it is necessary to evaluate a greater

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to 80 percent of the organic load on the existing treatment facilities. A wastewater characterization survey indicated that segregation and separate treatment of the more concentrated waste streams would provide an efficient and economically attractive means to enhance the overall wastewater treatment program. However, it was also recognized that the characteristics of the selected streams would preclude effective secondary treatment without appropriate pretreatment. The pH varied from 2 to 10, but usually the mean was close to 6, due to in-plant neutralization units. The COD ranged between 1,000 mg/l and 24,000 mg/l. For two major streams, the means of the COD were 4,000 mg/l and 5,500 mg/l; means of the BOD_5 were 1,700 mg/l and 2,600 mg/l with a range from 400 mg/l to 8,000 mg/l; the means of the TSS values were 450 mg/l and 700 mg/l with a range of 40 mg/l to 5,000 mg/l. Obviously, effective pretreatment was imperative for successful application of secondary biological treatment. Concern centered about not only the fluctuating pH, but also the periodic high solids and organic loadings. In fact, these inordinate wastewater characteristics, dictated that the proposed treatment system be proven and refined by the construction and operation of a pilot unit. Primary treatment consisted of individual equalization, pH adjustment and sedimentation. The pH was adjusted to 8.5 - 10.5 with the use of lime. Co-precipitation was quite evident upon mixing of the two streams, and this process was enhanced by pH adjustment.

The third case, a Viscose Rayon Plant, produced both acid and alkaline waste streams. The alkaline wastes had a pH generally in excess of 10 and contained relatively high concentrations of organics. The acid waste stream characteristically exhibited a pH of less than 4, BOD_5 concentration of less than 100 mg/l, zinc levels ranging from 15 to 20 mg/l, and low suspended solids. Upon mixing these two streams, co-precipitation occurred which resulted in the removal of significant quantities of dissolved organics. Bench-scale treatability studies indicated

that the co-precipitation phenomena could be enhanced and zinc removal accomplished by lime coagulation/sedimentation pretreatment.

CASE I -- COMBINED REGIONAL TREATMENT

Bench-scale tests were performed on samples gathered from nine potential participants, and pilot-plant design was then predicted on the results of these efforts. Detailed waste characterization studies indicated that the integrated waste stream would require neutralization prior to biological treatment, but rather unimpressive results from chemical coagulation/sedimentation pretreatment was observed. However, for two of the waste streams, as much as 50 percent of the COD could be removed following neutralization, alum coagulation, flocculation, and clarification. Since these wastes contained only small quantities of suspended solids in their raw state, the organic removals evidently resulted from the precipitation of soluble constituents. Economics dictated the use of lime for neutralization.

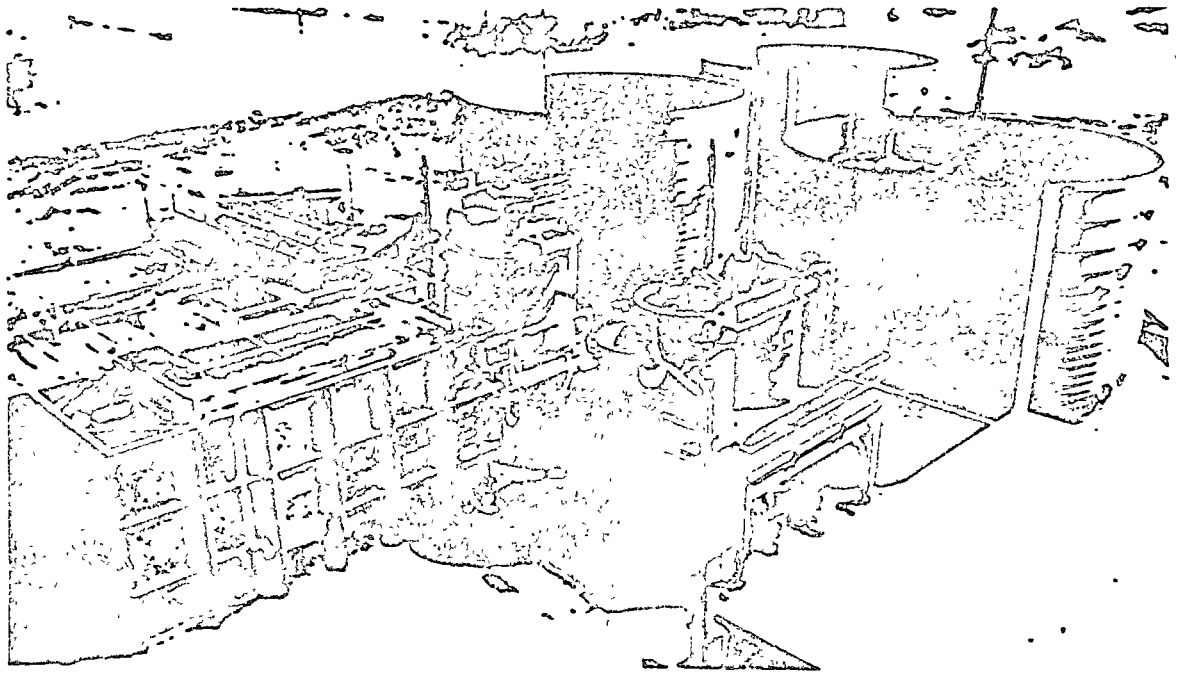
The completed pilot used in these studies is shown in Fig. 1, and the process is illustrated in Fig. 2. Wastewater from the various participants was transported to the unit by tank truck and stored in two 71,000 gallon wood stave tanks. Another wooden tank of similar size was used for equalization.

The system incorporated provisions for two stage neutralization, however, it soon became apparent that a stable pH could be maintained by adding lime slurry to only the first rapid mix unit. About 350 mg/l of hydrated lime was required to maintain an effluent pH of 7.5. The generation of a stringy floc could be observed in the rapid mix basin.

Effluent from the neutralization tanks was pumped to the primary clarifier shown in Fig. 3. This clarifier was ten feet in diameter. It was hoped that lime addition would produce a heavy sludge and enhance higher overflow rates. Unfortunately,

REGIONAL TREATMENT SYSTEM

PILOT PLANT



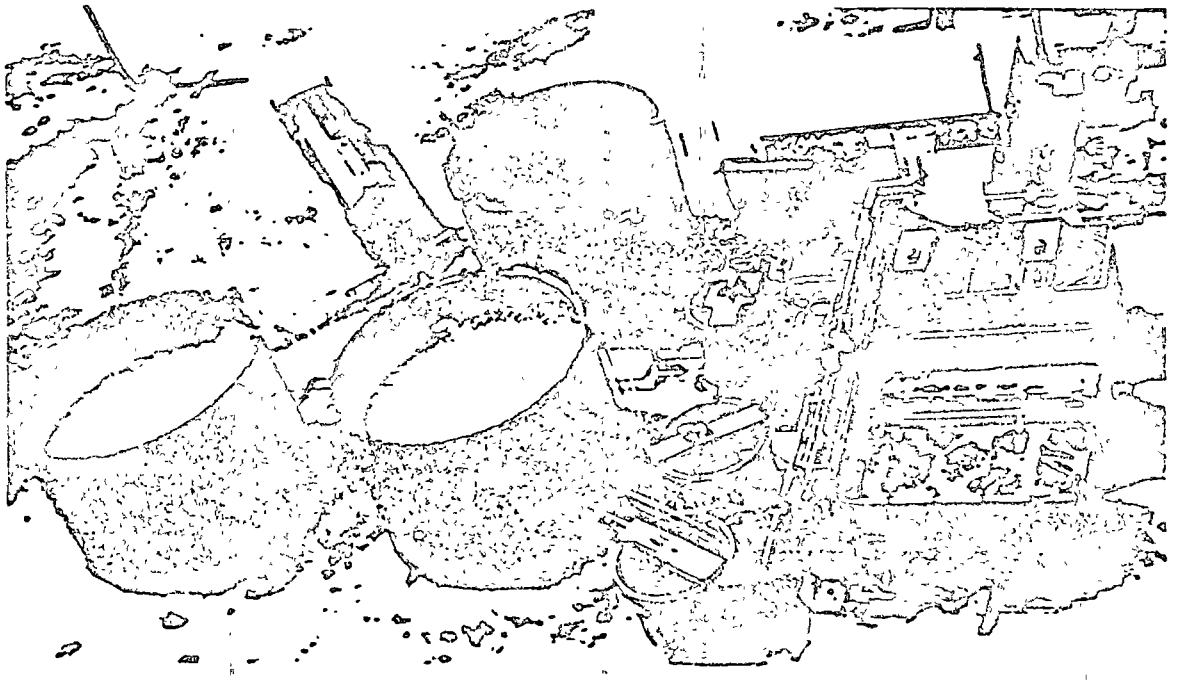


FIGURE 1

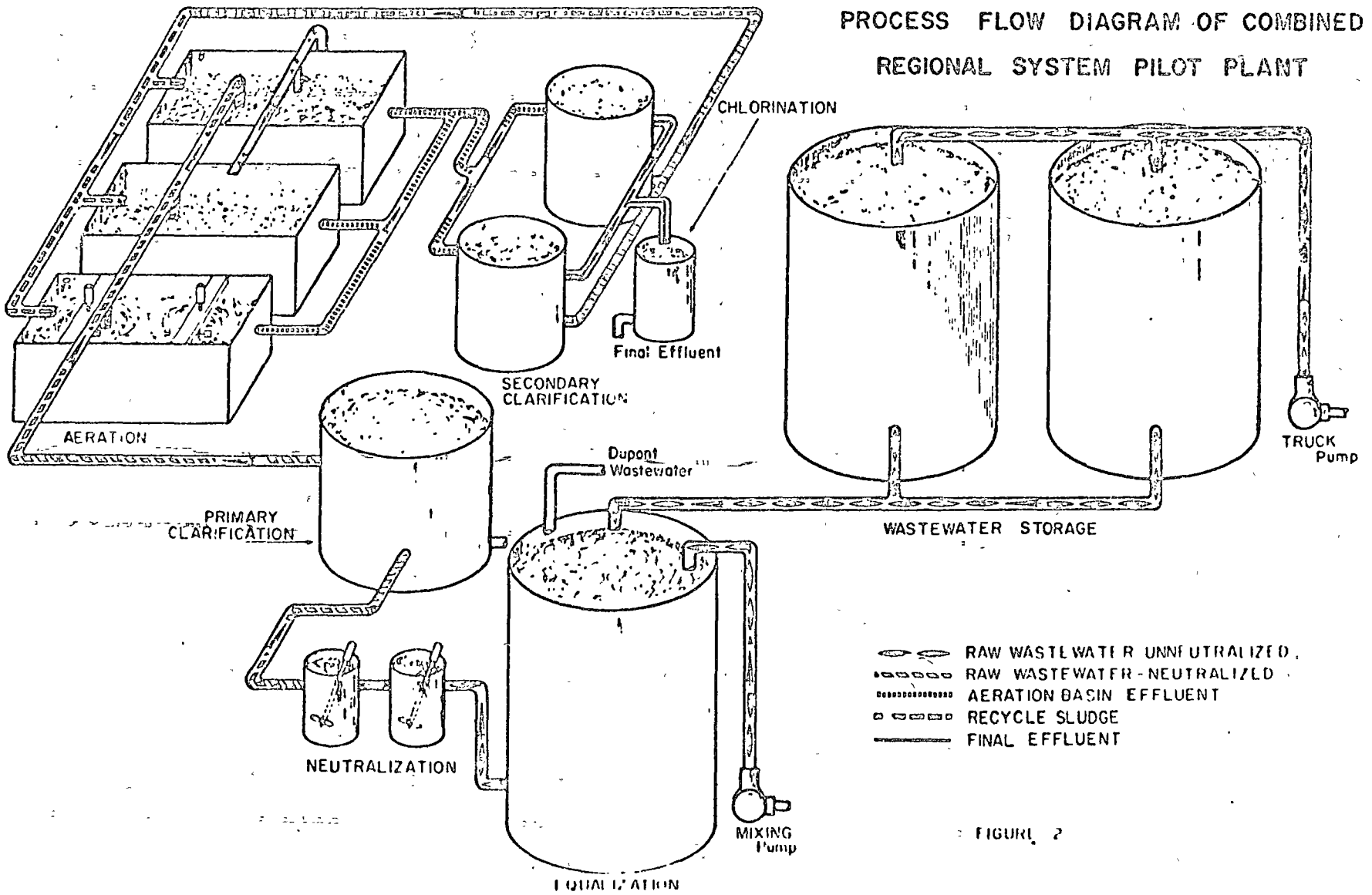

PROCESS FLOW DIAGRAM OF COMBINED
REGIONAL SYSTEM PILOT PLANT
CHLORINATION
Final Effluent
SECONDARY
CLARIFICATION
AERATION
TRUCK
Pump
Dupont
Wastewater
PRIMARY
CLARIFICATION
WASTEWATER STORAGE
NEUTRALIZATION
MIXING
Pump
EQUALIZATION
RAW WASTEWATER UNNEUTRALIZED
RAW WASTEWATER - NEUTRALIZED
AERATION BASIN EFFLUENT
RECYCLE SLUDGE
FINAL EFFLUENT

FIGURE 2

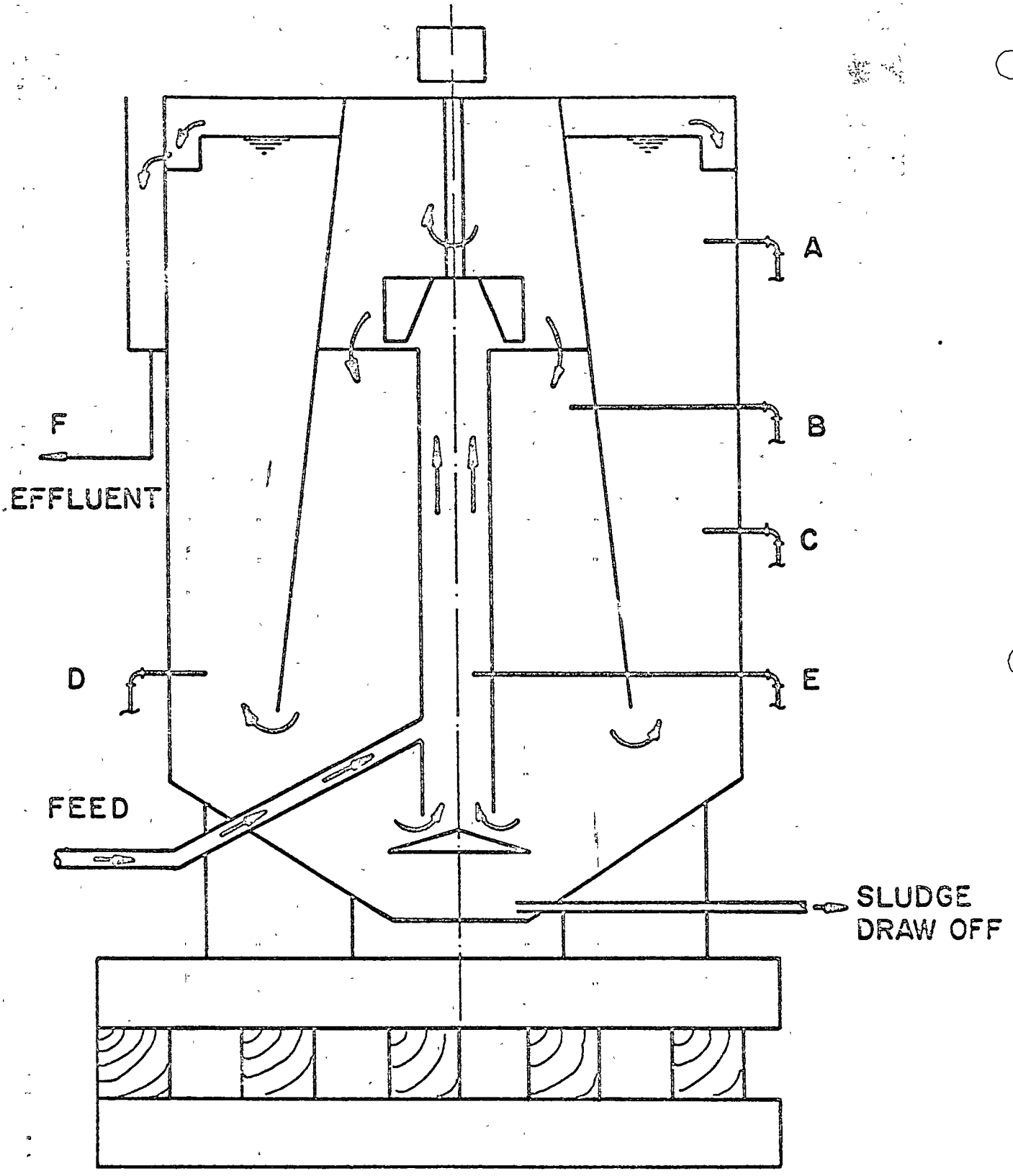


FIG. 3

REACTOR CLARIFIER SAMPLING POINTS

solids carry-over occurred whenever the reactor turbine was used. Attempts to improve operation by varying the speed of the flocculator turbine and by adding various polyelectrolytes proved unsuccessful and the unit was used during the remainder of the test program as a normal centerfeed clarifier.

Dye studies were performed to investigate the possibility that the turbine was inducing turbulence into the settling zone. However, a study of the hydraulic characteristics indicated that the performance of the reactor clarifier was attributed to the basic nature of the suspension rather than the equipment.

Bench-scale testing conducted concurrently with pilot-plant operations indicated that flocculation significantly improved the settling characteristics of the neutralized wastewater. Since the turbine, when operated at low speed, served as a flocculator, its use should have enhanced clarifier performance. Conversely, the high concentration of suspended organic solids caused the neutralized waste to behave as a flocculant suspension where zone settling velocity decreased with increasing solids concentration after an optimum was reached at approximately 2,000 mg/l. Evidently any positive value obtained from the turbine as a flocculator was overcome by its internal recycle function which served to maintain a higher than optimum slurry concentration in the settling zone.

The results achieved by lime pretreatment are illustrated in Fig. 4 where influent and effluent BOD_5 are presented in terms of percent occurrence. Overall BOD_5 removal averaged 37 percent. The fact that much of the soluble organics were removed is evidenced by analyses of filtered samples which showed that approximately ___ percent of the BOD_5 removed could not be attributed to influent suspended solids. Organic removals in terms of COD and TOC are shown in Table 2.

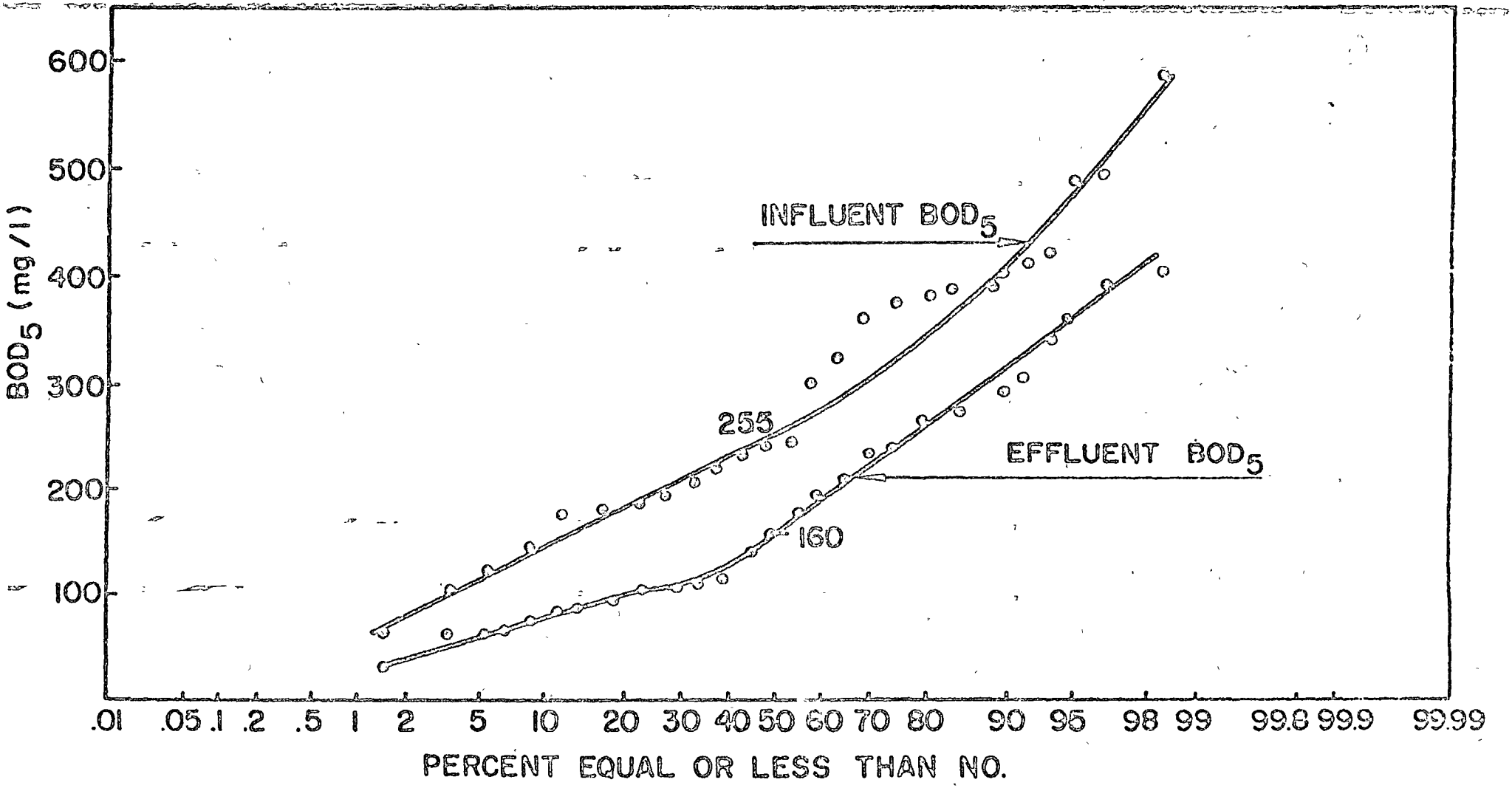


FIG. 4. EFFECTIVNESS OF PRIMARY TREATMENT FOR PROPOSED REGIONAL TREATMENT PLANT.

Table 2. Soluble Organic Removals by Lime Pretreatment*

Results	BOD_5	COD	TOC
Mean Filtered influent (mg/l)	168	464	201
Mean filtered effluent (mg/l)	131	408	155
Mean removal (mg/l)	37	56	46
Mean removal (%)	24	13	23

*All data from filtered samples

CASE II - INTEGRATED REFINERY/PETROCHEMICAL INSTALLATION

Two waste streams were selected for the integrated refinery/petrochemical study. Pretreatment was obviously required as influent oil and suspended solids concentrations were occasionally more than an order of magnitude above the accepted limits for successful biological treatment. Neutralization was also a necessity as the influent pH ranged between 2.0 and 10.0 with a mean of 6.0. It was also recognized that pretreatment would provide the additional benefit of removing a portion of the soluble organic loading since co-precipitation occurred when the pH of the commingled waste streams was increased.

Air flotation on a bench-scale was unsuccessful and gravity separation of oils and solids from the neutralized waste was only marginally successful. However, it was found that a settleable flocculant suspension could be developed at a pH above 8.0. On this basis, a pilot plant was designed and constructed to test and refine treatment alternatives. The pilot unit incorporated facilities similar to those described for the regional system, i.e., equalization, rapid mixing with chemical addition, primary clarification, and secondary biological treatment. Chemical addition provided for pH adjustment, floc formation and increased settling velocities.

The pilot unit was equipped so that either lime or caustic might be added for pH control. Moreover, facilities were available for adding a soda ash solution. Feeding equipment for adding polyelectrolytes was provided and eventually facilities were provided to add powdered limestone slurry. The latter was used as a weighting agent.

Both caustic and lime were tested for pH control, but as anticipated the lime proved to be more effective. The lime not only cost one-fifth as much as the caustic per equivalent weight of base, but it materially enhanced settling of the floc. Hydrated lime was used as the primary source of base throughout

the program. Dosage ranged from 250 to 900 mg/l to obtain pH levels of 8.0 to 11.0. An operating pH of about 8.5 provided optimum floc formation and settling. A lime dosage of 350 mg/l was required. Massive lime addition did present a potential problem in that the available natural alkalinity was insufficient to precipitate all of the calcium and the unstable effluent interferred with subsequent treatment steps.

Concern over the fate of these excess calcium ions together with anticipated problems in controlling the pH of the mixed liquor prompted the addition of soda ash. Drastic pH reductions to below four had occurred during the bench-scale biological treatability studies. This low pH problem is a fairly common occurrence when treating some refinery wastes. It was hoped that the soda ash would precipitate the excess calcium ions, enhance the settleability of the floc, and buffer the biological process against detrimental pH changes. It was found that the natural biological reduction in pH from an influent of 8.5 to a mean of 7.0 shifted the carbonate-bicarbonate balance and reduced the carbonate ions available for calcium carbonate precipitation to approximately one-twenty fifth of that entering the aeration basin. The result being that the primary effluent was rendered more stable by biological treatment and soda ash addition was not required for this purpose. Drastic pH shifts did not occur in the pilot unit and soda ash proved to be unnecessary as a buffer. Furthermore, cost analysis indicated that a weighting agent could be applied more effectively in the form of powdered limestone.

The primary clarifer was operated for approximately two months at overflow rates ranging between 400 to 1,100 gpd/ft^2. The pilot unit could be operated either as a reactor clarifier or in the conventional centerfeed configuration. Similar to the regional treatment system, the flocculant suspension responded favorably to turbine flocculation but the internal recyle had a

detrimental effect on performance. In both cases, a true flocculator clarifier would have been the optimum equipment selection.

Actual performance can best be characterized by extended periods of high efficiency punctuated by periodic gross discharges of oily sludge. Each failure could be traced to abnormally high influent oil concentrations. Normally, the influent oil remained less than 200 mg/l but on occasion jumped to over 700 mg/l which in turn triggered a clarification failure. This problem was eventually overcome by operating the unit at an overflow rate of approximately 600 gpd/ft^2 and adding massive quantities of weighting agent when influent oil levels rose significantly.

After the appropriate operational techniques had been perfected, effluent oil and suspended solids concentration could be maintained consistantly below 50 mg/l. Removals of COD in the primary treatment unit are shown in Fig. 5. Approximately 40 percent of the influent loading, or a total of 1,700 mg/l of COD was removed. Oil and grease removal ranged from 100 to 5,000 mg/l with a mean of approximately 500 mg/l.

Considering the characteristics of the waste streams, it is believed that lime coagulation followed by sedimentation offered the only workable alternative for effective oil and suspended solids removal. Furthermore, this technique provided the added attraction of taking advantage of co-precipitation to assist in the removal of significant quantites of dissolved organics.

CASE III - VISCOSE RAYON PLANT

The third case for application of lime in the primary treatment unit involved a synthetic fibers plant. Although the installation also included a polyester facility, most of the significant waste streams were generated in the course of viscose rayon production.

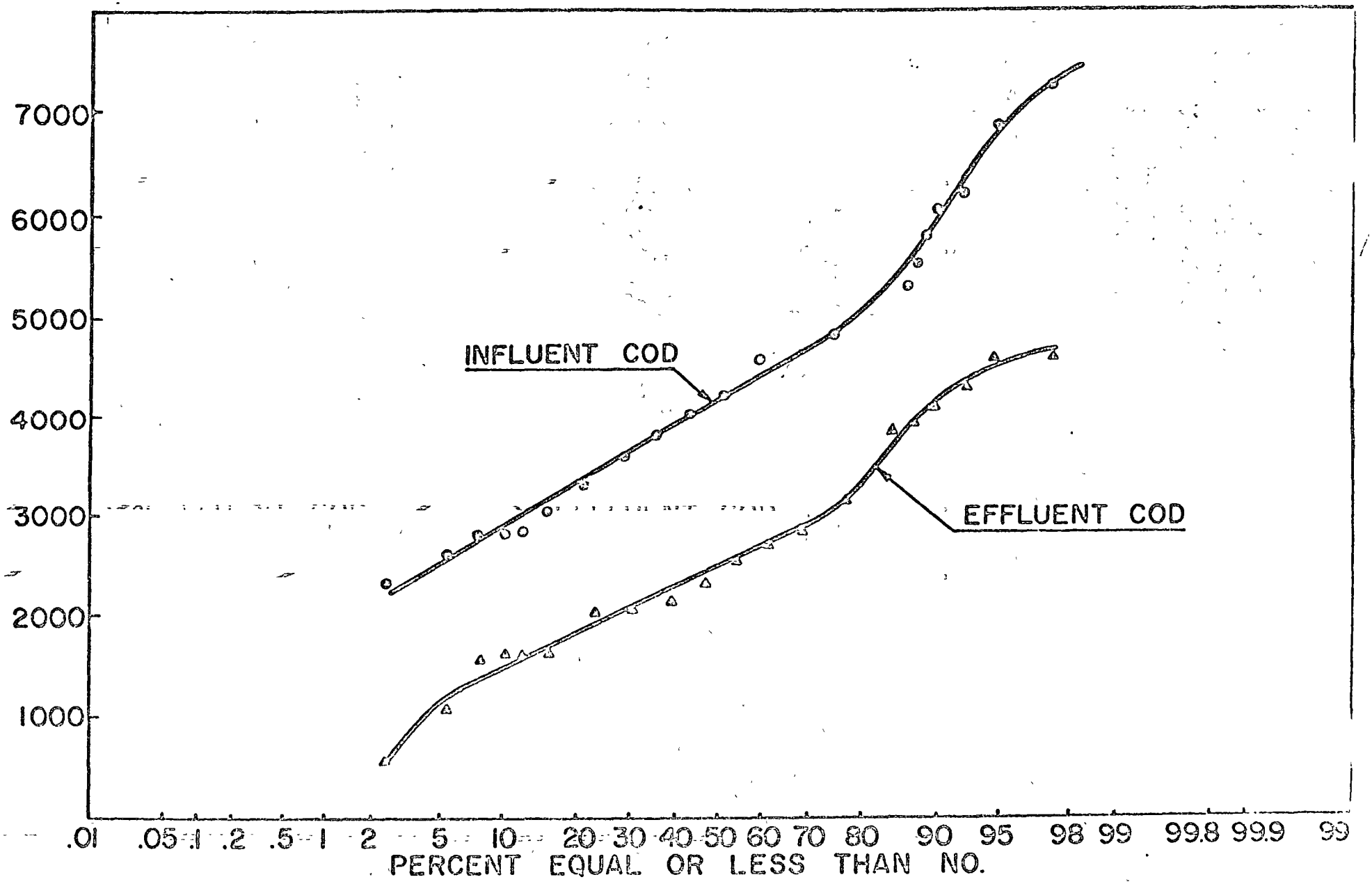


FIG. 5. EFFECTIVENESS OF PRIMARY TREATMENT FOR INTEGRATED REFINERY / PETROCHEMICAL FACILITY.

These wastes streams can generally be catagorized as either alkaline or acid. The alkaline waste streams are produced while disolving cellulose to form viscose. Cellulose is made soluble in carbon disulfide under alkaline conditions and wastes are generated through the separation of unusable hemicellulose or by normal process spills and losses. These wastes have a pH ranging from 10 to 11, a BOD_5 of approximately 300 mg/l, a COD of about 450 mg/l and contain negligible quantities of zinc or other heavy metals. In the next process step, the dissolved cellulose, (viscose) is precipitated and polymerized by extrusion or spinning in an acid bath. Zinc is added to the sulfuric acid bath to enhance the toughness of the rayon fiber.

The wastes generated during the acid process characteristically exhibited a pH of less than 4, a BOD_5 of less than 100 mg/l, and zinc concentrations ranging from 15 to 20 mg/l. When combined, the two streams had a mean flow rate of approximately 7 $\bar{M}$GD with peak flows of up to 9 $\bar{M}$GD.

The reaction which takes place upon mixing the two waste streams is essentially the same as that used in the production of rayon, i.e., the acid waste precipitates and polymerizes a portion of the soluble cellulose remaining in the alkaline waste stream. Some previous treatment schemes took advantage of this phenomena by mixing the two streams prior to sedimentation in large earthen ponds. Unfortunately, variations in the characterstics of the alkaline waste coupled with difficulties in maintaining good settling in the ponds resulted in inefficient organic removals and did nothing to reduce effluent zinc concentration.

The proposed treatment system took advange of the natural co-precipitation of organics but optimized it to achieve maximum removals. The first step in design involved a detailed wastewater survey to insure that all contaminated wastes were collected and routed to the new treatment site. Bench-scale treatability studies were then performed to develop design criteria with the specific objectives of essentially complete zinc removal and maximum organic precipitation.

The bench-scale test revealed that once the soluble cellulose had come in contact with an acid environment and precipitated it remained insoluble even at an elevated pH. Furthermore, the addition of lime to the commingled waste not only removed zinc, but also coagulated the precipitated cellulose. As shown in Fig. 6, effluent concentrations of approximately 0.5 mg/l zinc could be achieved at a pH of less than 9.0. The effectiveness of lime coagulation in organic removal is illustrated in Fig. 7. On the average, 300 mg/l of lime were required to obtain a design pH of 8.5 with maximum peak dosages of up to 750 mg/l. It is anticipated that lime coagulation/sedimentation will reduce the organics by 65 to 70 percent and achieve 95 percent or better zinc removal.

The proposed treatment facilities consist of alkaline equalization, premix and rapid mix basins, chemical storage and feed facilities, and a flocculator clarifier. Cellulose precipitation will take place in the premix basin upon commingling of the two waste streams. Lime will be added in the rapid mix basin.

The bench-scale studies indicated that the lime floc settled well and settling was enhanced by gentle flocculation, but the floc was susceptable to shear. To compensate for this problem, mixing will be accomplished with low-speed, large-diameter turbines. The tendency for floc destruction will be reduced by using a low-speed screw pump to lift the wastewater to the flocculator clarifier. The clarifer will provide approximately 15 minutes of low intensity flocculation and will operate at a mean overflow rate of 900 gpd/ft^2.

Although lime was selected as the primary chemical for pH adjustment, a backup system was provided to feed caustic. The system was instrumented for automatic addition of sulfuric acid to the premix basin for precipitation of dissolved organics in the case of temporary suspension of waste acid releases.

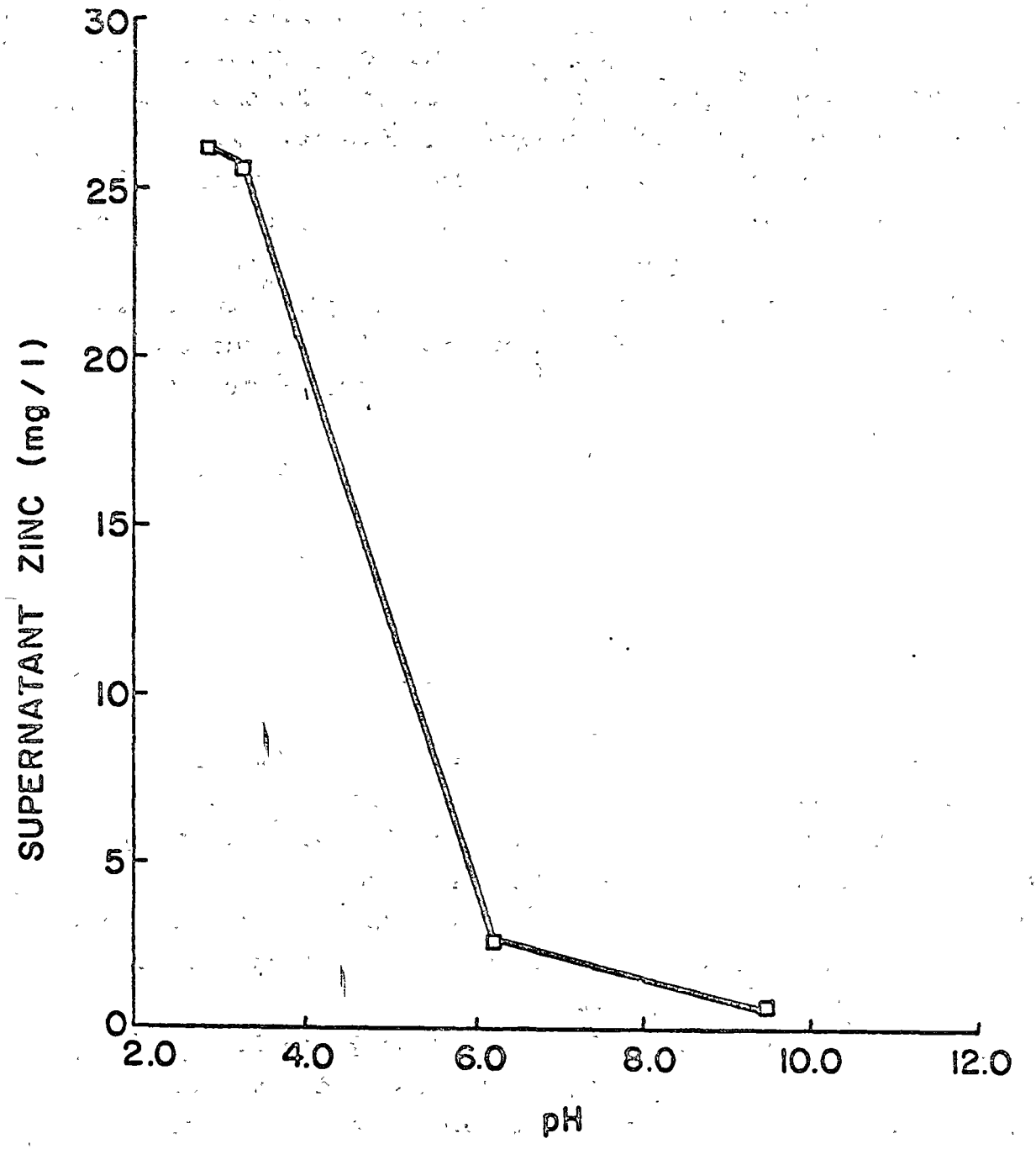


FIG. 6

ZINC REMOVAL BY LIME ADDITION

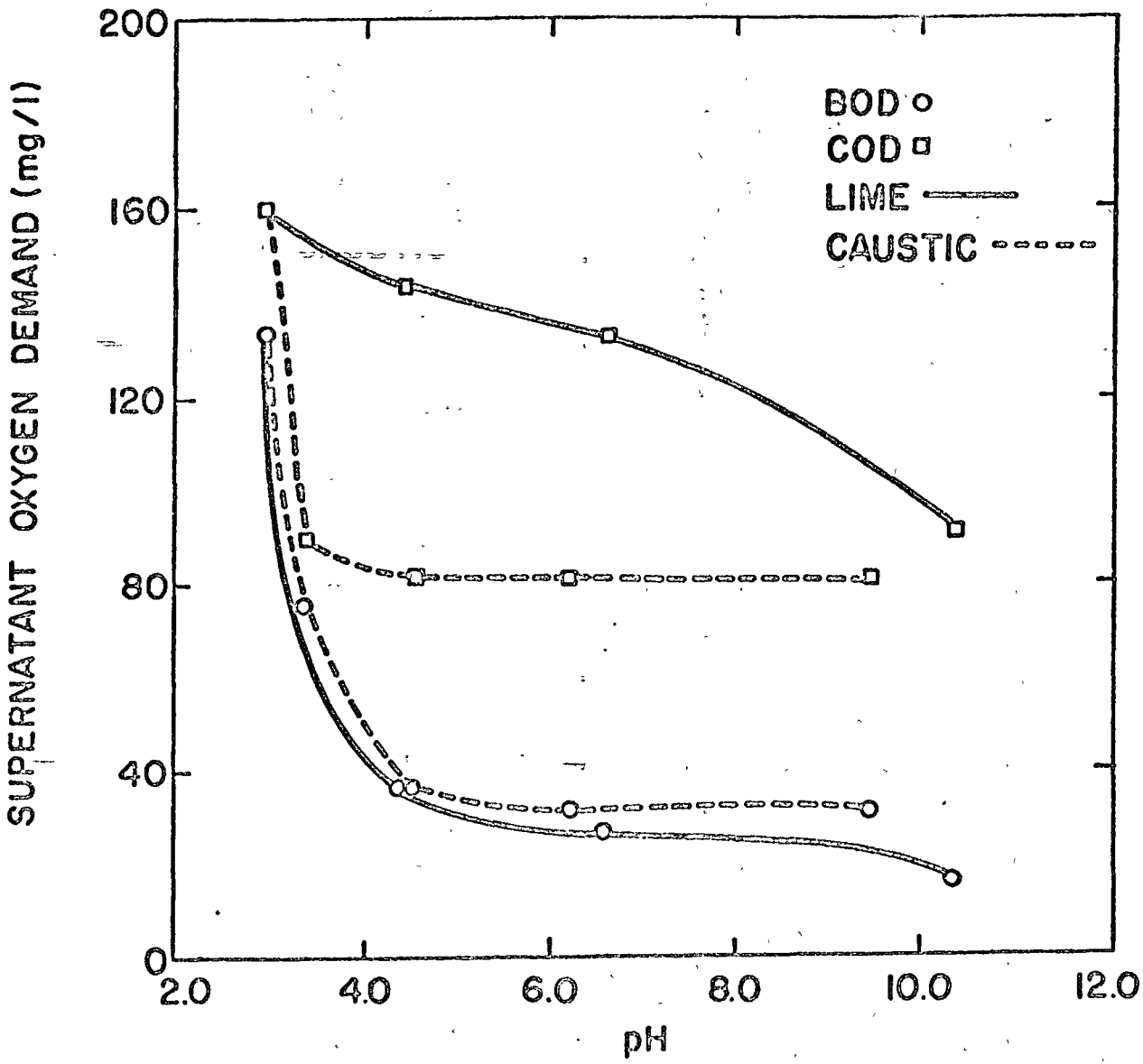


FIG. 7

MOVAL OF ORGANICS THROUGH LIME COAGULATION AND SEDIMENTATION

SUMMARY

Three case histories have been presented to illustrate the potential of lime coagulation/sedimentation for industrial wastewater pretreatment. In each case, lime pretreatment served not only to adjust pH and reduce contaminant concentrations to a level suitable for secondary biological treatment, but also removed significant quantities of dissolved organics. These removals of dissolved organics are of particular significance because the precipitated constituents are generally large molecules or polyermized entities and these are generally difficult to degrade biologically.

Lime pretreatment represents a viable process alternative which should be considered in many cases. Therefore, in many treatability investigations the scope of the study should be broadened to include evaluation of coagulation/sedimentation pretreatment

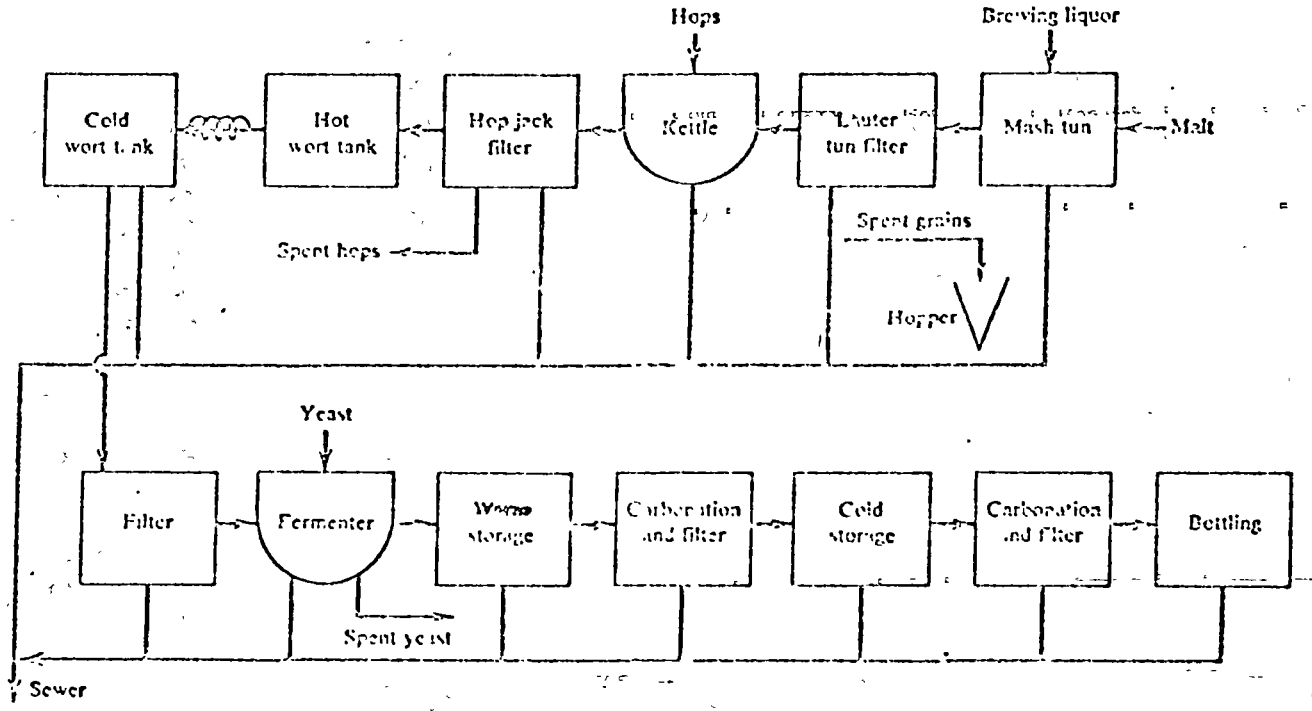
REFERENCES

1. Gloyna, E. F. and W. W. Eckenfelder, Water Quality Improvement by Physical and Chemical Processes, Vol. 3, University of Texas Press, Austin, Texas, (1970).

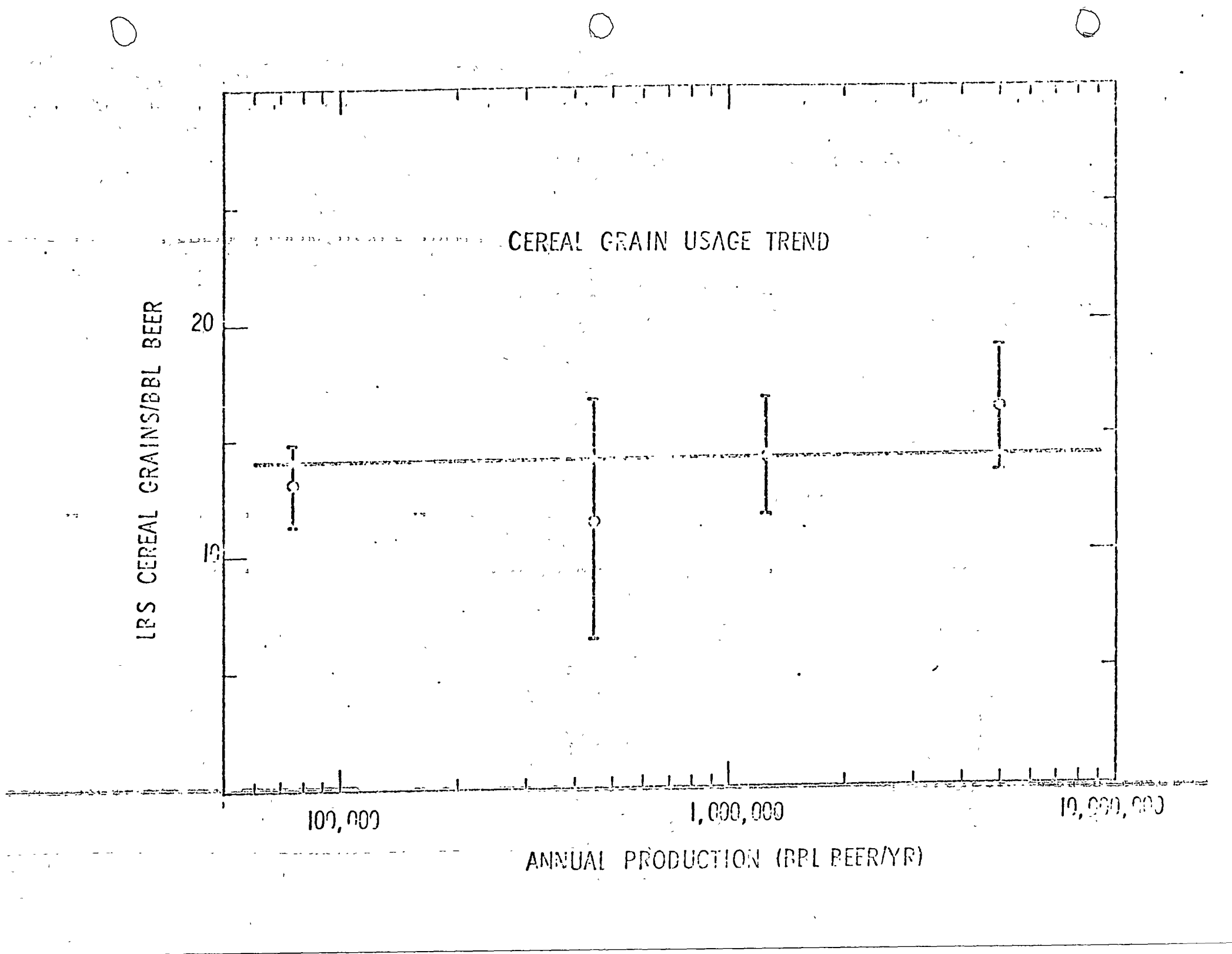
2. Ford, D. L. and J. Eller, Unpublished Reports, Engineering-Science, Inc., (1973).

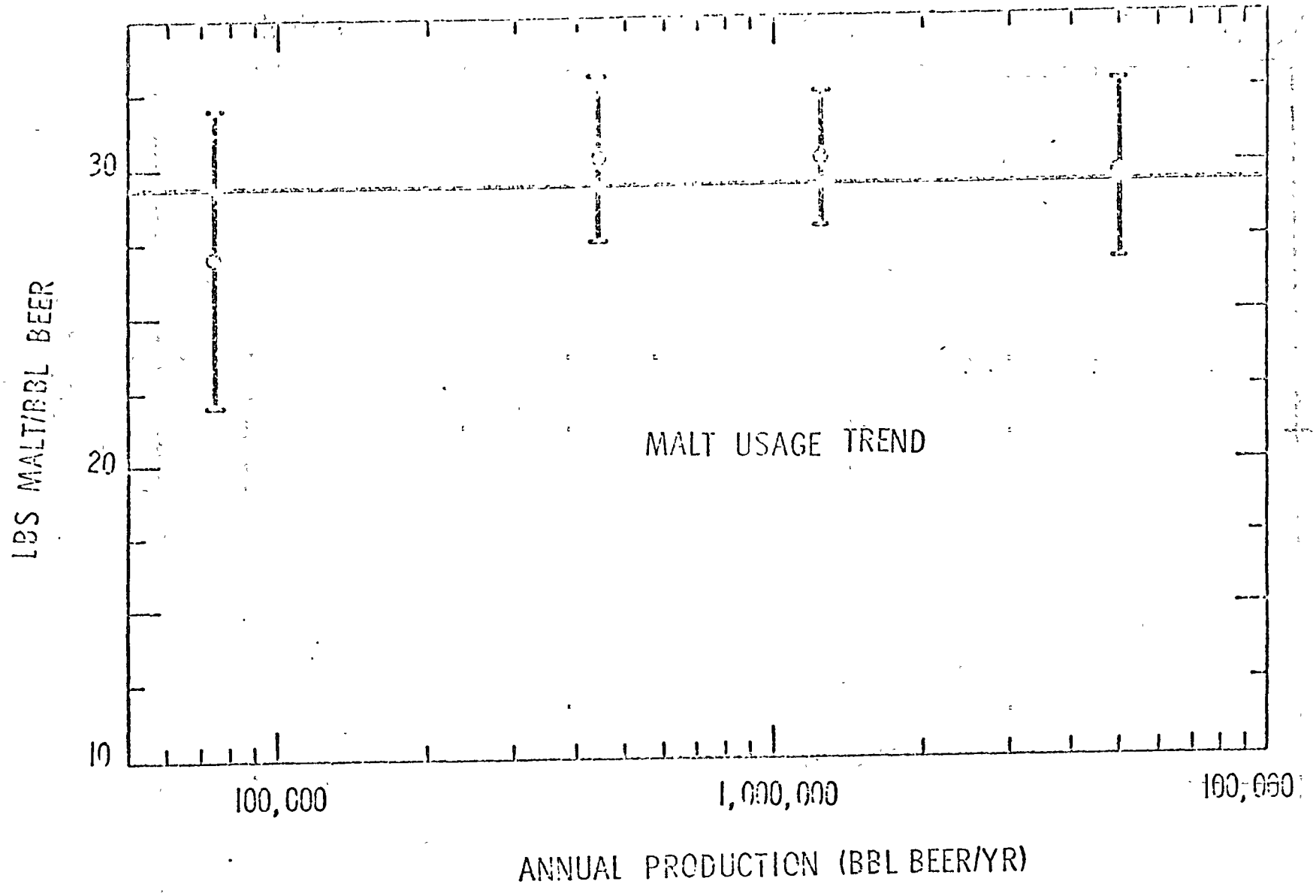
INITIAL RESPONSE TO BREWERY WASTE TREATMENT SURVEY

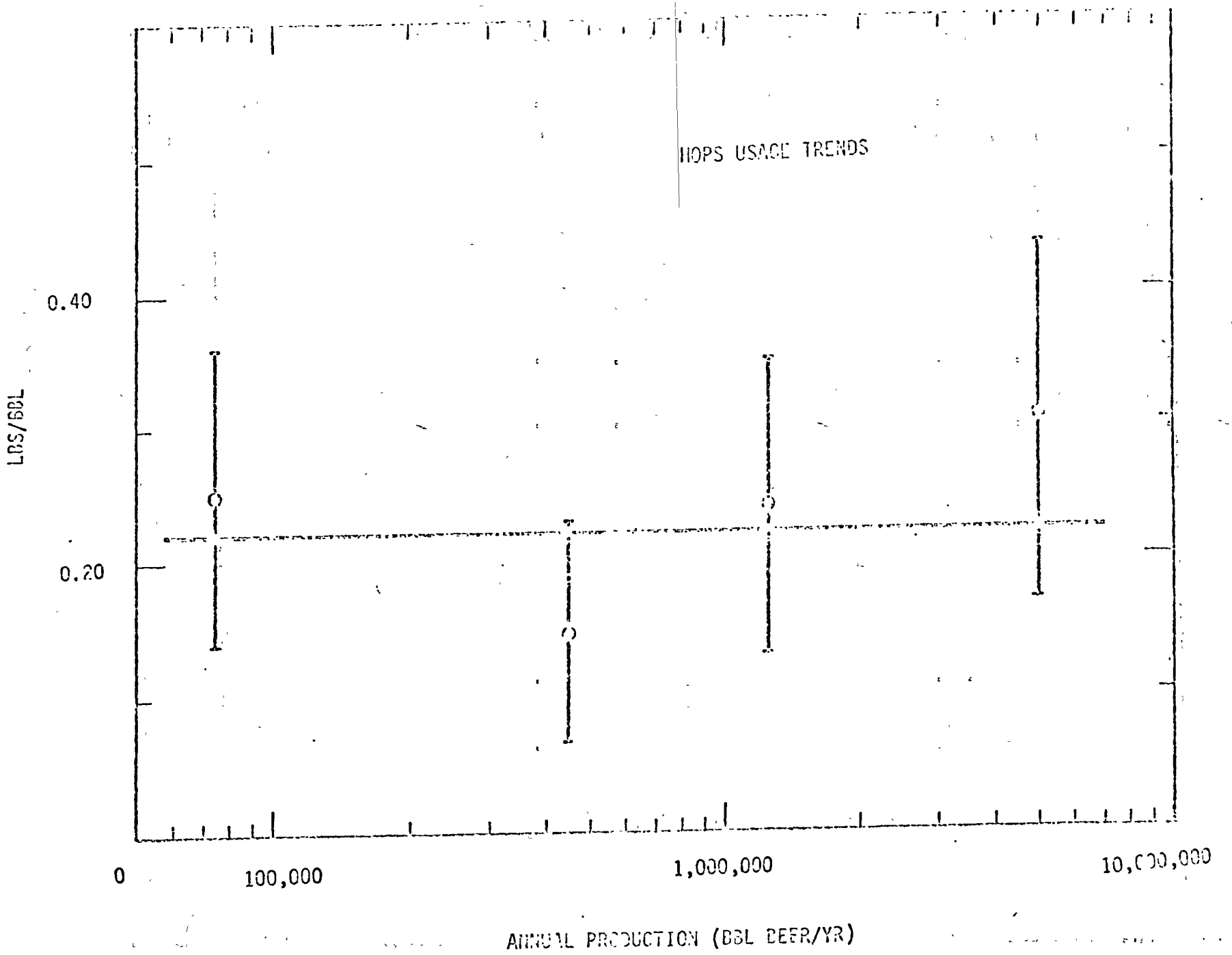
ANNUAL PRODUCTION, P, BBLS.	NUMBER OF REPLIES
$P < 150{,}000$	6
$150{,}000 < P < 750{,}000$	9
$750{,}000 < P < 1{,}500{,}000$	20
$1{,}500{,}000 < P$	18

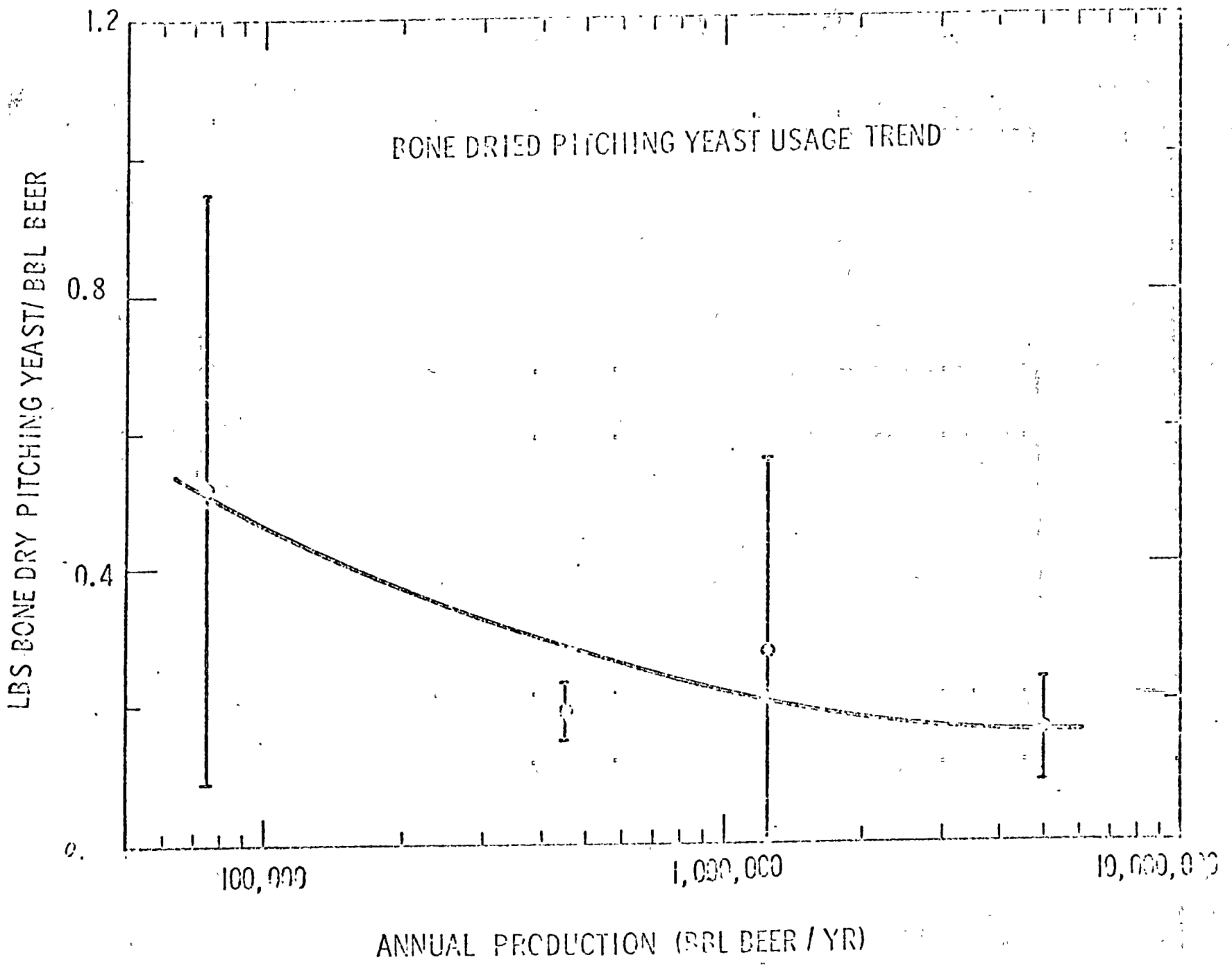


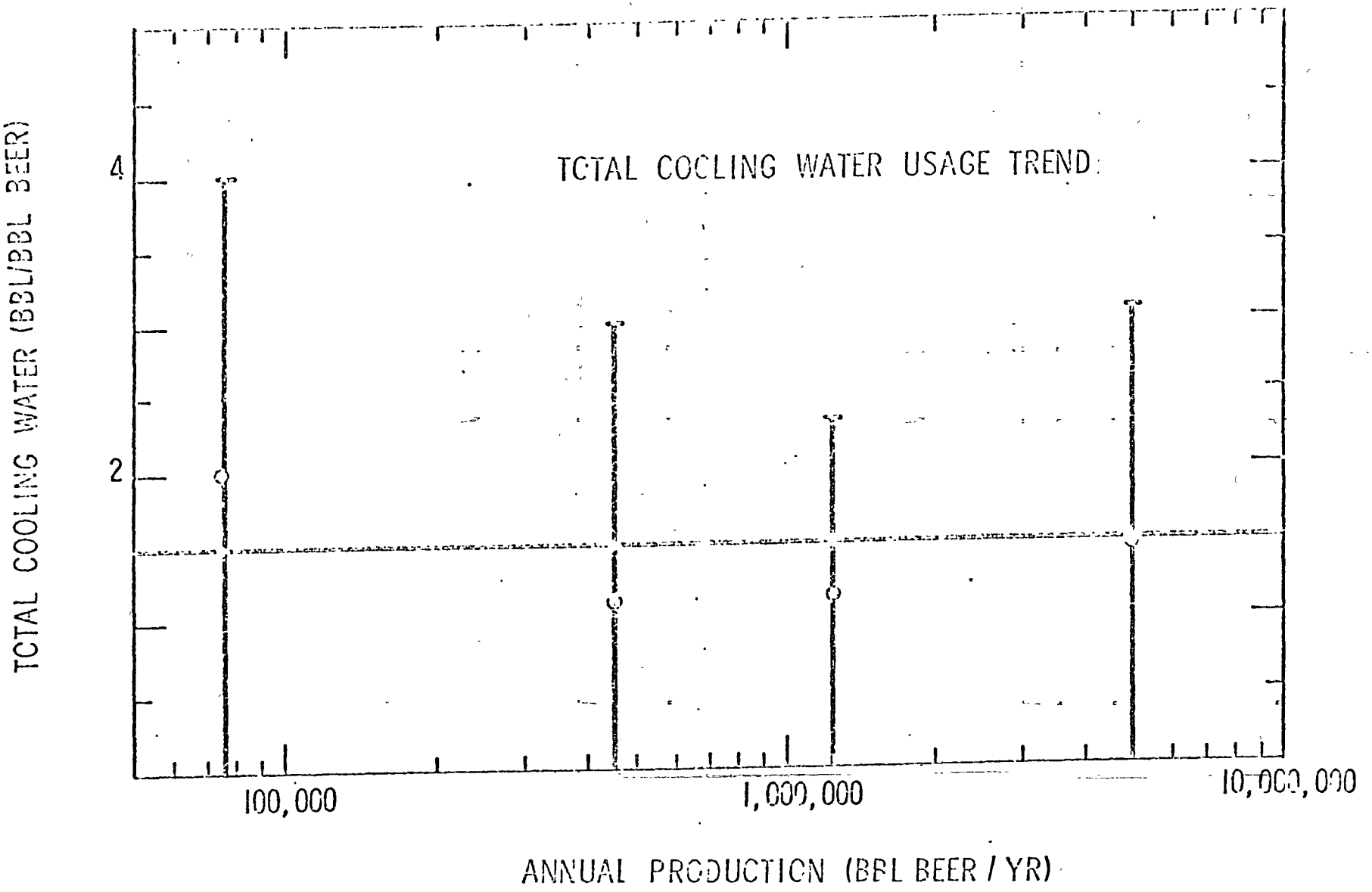
Sequence of process operations

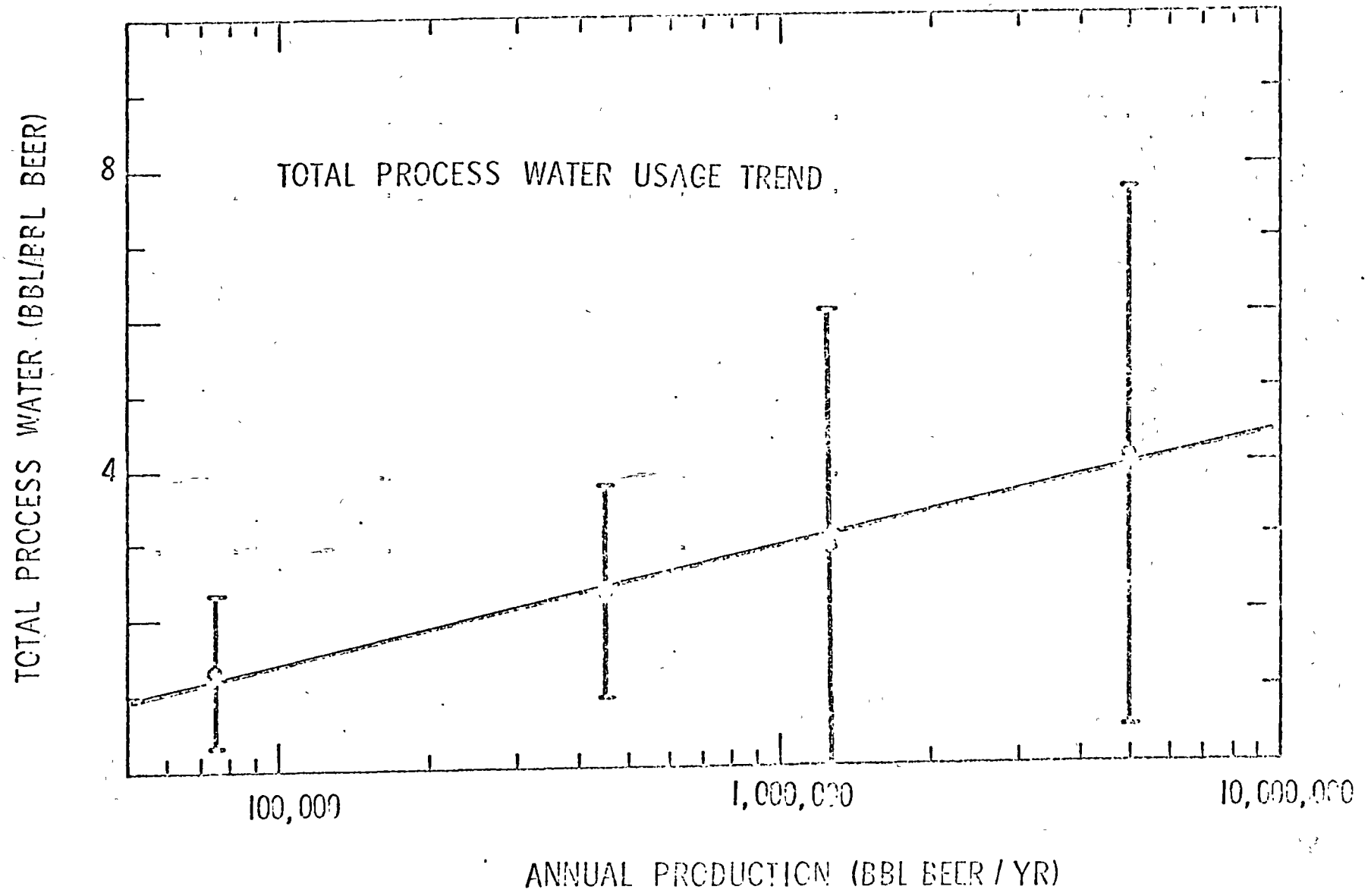

CEREAL GRAIN USAGE TREND
LBS CEREAL GRAINS/BBL BEER
20
19
100,000
1,000,000
10,000,000
ANNUAL PRODUCTION (BBL BEER/YR)

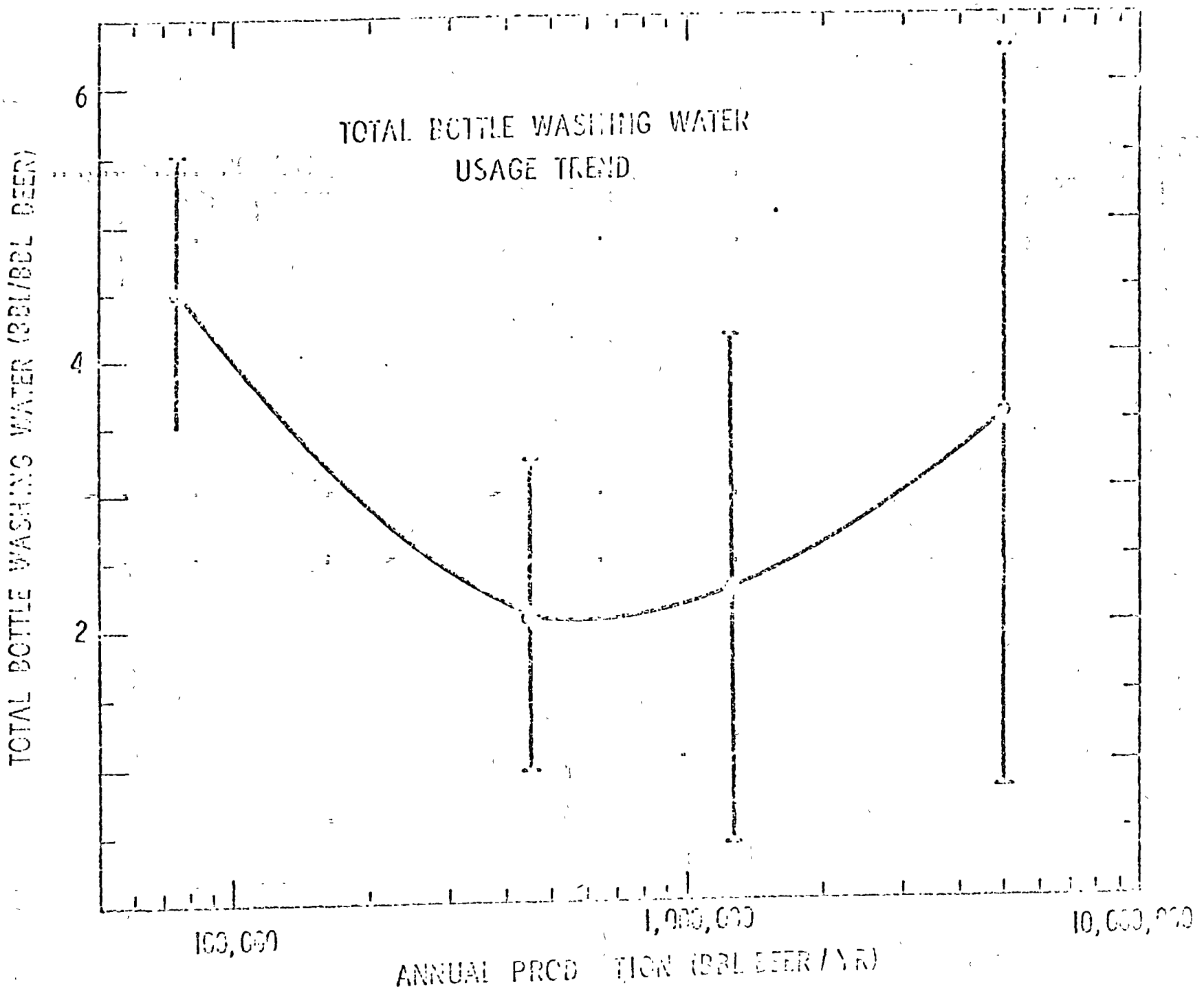

MALT USAGE TREND
LBS MALT/BBL BEER
30
20
10
100,000
1,000,000
10,000,000
ANNUAL PRODUCTION (BBL BEER/YR)

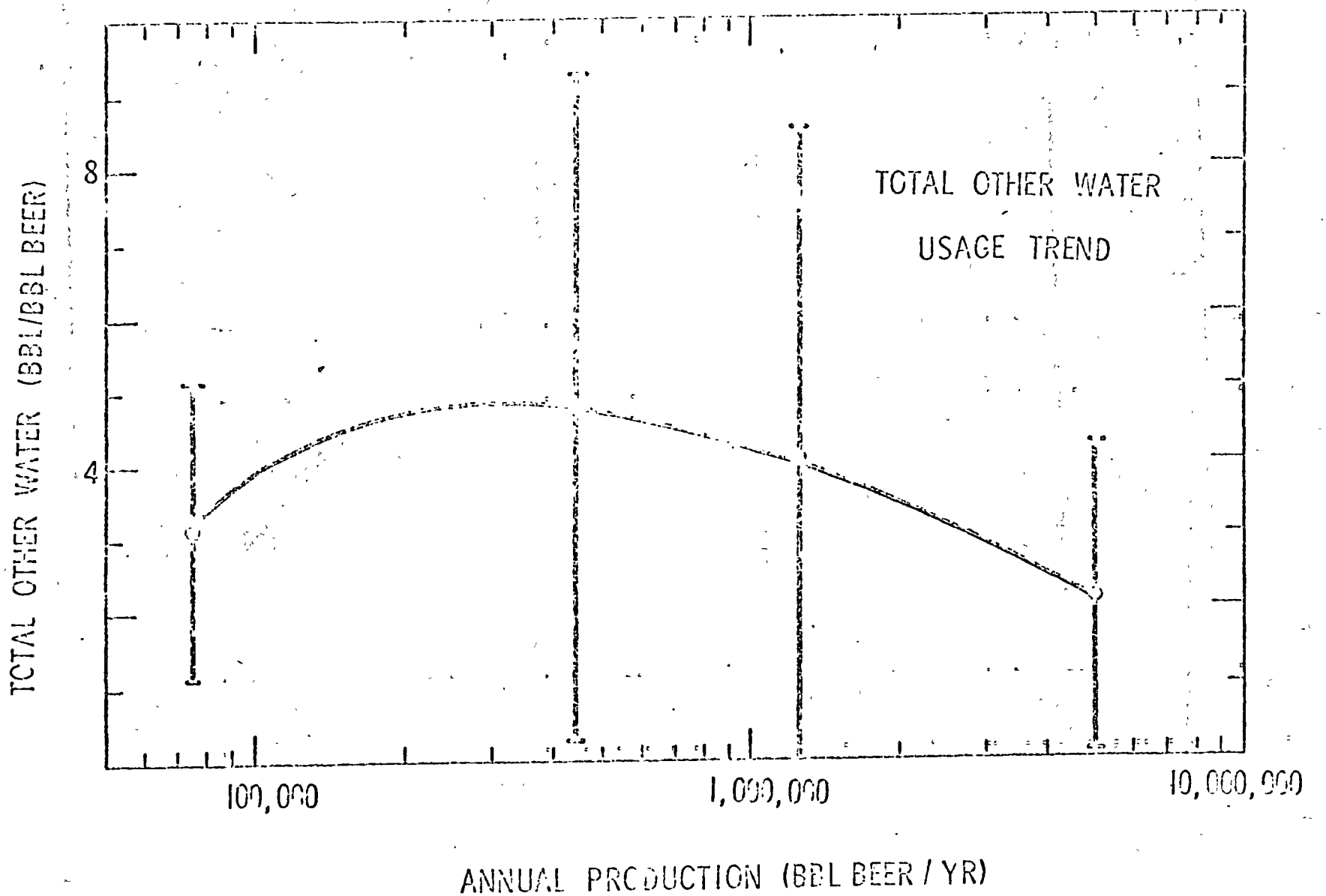

HOPS USAGE TRENDS
0.40
0.20
LBS/BBL
0
100,000
1,000,000
10,000,000
ANNUAL PRODUCTION (BBL BEER/YR)

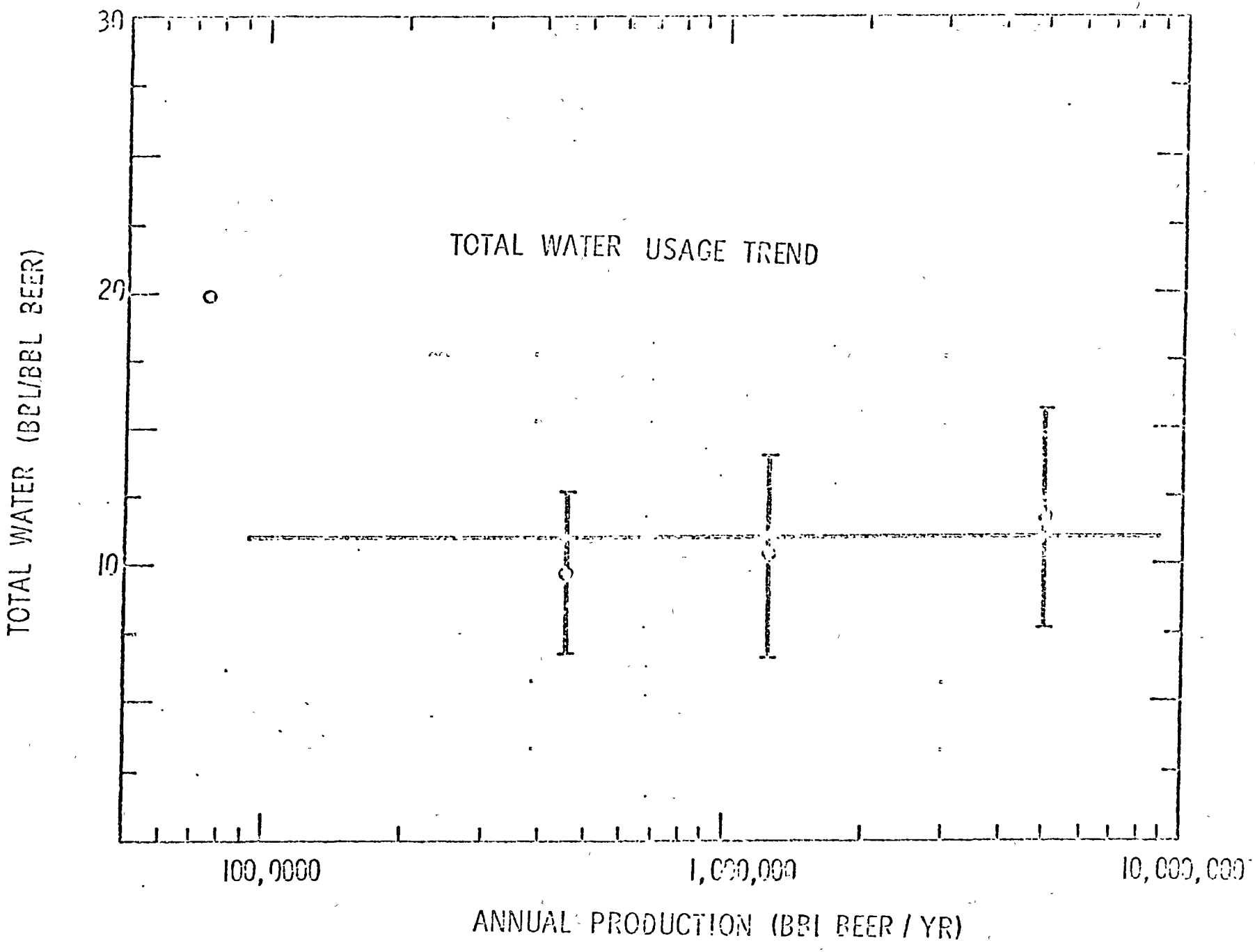

BONE DRIED PITCHING YEAST USAGE TREND
LBS BONE DRY PITCHING YEAST/ BBL BEER
1.2
0.8
0.4
0.
100,000
1,000,000
10,000,000
ANNUAL PRODUCTION (BBL BEER / YR)

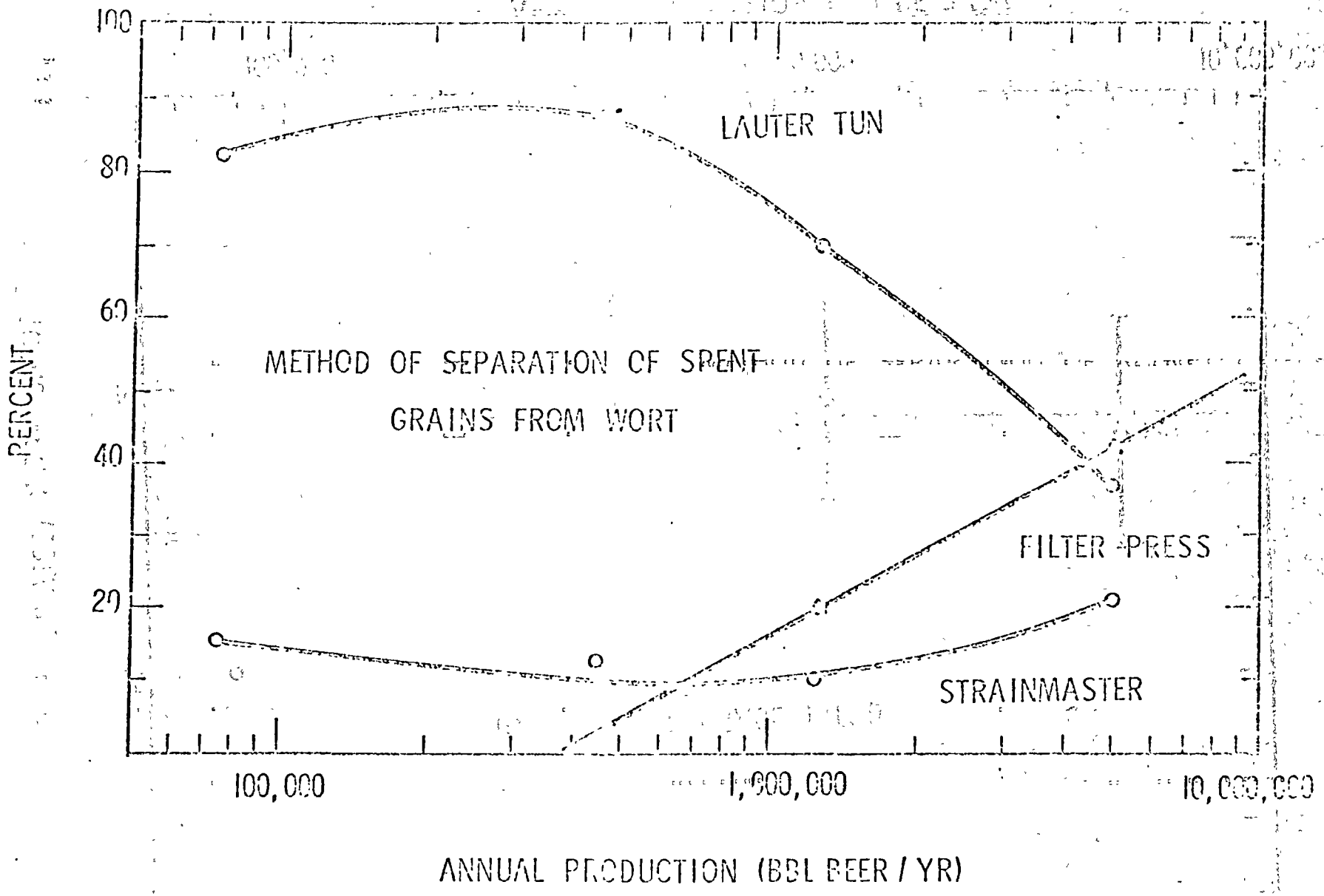

TOTAL COOLING WATER USAGE TREND
TOTAL COOLING WATER (BBL/BBL BEER)
4
2
100,000
1,000,000
10,000,000
ANNUAL PRODUCTION (BBL BEER / YR)

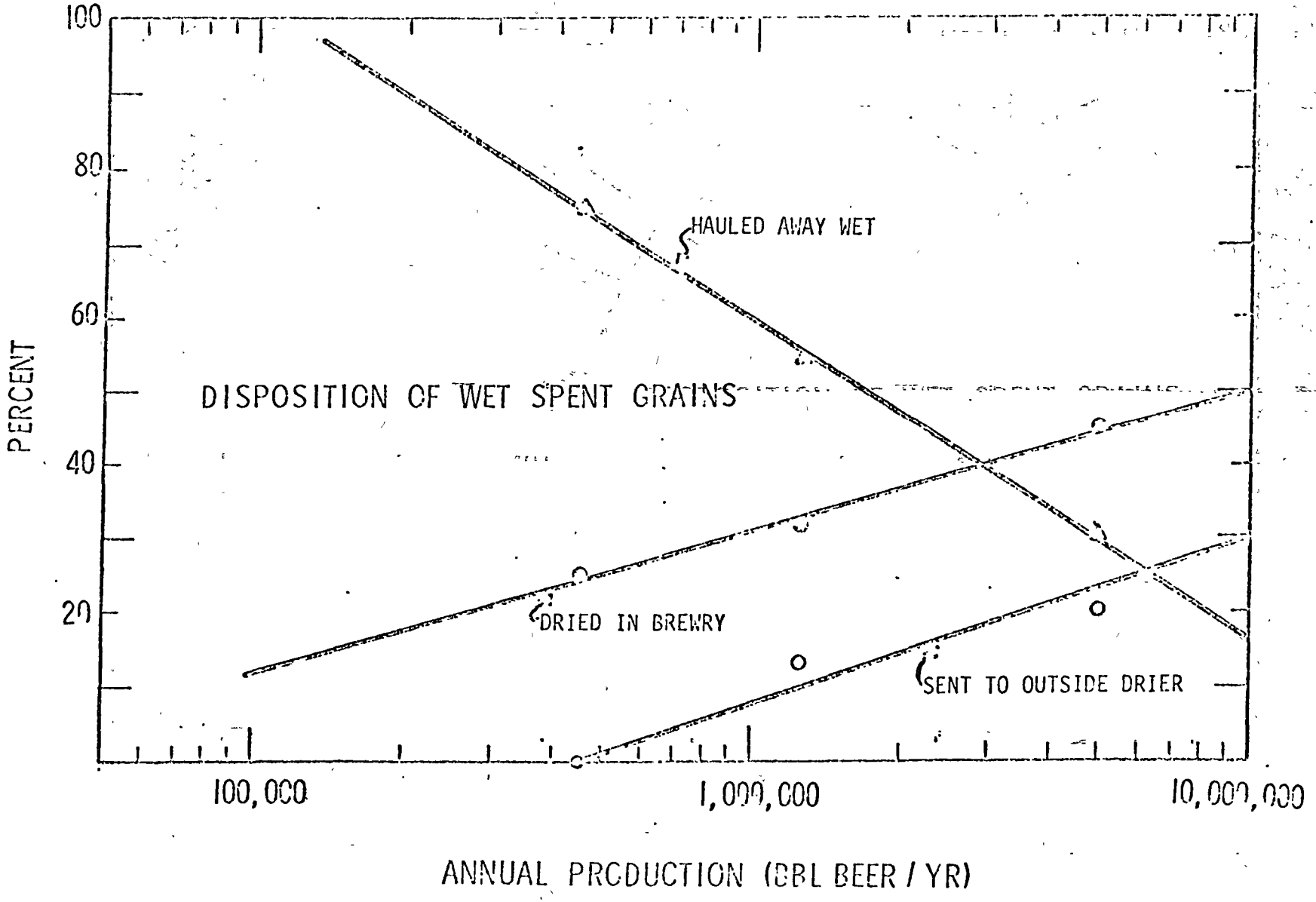

TOTAL PROCESS WATER USAGE TREND
TOTAL PROCESS WATER (BBL/BBL BEER)
8
4
100,000
1,000,000
10,000,000
ANNUAL PRODUCTION (BBL BEER / YR)

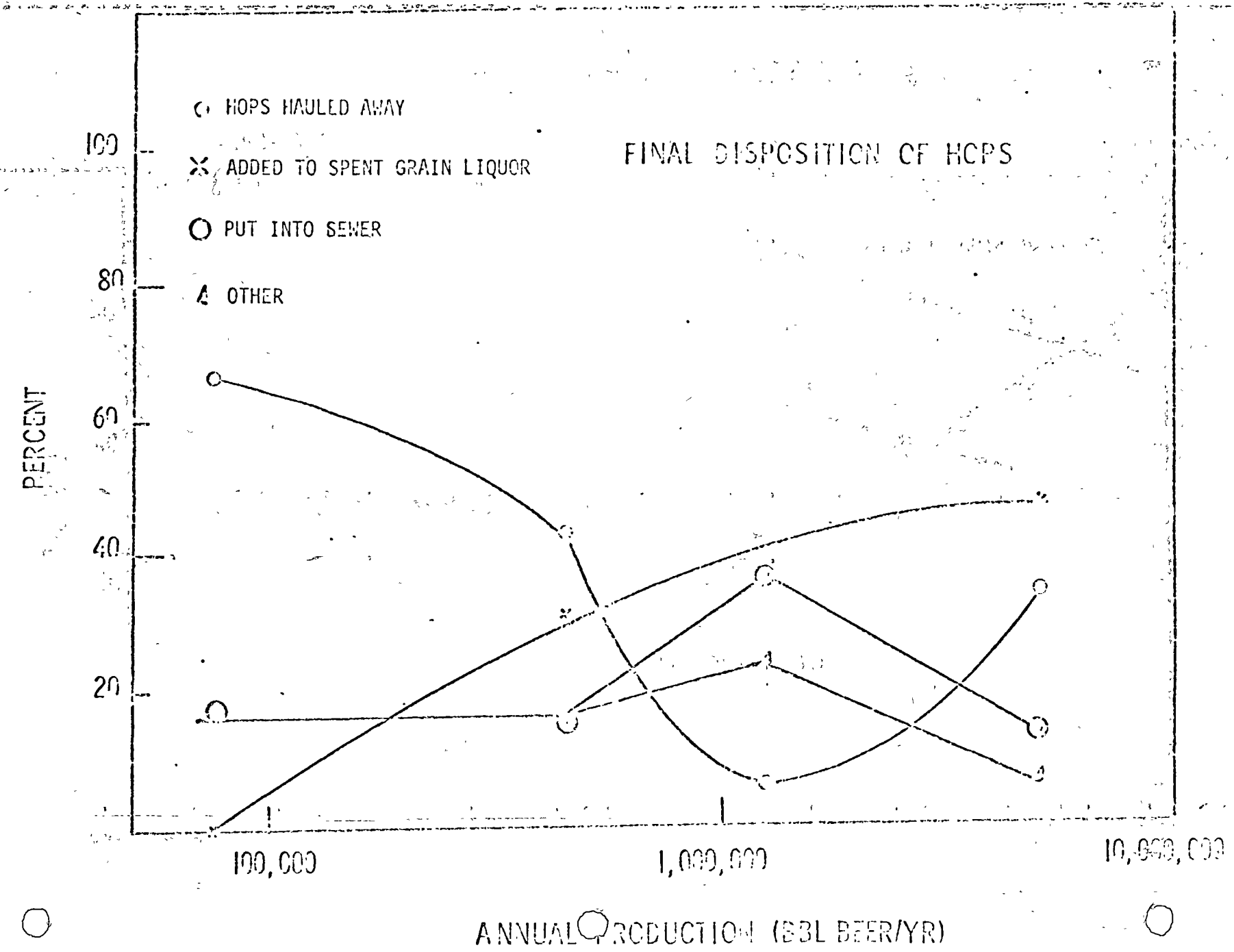

TOTAL BOTTLE WASHING WATER
USAGE TREND
TOTAL BOTTLE WASHING WATER (BBL/BBL BEER)
6
4
2
100,000
1,000,000
10,000,000
ANNUAL PRODUCTION (BBL BEER/YR)

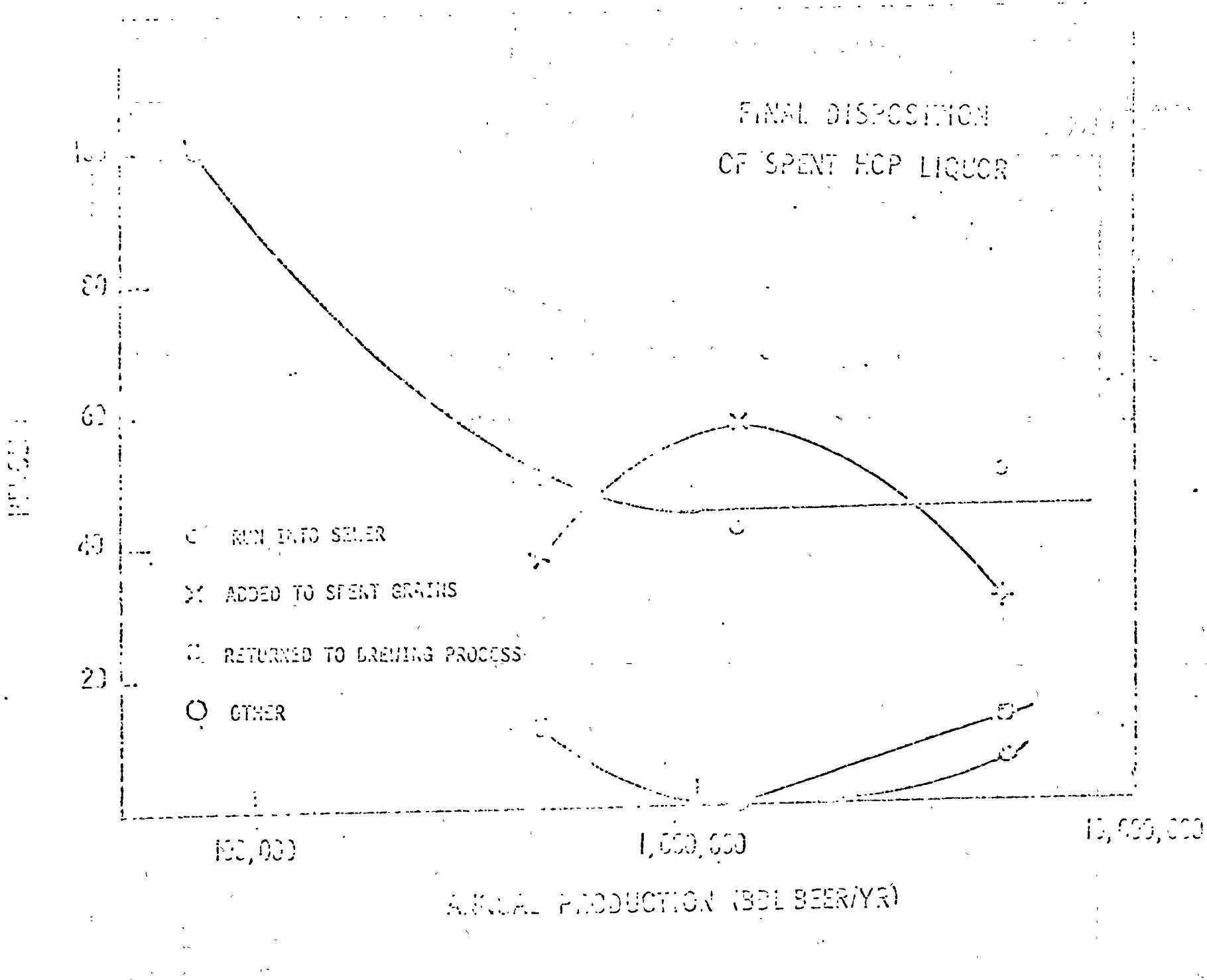

TOTAL OTHER WATER
USAGE TREND
TOTAL OTHER WATER (BBL/BBL BEER)
8
4
100,000
1,000,000
10,000,000
ANNUAL PRODUCTION (BBL BEER / YR)

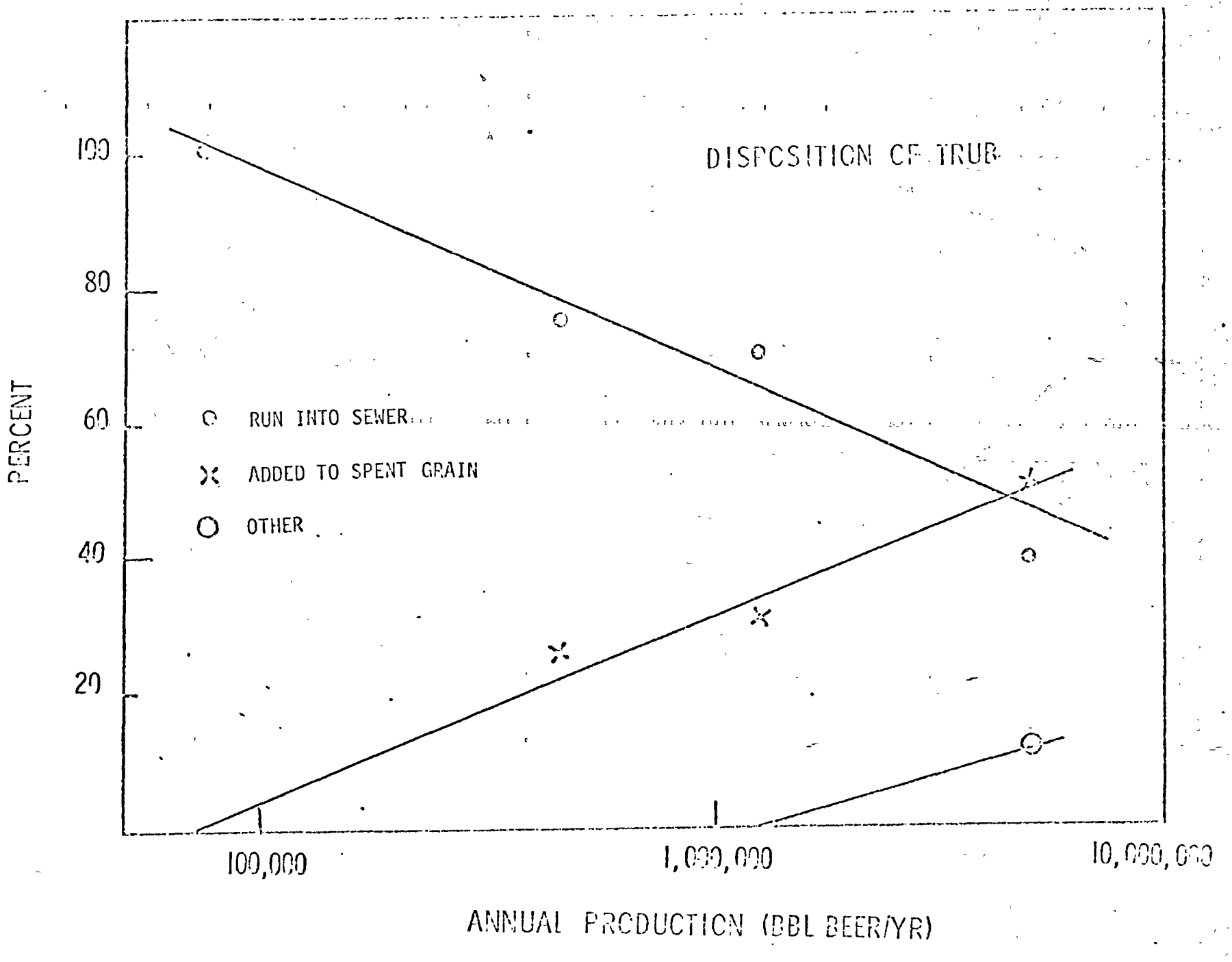

TOTAL WATER USAGE TREND
TOTAL WATER (BBL/BBL BEER)
30
20
10
100,0000
1,000,000
10,000,000
ANNUAL PRODUCTION (BBL BEER / YR)


100
80
60
40
20
PERCENT
METHOD OF SEPARATION OF SPENT GRAINS FROM WORT
LAUTER TUN
FILTER PRESS
STRAINMASTER
100,000
1,000,000
10,000,000
ANNUAL PRODUCTION (BBL BEER / YR)


100
80
60
40
20
PERCENT
DISPOSITION OF WET SPENT GRAINS
HAULED AWAY WET
DRIED IN BREWRY
SENT TO OUTSIDE DRIER
100,000
1,000,000
10,000,000
ANNUAL PRODUCTION (BBL BEER / YR)


HOPS HAULED AWAY
ADDED TO SPENT GRAIN LIQUOR
PUT INTO SEWER
OTHER
FINAL DISPOSITION OF HOPS
PERCENT
100
80
60
40
20
100,000
1,000,000
10,000,000
ANNUAL PRODUCTION (BBL BEER/YR)


FINAL DISPOSITION
OF SPENT HOP LIQUOR
80
60
40
20
RUN INTO SEWER
ADDED TO SPENT GRAINS
RETURNED TO BREWING PROCESS
OTHER
1,000,000
ANNUAL PRODUCTION (BBL BEER/YR)


DISPOSITION OF TRUB
100
80
60
40
20
PERCENT
RUN INTO SEWER
ADDED TO SPENT GRAIN
OTHER
100,000
1,000,000
10,000,000
ANNUAL PRODUCTION (BBL BEER/YR)

A BREWHOUSE

B FERMENTATION

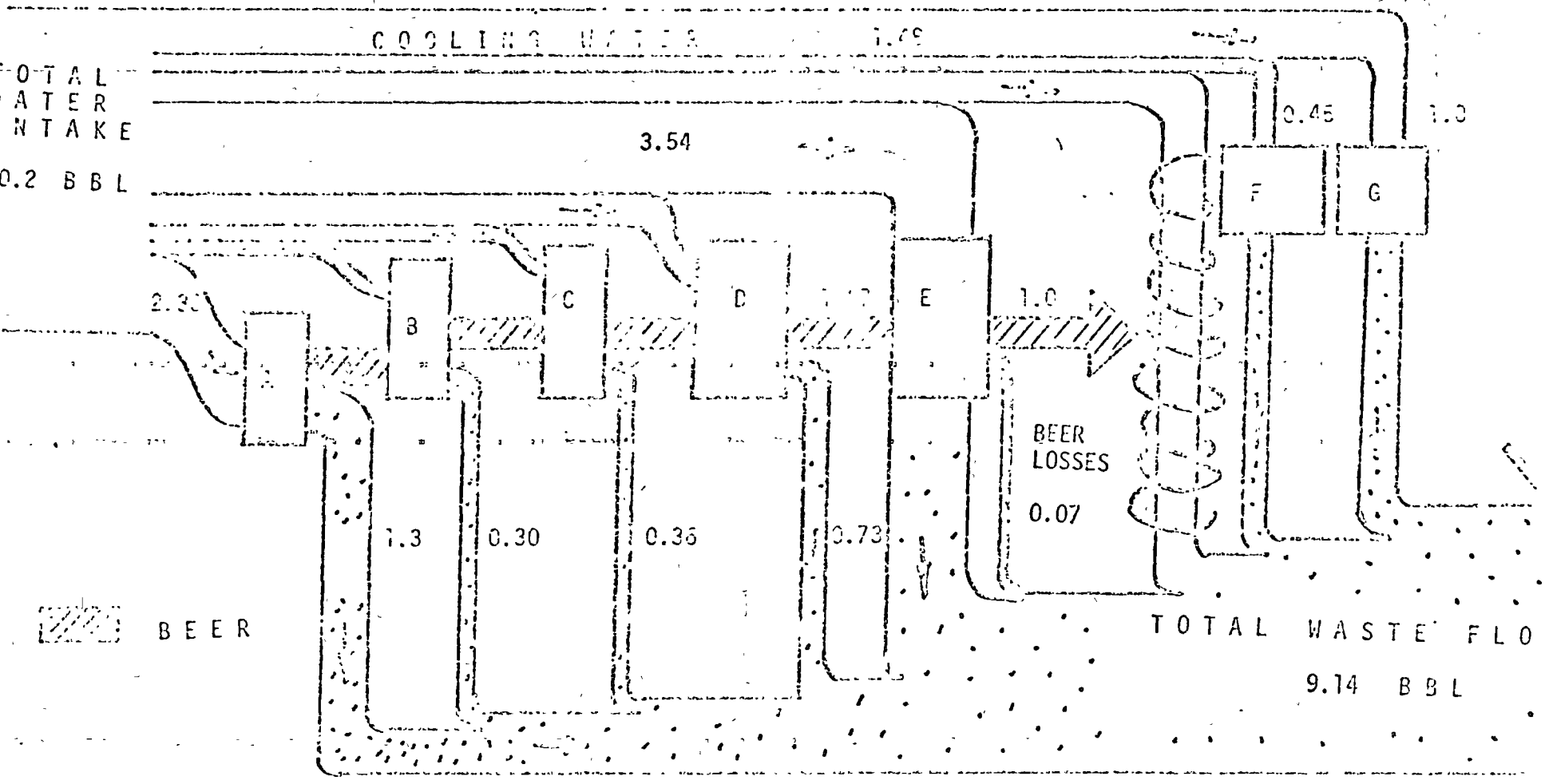
C AGING

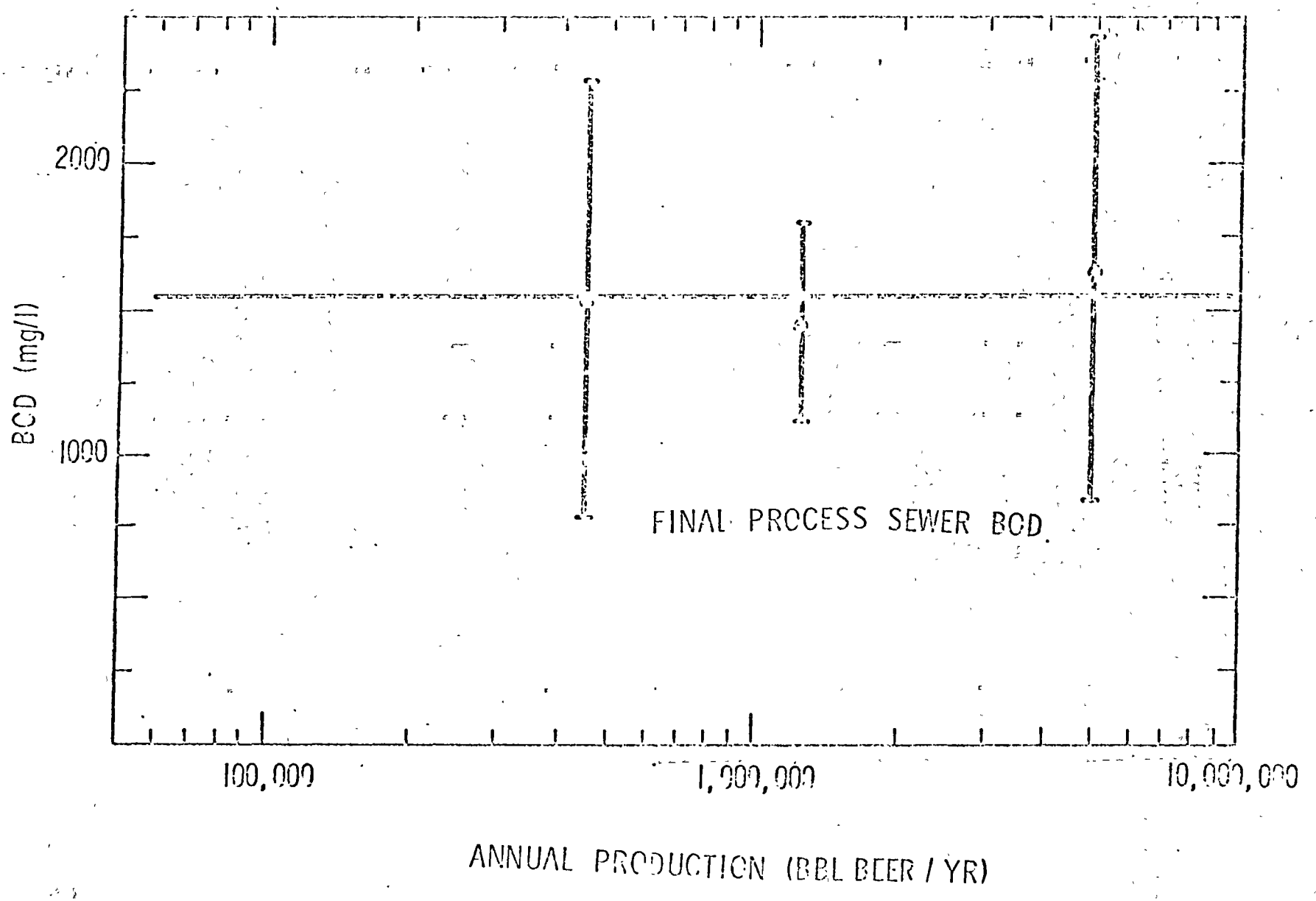
D FILTRATION AND WASHDOWN

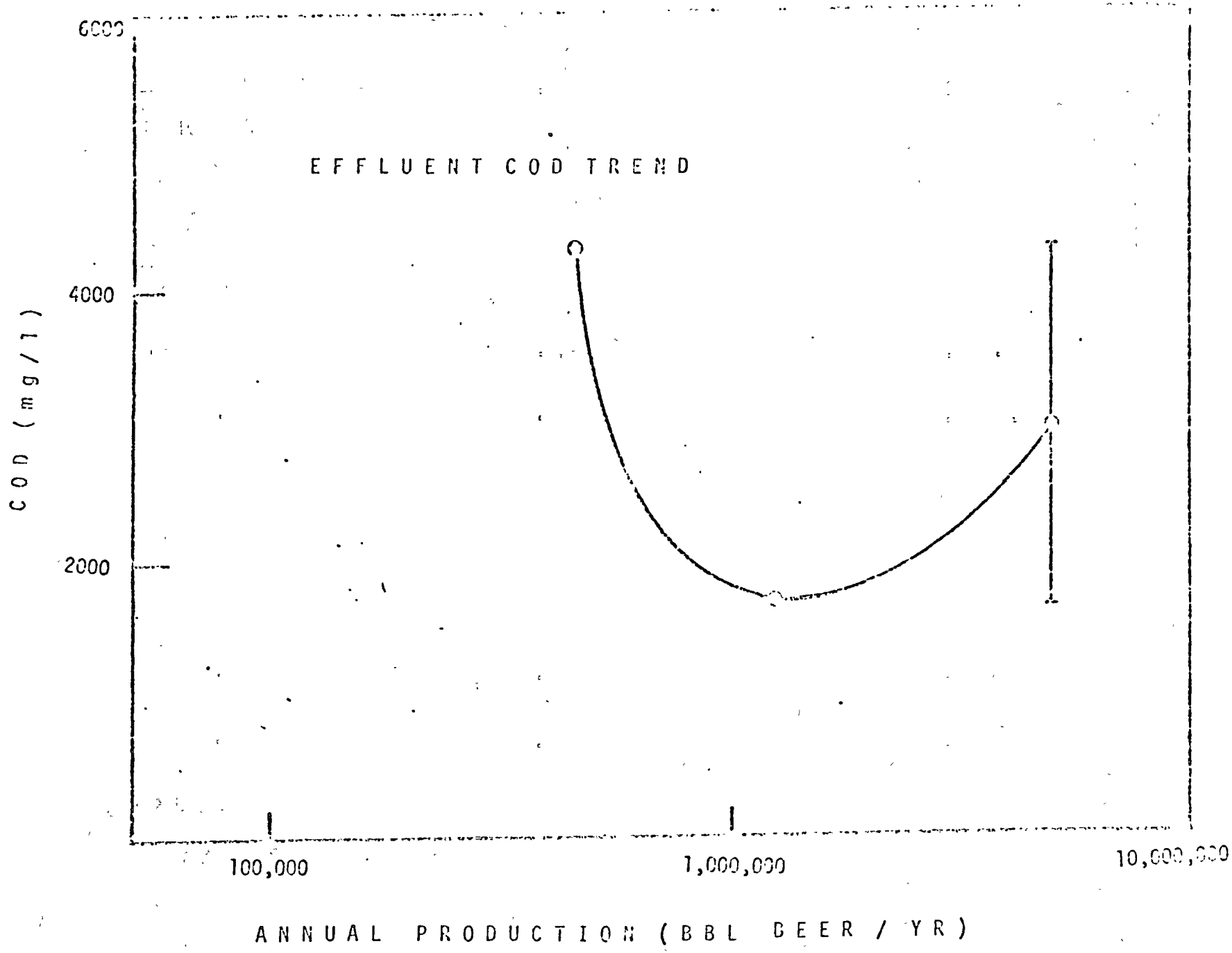
E BOTTLING

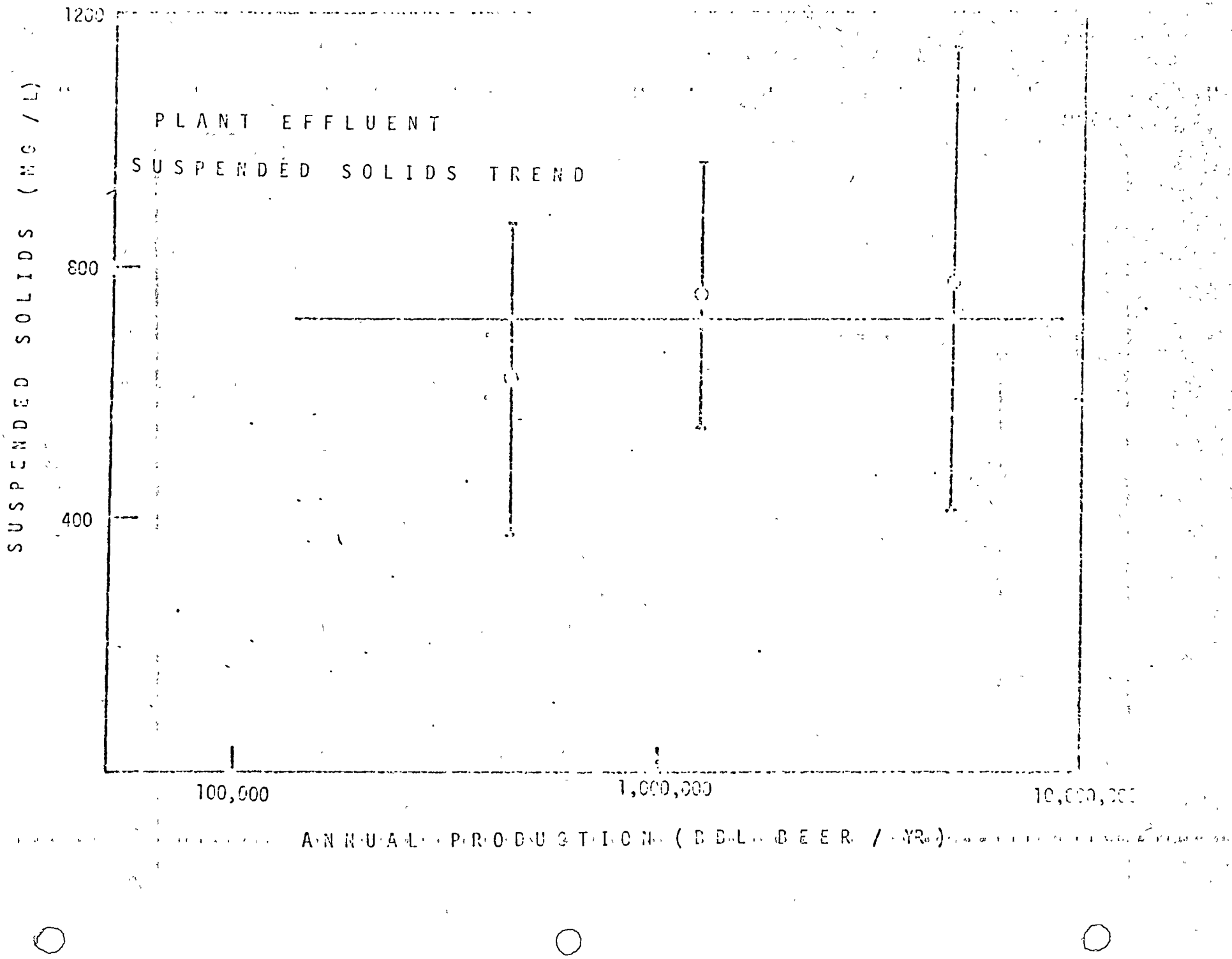
F HOUSE CLEANING

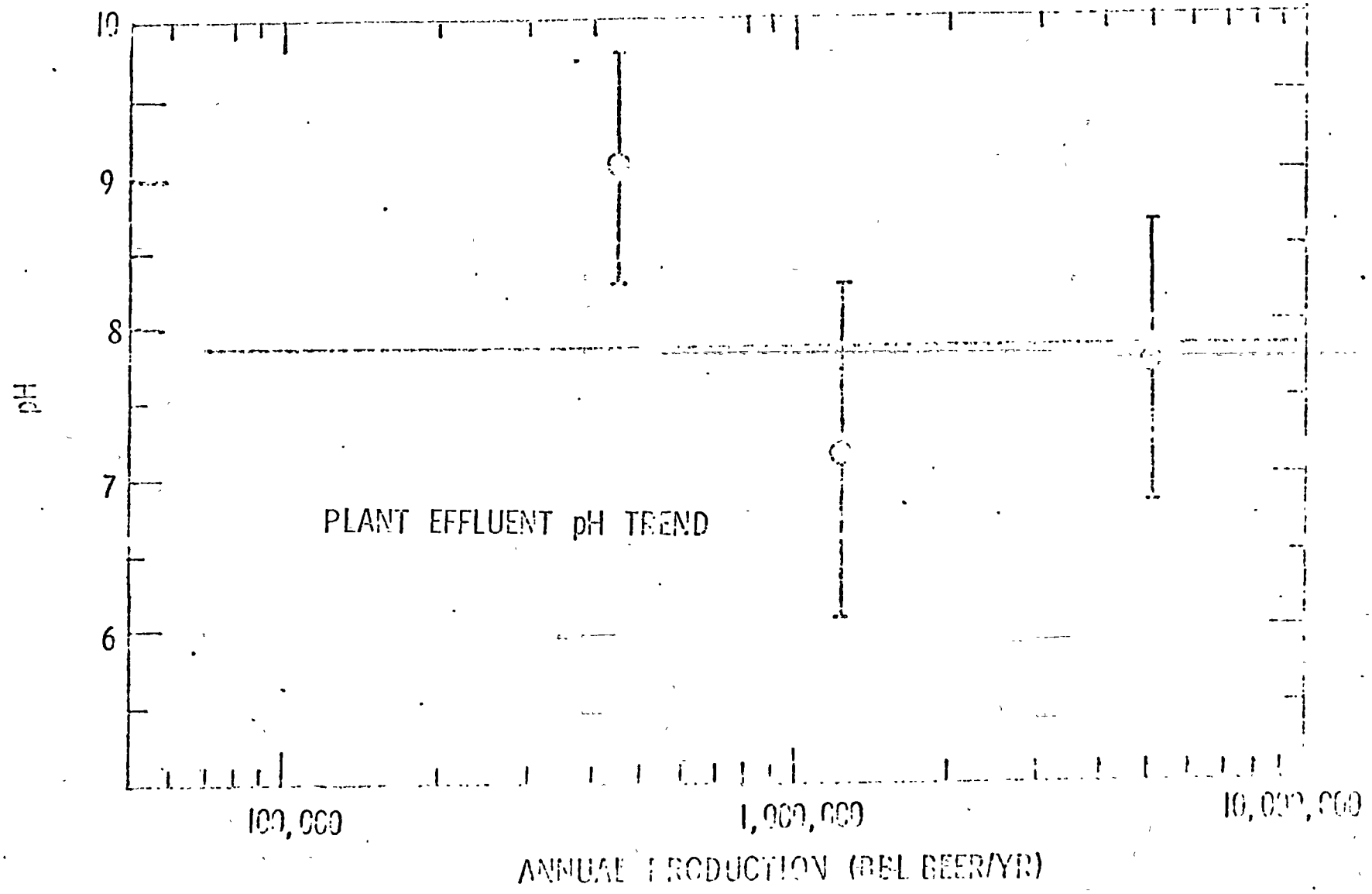
G OTHER




2000
1000
BOD (mg/l)
FINAL PROCESS SEWER BOD
100,000
1,000,000
10,000,000
ANNUAL PRODUCTION (BBL BEER / YR)

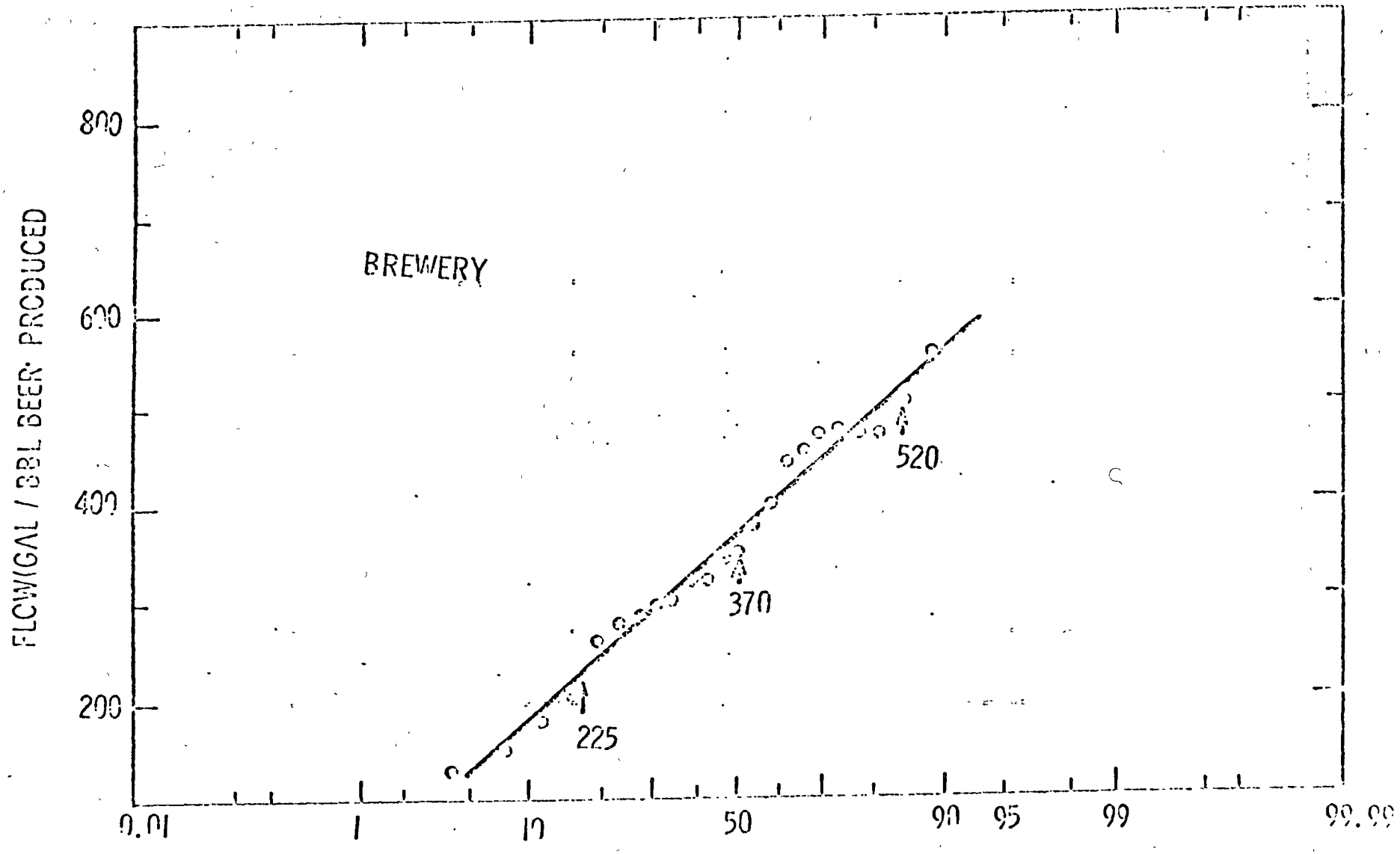

EFFLUENT COD TREND
6000
4000
2000
COD (mg/l)
100,000
1,000,000
10,000,000
ANNUAL PRODUCTION (BBL BEER / YR)

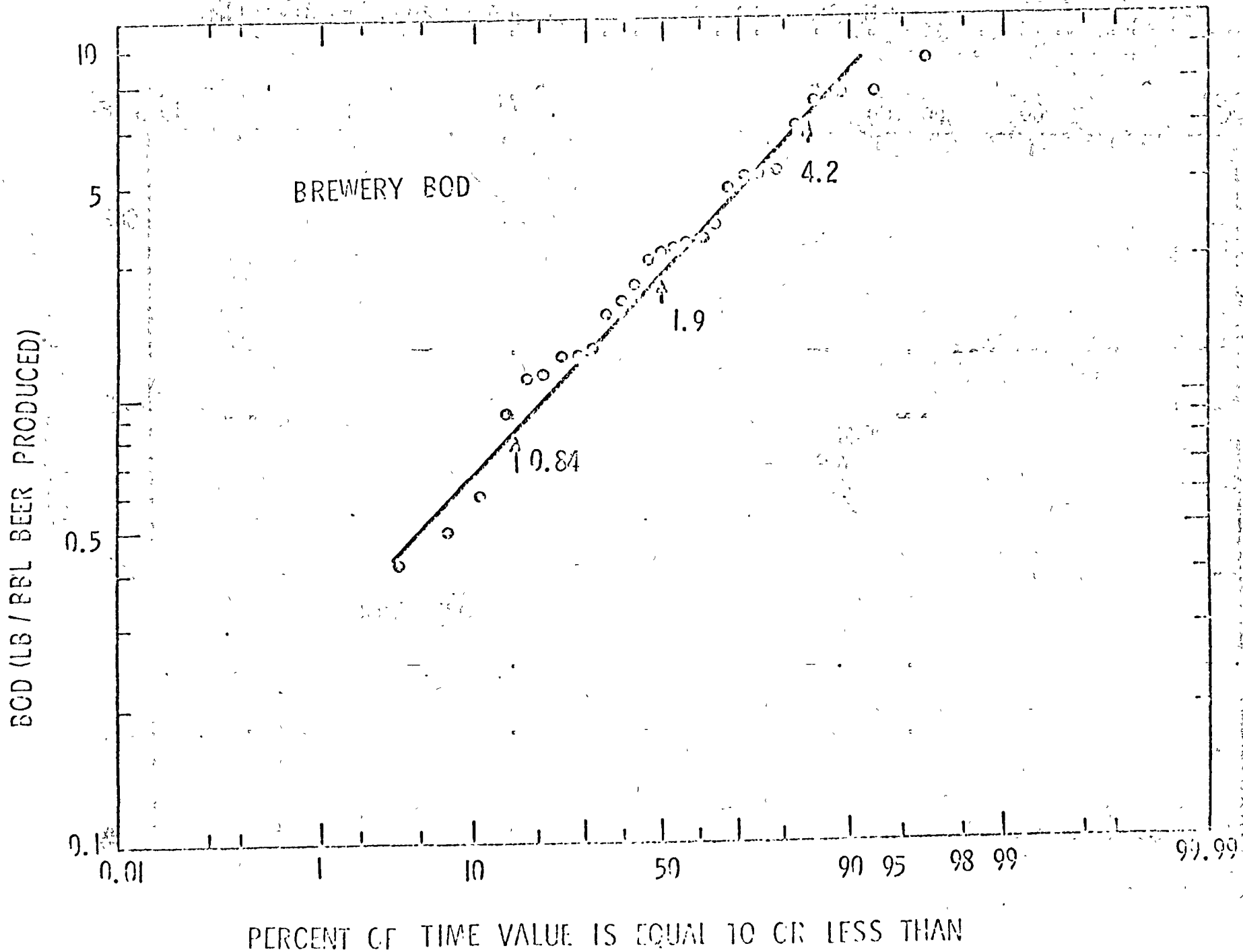

PLANT EFFLUENT
SUSPENDED SOLIDS TREND
SUSPENDED SOLIDS (MG / L)
1200
800
400
100,000
1,000,000
ANNUAL PRODUCTION (BBL BEER / YR.)

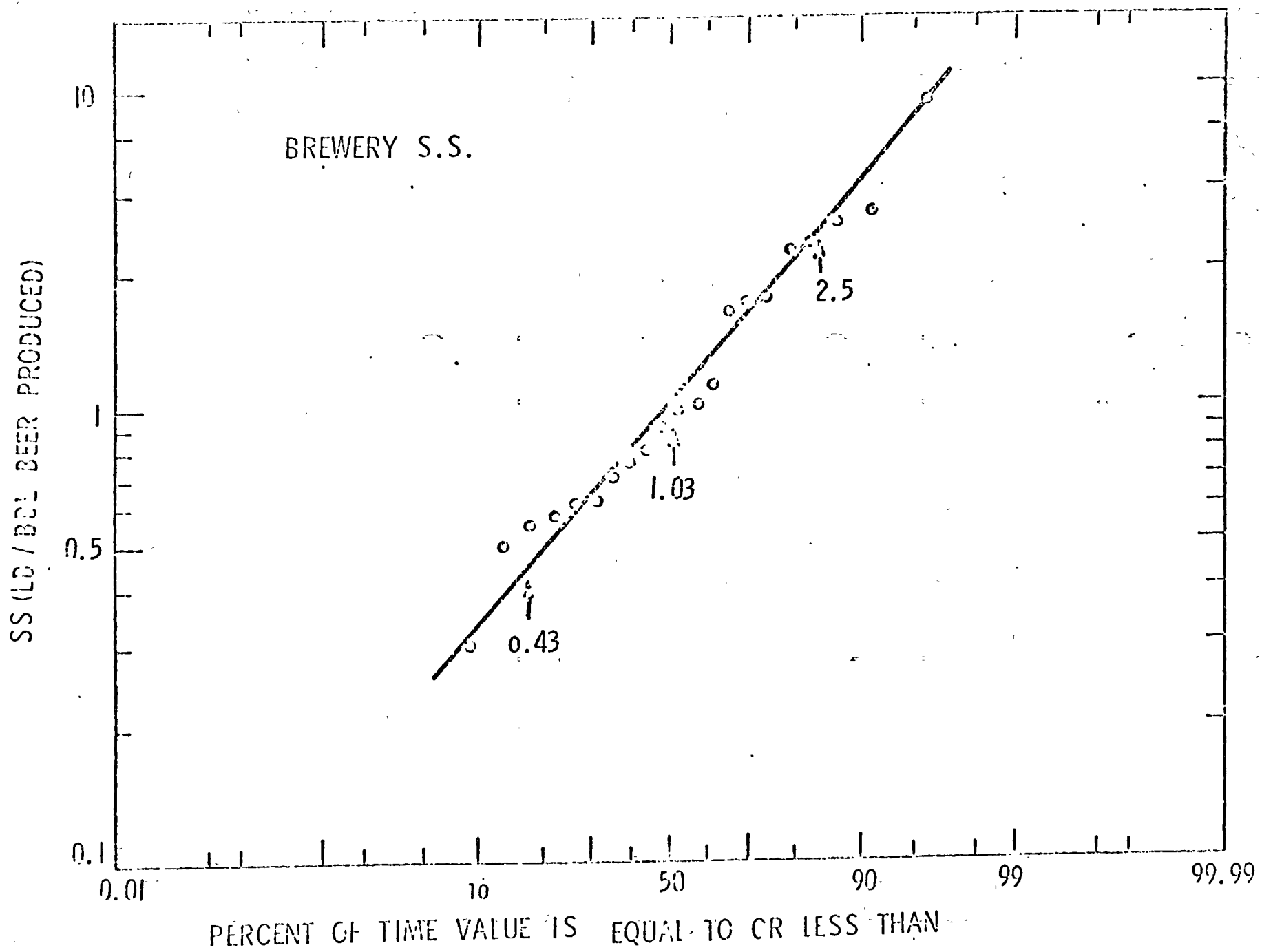

10
9
8
7
6
pH
PLANT EFFLUENT pH TREND
100,000
1,000,000
10,000,000
ANNUAL PRODUCTION (BBL BEER/YR)

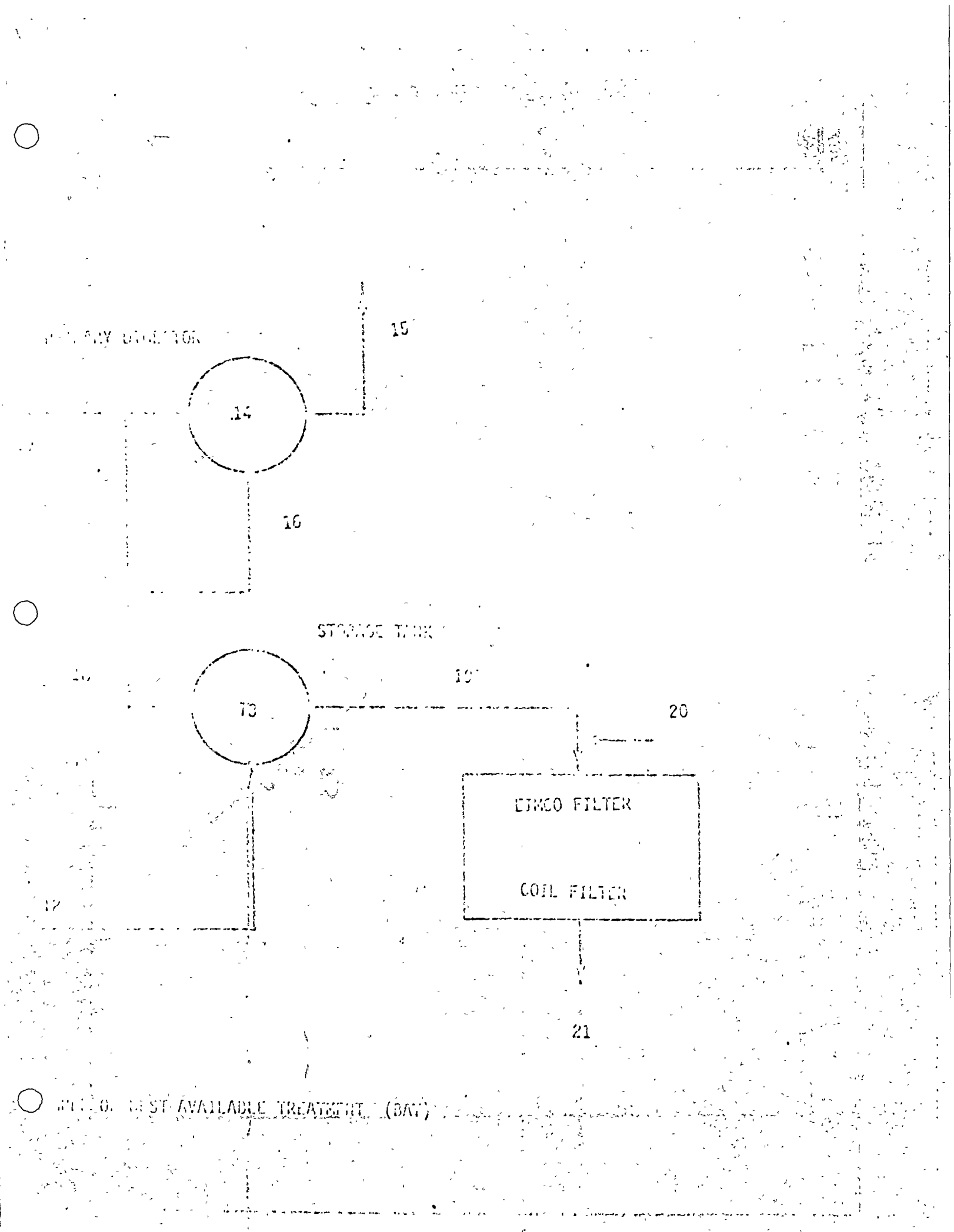
WASTE CHARACTERIZATION

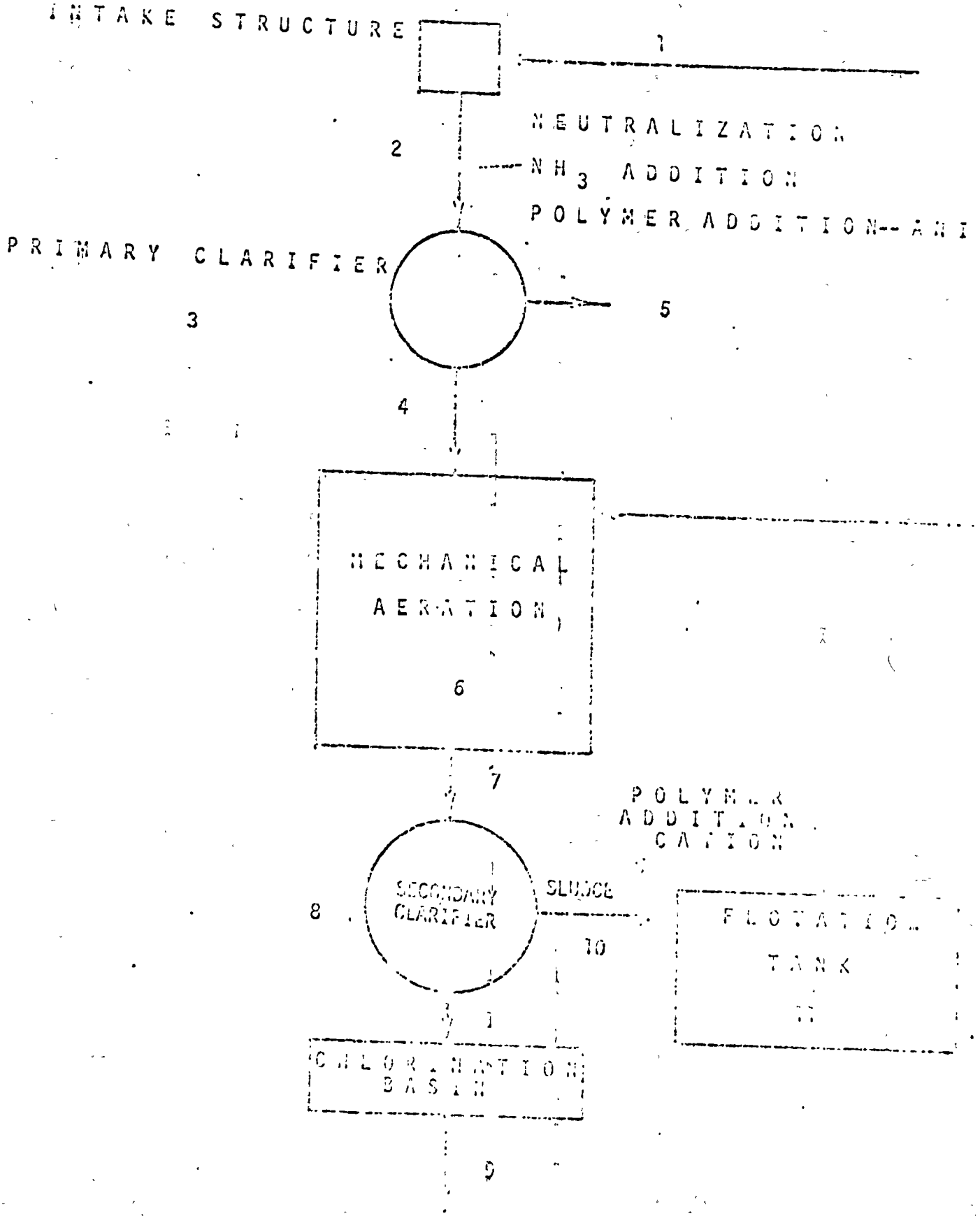
ANNUAL PRODUCTION 100,000 BBL	P>15	7.5<P<15	1.5<P<7.5
Process Low	9.1	8.5	6.7
Cooling Water Flow	2.0	.2	---
SS mg/l	770	760	62[illegible]
COD mg/l	3,000	1,700	4,30[illegible]
BOD mg/l	1,500	1,400	1,500
#BOD /BBL	3.8	3.3	2.8
pH	7.7	6.9	9.0
Process Temp^{o} F	82	91	.6[illegible]

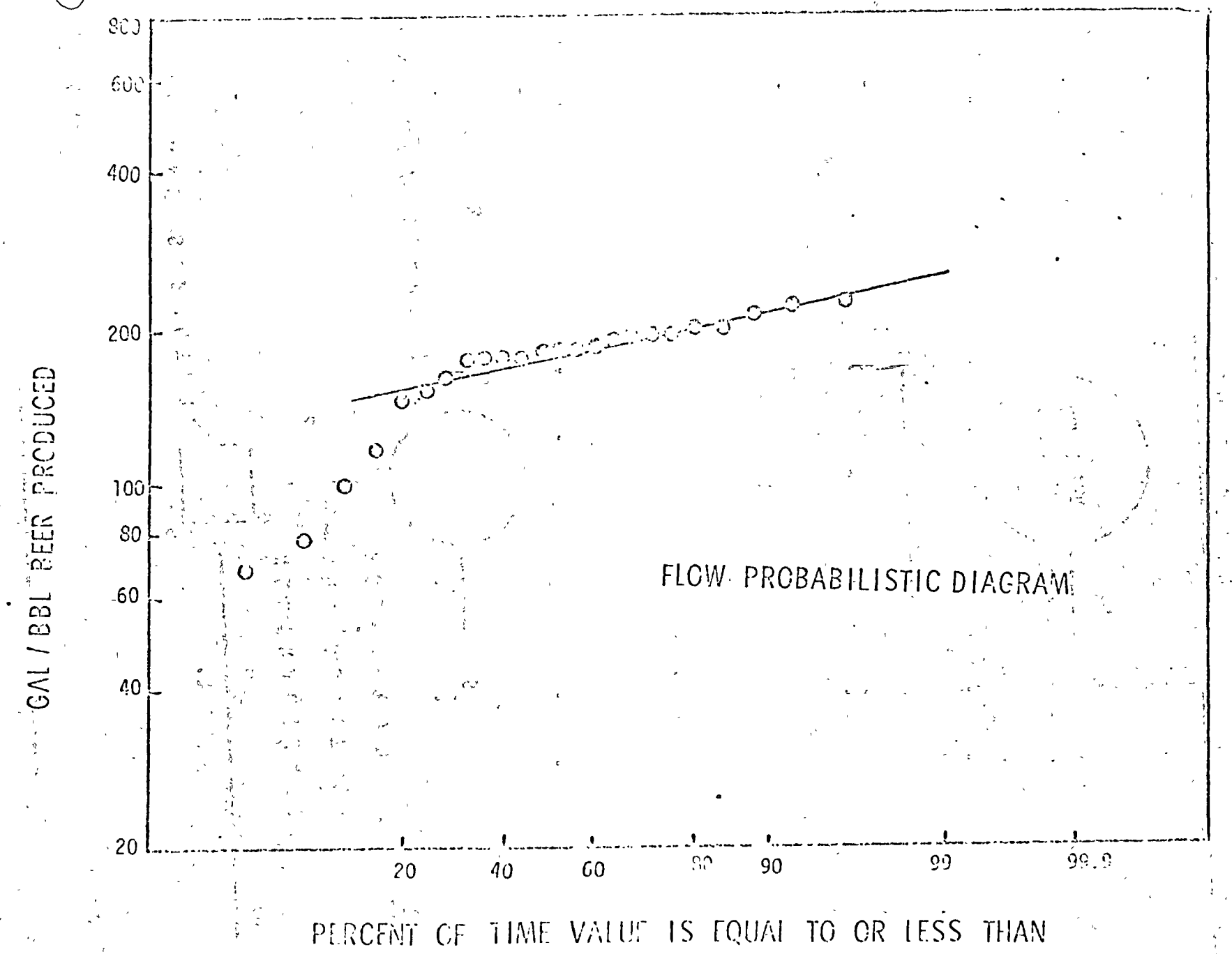

BREWERY
FLOW/GAL / BBL BEER PRODUCED
800
600
400
200
520
370
225
0.01
1
10
50
90
95
99
99.99
PERCENT OF TIME VALUE IS EQUAL TO OR LESS THAN

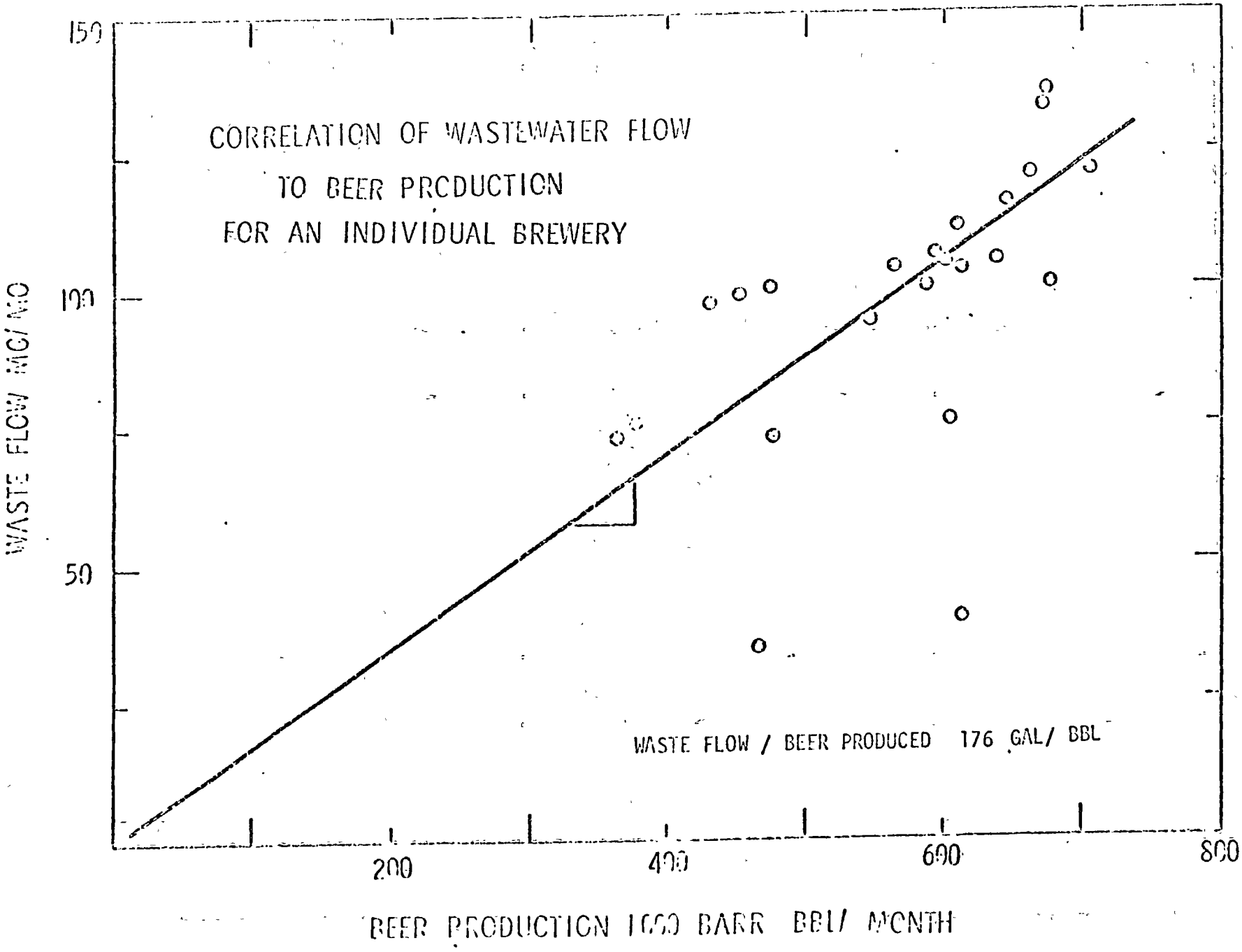

BREWERY BOD
10
5
1
0.5
0.1
0.84
1.9
4.2
BOD (LB / BBL BEER PRODUCED)
0.01
1
10
50
90
95
98
99
99.99
PERCENT OF TIME VALUE IS EQUAL TO OR LESS THAN

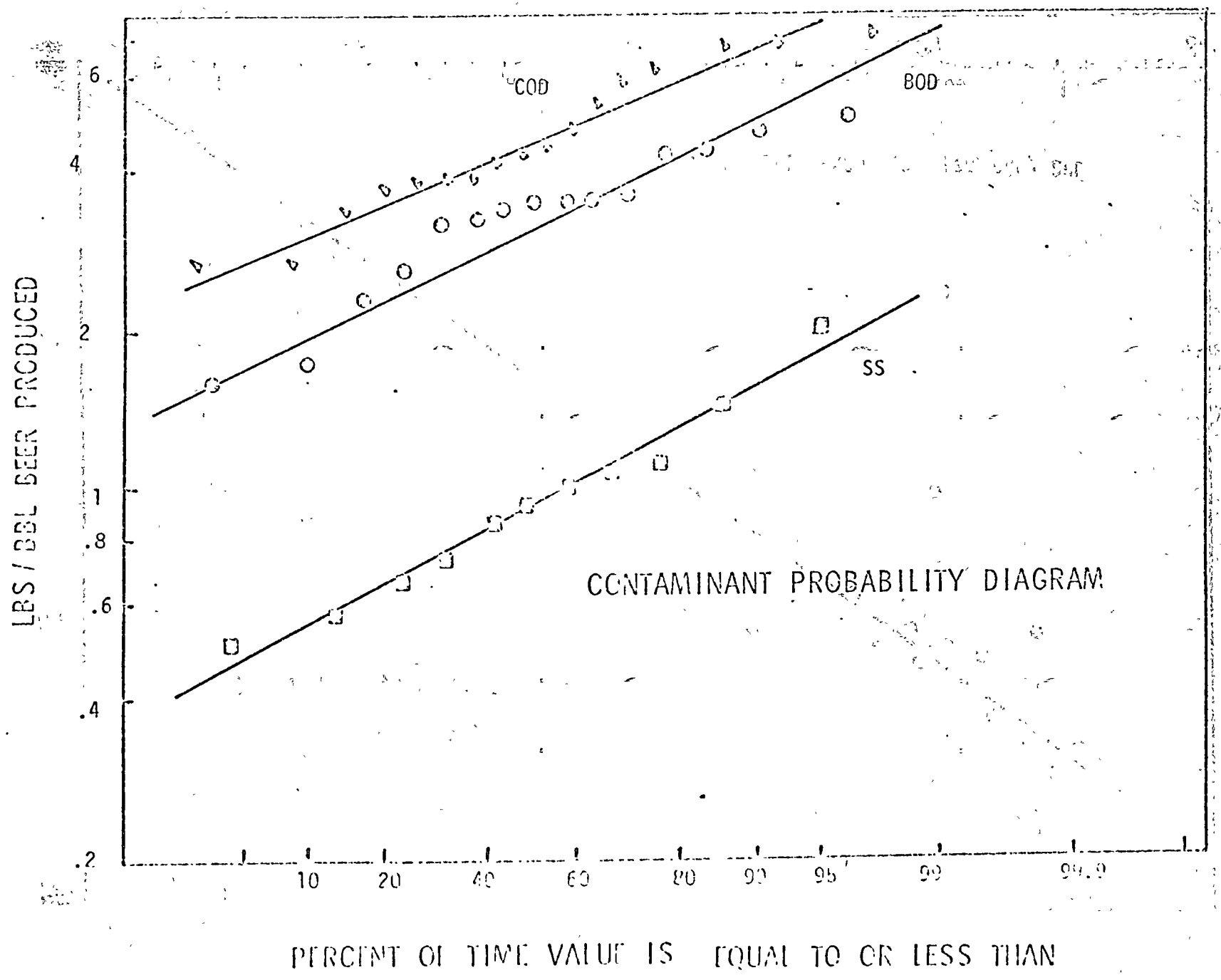

BREWERY S.S.
SS (LB / BBL BEER PRODUCED)
10
1
0.5
0.1
0.01
10
50
90
99
99.99
0.43
1.03
2.5
PERCENT OF TIME VALUE IS EQUAL TO OR LESS THAN

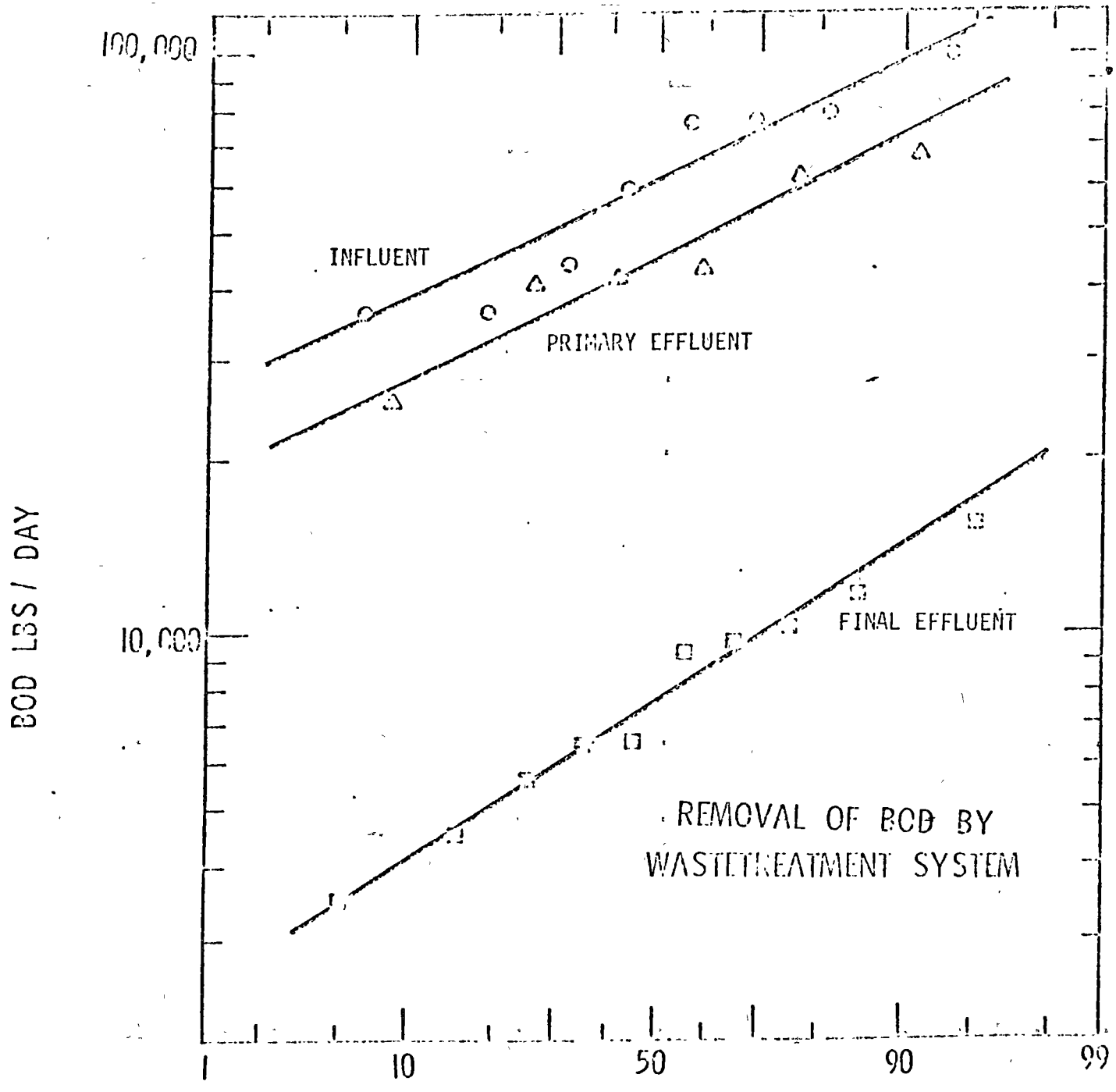

15
14
16
STORAGE TANK
19
13
20
DEMCO FILTER
COIL FILTER
12
21

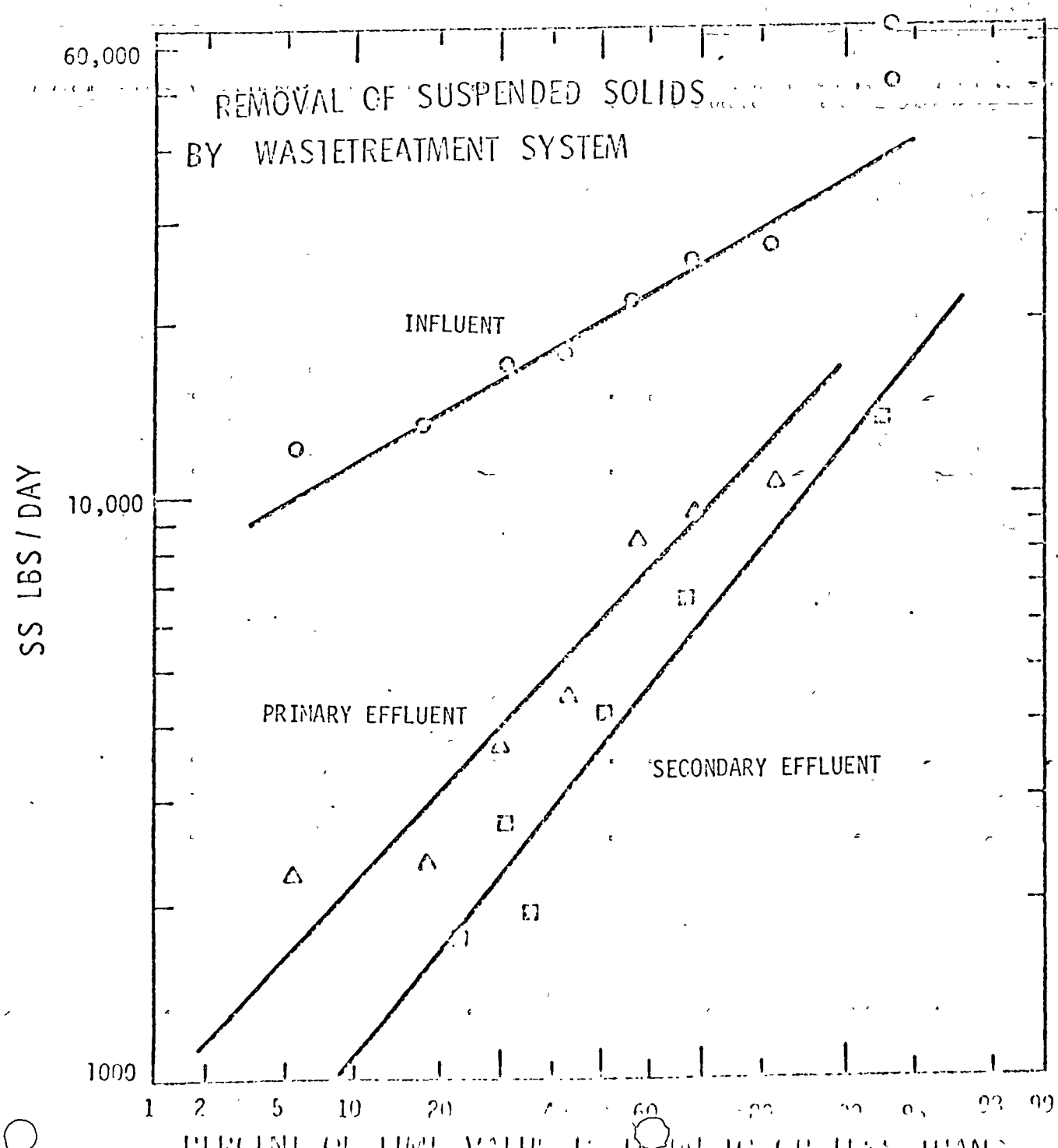

INTAKE STRUCTURE
1
NEUTRALIZATION
2
NH3 ADDITION
POLYMER ADDITION--ANIO
PRIMARY CLARIFIER
3
5
4
MECHANICAL AERATION
6
7
POLYMER ADDITION CATION
SECONDARY CLARIFIER
SLUDGE
8
10
FLOTATION TANK
11
CHLORINATION BASIN
9

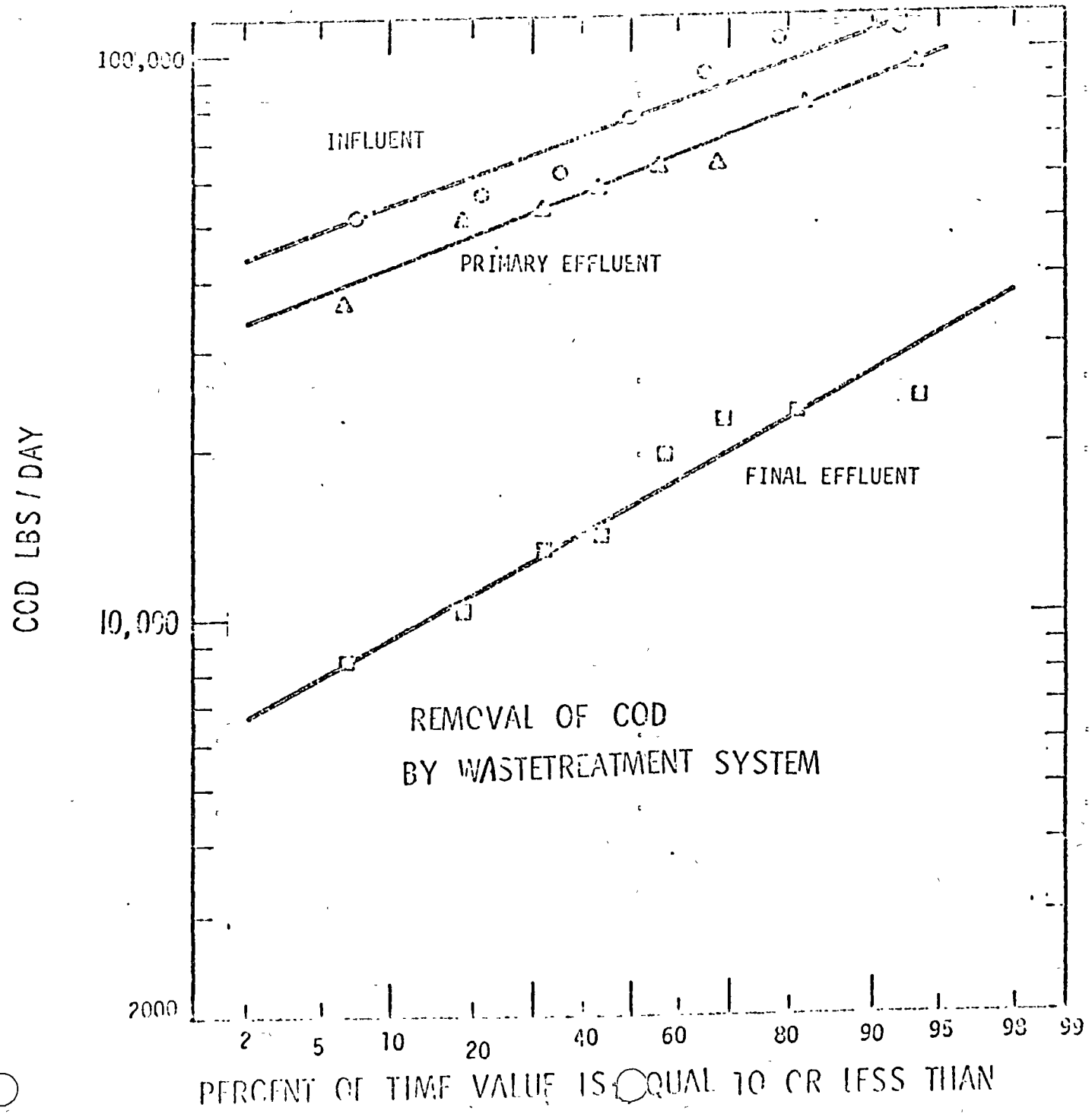

800
600
400
200
100
80
60
40
20
GAL / BBL BEER PRODUCED
FLOW PROBABILISTIC DIAGRAM
20
40
60
80
90
99
99.9
PERCENT OF TIME VALUE IS EQUAL TO OR LESS THAN

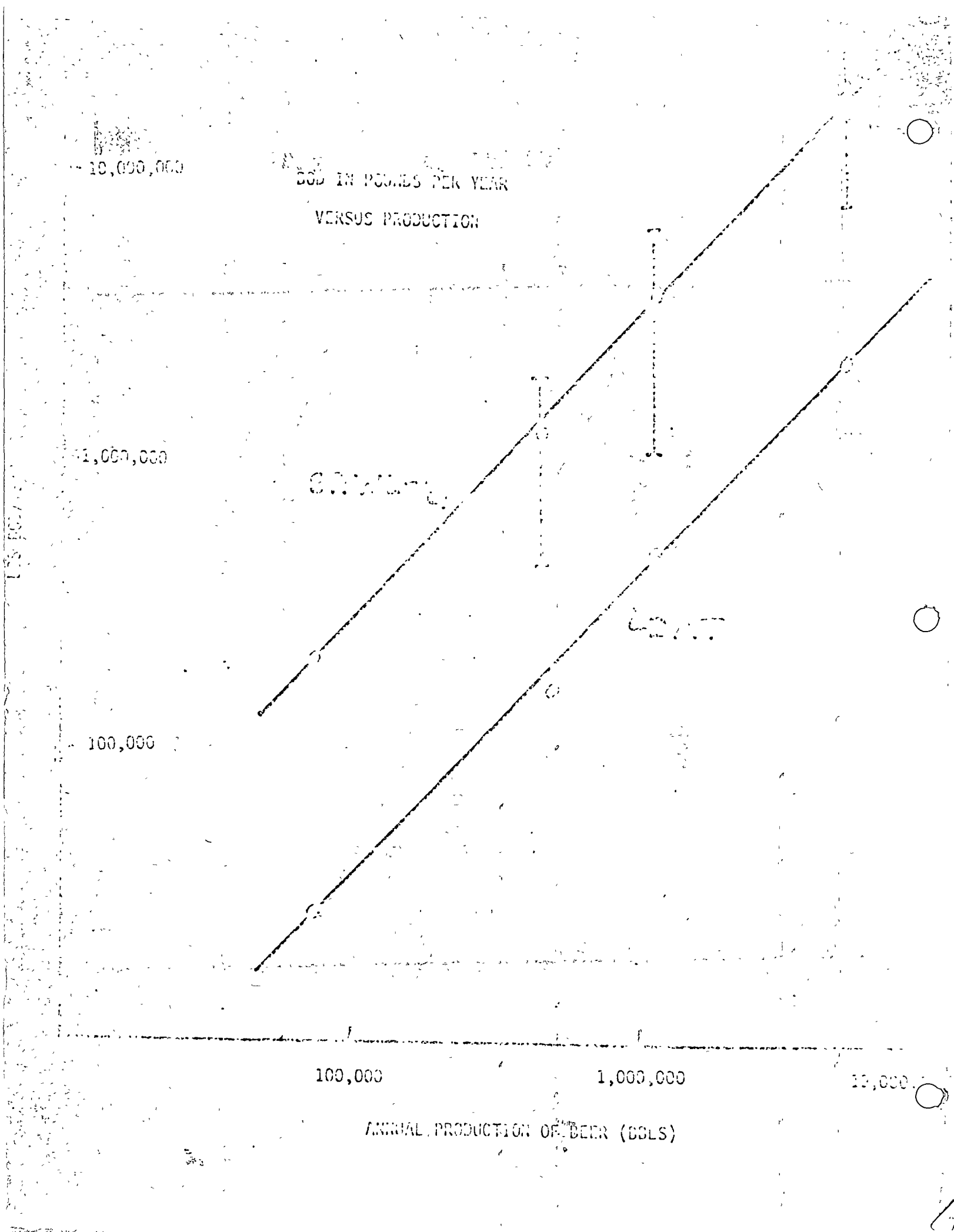

CORRELATION OF WASTEWATER FLOW
TO BEER PRODUCTION
FOR AN INDIVIDUAL BREWERY
WASTE FLOW / BEER PRODUCED 176 GAL/ BBL
150
100
50
200
400
600
800
WASTE FLOW 1000 GAL/ MO
BEER PRODUCTION 1000 BARR BBL/ MONTH


COD
BOD
SS
CONTAMINANT PROBABILITY DIAGRAM
LBS / BBL BEER PRODUCED
6
4
2
1
.8
.6
.4
.2
10
20
40
60
80
90
95
99
99.9
PERCENT OF TIME VALUE IS EQUAL TO OR LESS THAN


100,000
10,000
BOD LBS / DAY
INFLUENT
PRIMARY EFFLUENT
FINAL EFFLUENT
REMOVAL OF BOD BY
WASTETREATMENT SYSTEM
1
10
50
90
99
PERCENT OF TIME VALUE IS EQUAL TO OR LESS THAN

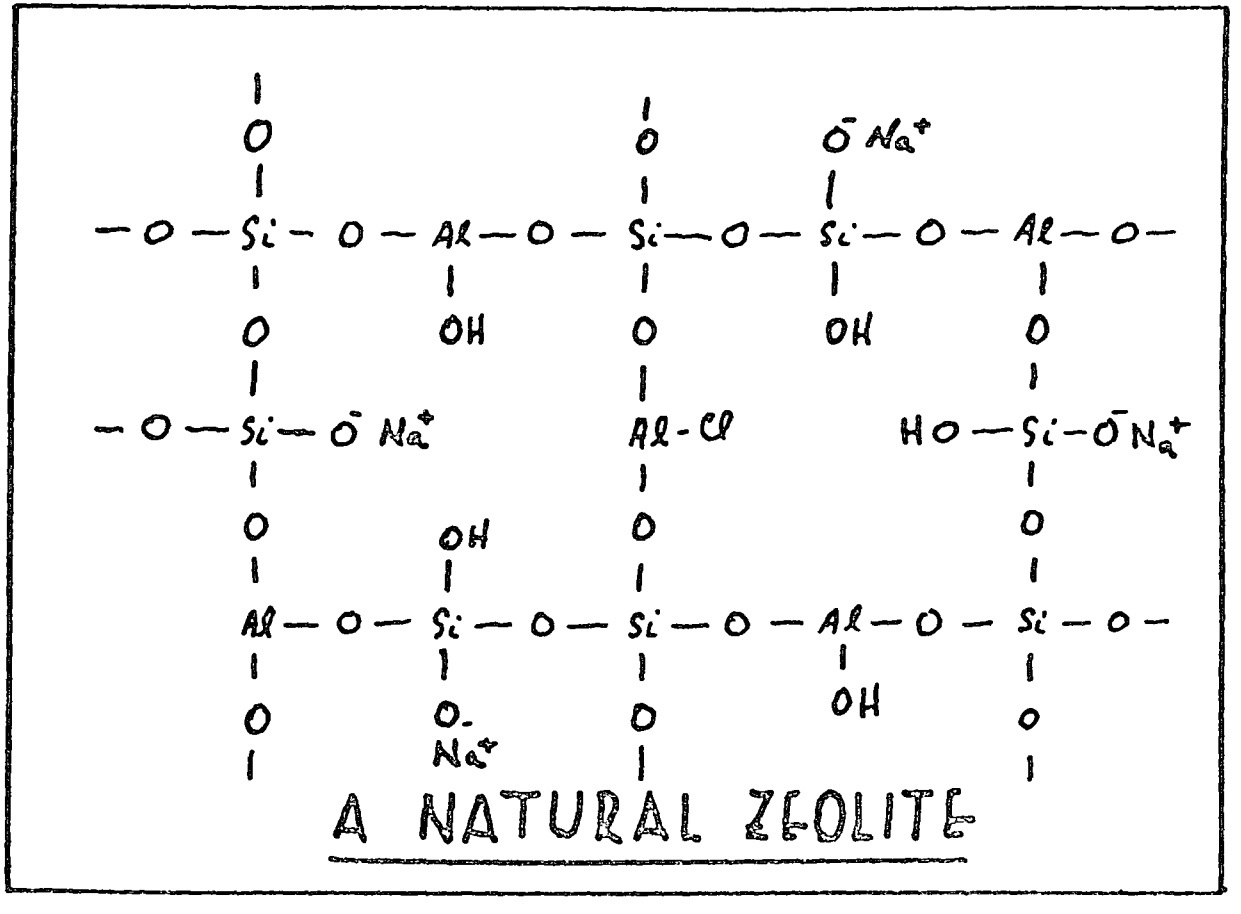

REMOVAL OF SUSPENDED SOLIDS
BY WASTETREATMENT SYSTEM
60,000
10,000
1000
SS LBS / DAY
INFLUENT
PRIMARY EFFLUENT
SECONDARY EFFLUENT
1
2
5
10
20
99

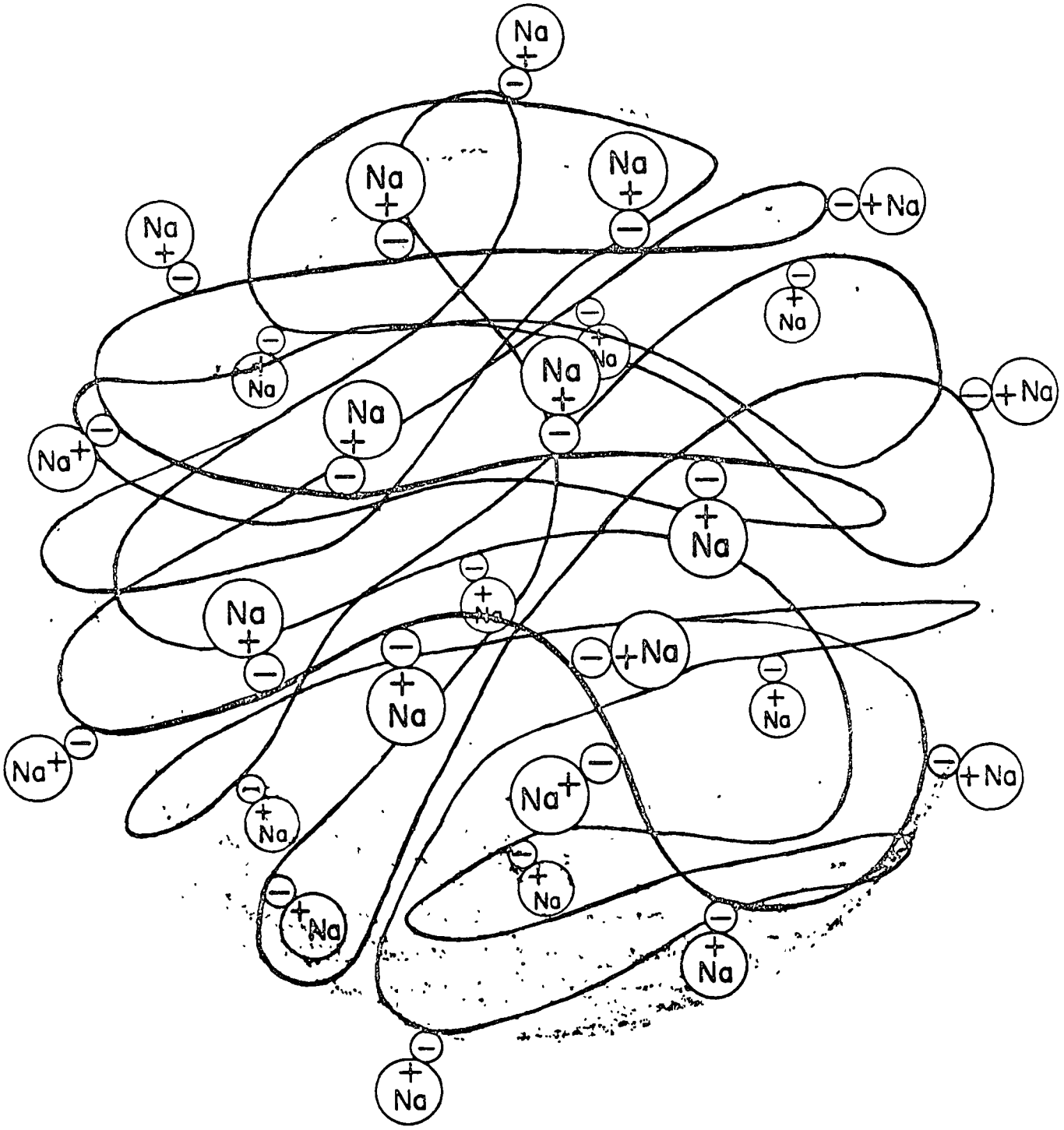

100,000
10,000
2000
COD LBS / DAY
INFLUENT
PRIMARY EFFLUENT
FINAL EFFLUENT
REMOVAL OF COD
BY WASTETREATMENT SYSTEM
2
5
10
20
40
60
80
90
95
98
99
PERCENT OF TIME VALUE IS EQUAL TO OR LESS THAN


10,000,000
BOD IN POUNDS PER YEAR
VERSUS PRODUCTION
1,000,000
100,000
100,000
1,000,000
ANNUAL PRODUCTION OF BEER (BBLS)

ION EXCHANGE

M. J. Humenick


A NATURAL ZEOLITE



Model of a cation exchanger, showing negatively charged exchange sites on the skeleton holding sodium ions like grapes on a vine.

Figure 1

ION EXCHANGE IS NOT NEW The process was studied by agricultural chemists more than a hundred years ago They found that certain types of soil containing silica and aluminum compounds had the ability of exchanging ions with those in water. These soils, called zeolites, were adapted for use in softening water in the early 1900's. The technology has grown rapidly. Today, ion exchange plays a fundamental role in industrial water engineering

Concepts and Terms

The conventional ion exchange materials used in water conditioning can be visualized as skeleton-like structures having many attached "exchange sites" (Figure 1) The skeleton is insoluble in water but is electrically charged, holding ions of opposite charge at the exchange sites

Exchange materials with negatively charged skeletons are referred to as cation exchangers since they attract positive ions; anion exchangers are positively charged and consequently, attract anions. The porous structure of ion exchange materials permits water to permeate the particle, affording good contact with the exchange sites.

If calcium ions, or cations of other species than sodium should approach a cation exchanger particle saturated with sodium ions, some of them may be captured by the exchanger. This would release sodium ions previously held at the exchange sites on the skeleton. An equilibrium is soon established between the distribution of these species on the exchanger and in the water surrounding the exchanger.

Laboratory studies of such equilibria show that an ion exchanger has a preference or "selectivity" for one species over another. This selectivity depends on ionic charge molecular weight, and solution concentration, (Figure 2) For example, a cation exchanger holds calcium ions more firmly than sodium ions when immersed in a weak solution, such as a typical natural water. For this reason, if a cation exchanger is originally saturated with sodium ions, it can be used to soften water, taking calcium out of the water and releasing sodium in exchange.

Fortunately, the selectivity between these species is reversed at high concentrations, so that a strong solution of brine can readily displace calcium from the exchange sites, "regenerating" the exchanger by returning sodium ions to their original positions on the exchanger skeleton.

The Measure of Exchange Capacity

Ion exchange materials in aqueous systems contain a large proportion of water. We might consider the ion exchange particle containing water to be a tiny vessel holding a salt solution The number of ion exchange sites in a unit volume, which is a measure of the "exchange capacity" of the ion exchange material, can be expressed in the same terms the chemist uses in defining the strength of a salt solution The chemist speaks of these solutions in terms of their "normality." "One normal solution" contains one equivalent weight of salt dissolved in a liter of solution. The ion exchange technologist speaks of the capacity of an ion exchanger in terms of "milliequivalents of exchange sites per milliliter of resin beads in a graduate." (Which is mathematically identical to equivalents per liter or normality). The normality of typical styrene-base cation exchangers is close to 2.0; that of typical strongly basic anion exchangers is about 1.3.

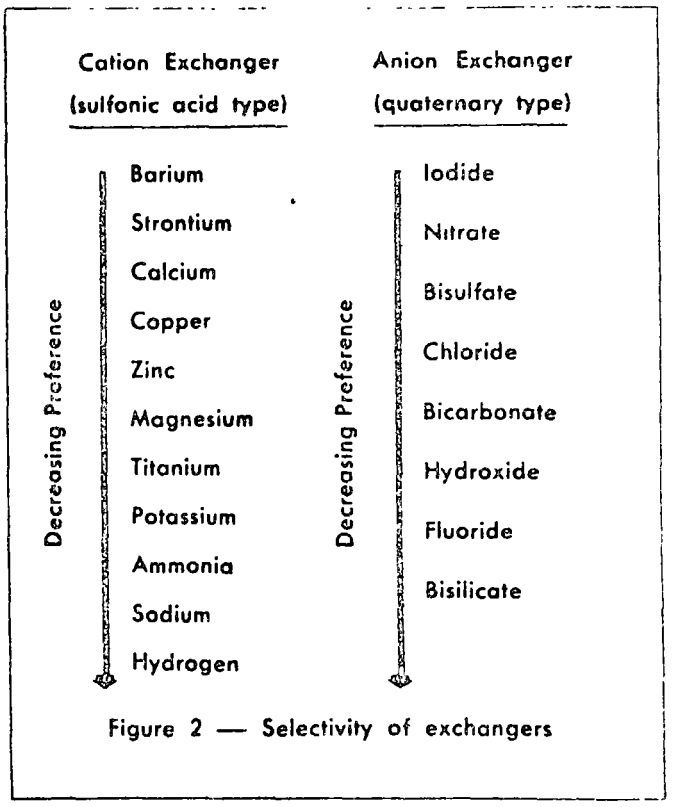


Figure 2 — Selectivity of exchangers

The long tradition in water chemistry of expressing hardness in "grains per gallon," has saddled ion exchange with a jargon all its own. One of the unfortunate results has been the expression of ion exchange capacity in "kilograins per cubic foot," (Kgr./cu. ft.). The factor for converting normality to kilograins per cubic foot is approximately 22 Most commercial styrene-type cation exchangers have a total capacity close to 40 Kgr./cu. ft. The strongly basic anion resins have capacities in the range of 28-30 Kgr./cu. ft.

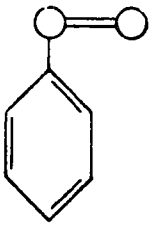
Ion Exchange Materials

The earliest ion exchange materials were either natural or synthetic zeolites — minerals produced from mixtures of aluminum salts and silicates. When these materials were converted to the sodium form by treatment with brine, they were capable of softening water quite effectively. However, capacity was low, and the mineral tended to dissolve, increasing the silica content of the finished water. Research in the late 1930's developed plastic materials (resins) which could be converted to ion exchangers by chemical processing. These resins greatly expanded the applications of ion exchange leading to such modern processes as demineralization — processes unattainable with the zeolite-type materials.

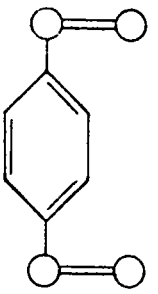
As an example of an ion exchanger fabricated of plastic materials, Figure 3 illustrates the construction of a cation exchanger built of two organic molecules, styrene and divinyl benzene. When a group of styrene molecules are treated under proper conditions of temperature and pressure, they will line up in a long chain, called a "polymer."

The styrene polymer would be too water-soluble after ion exchange sites have been added and not rigid enough

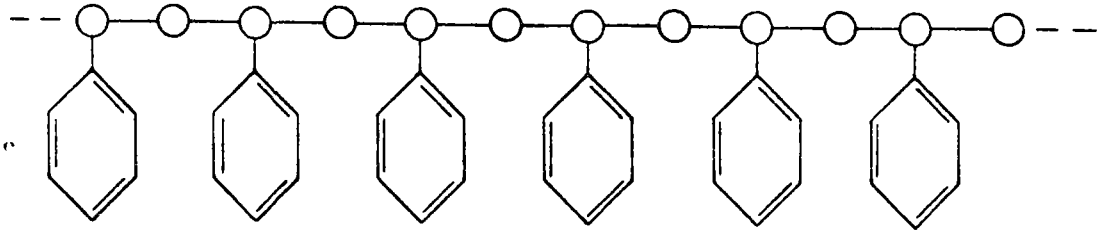
Styrene
(Vinyl Benzene)



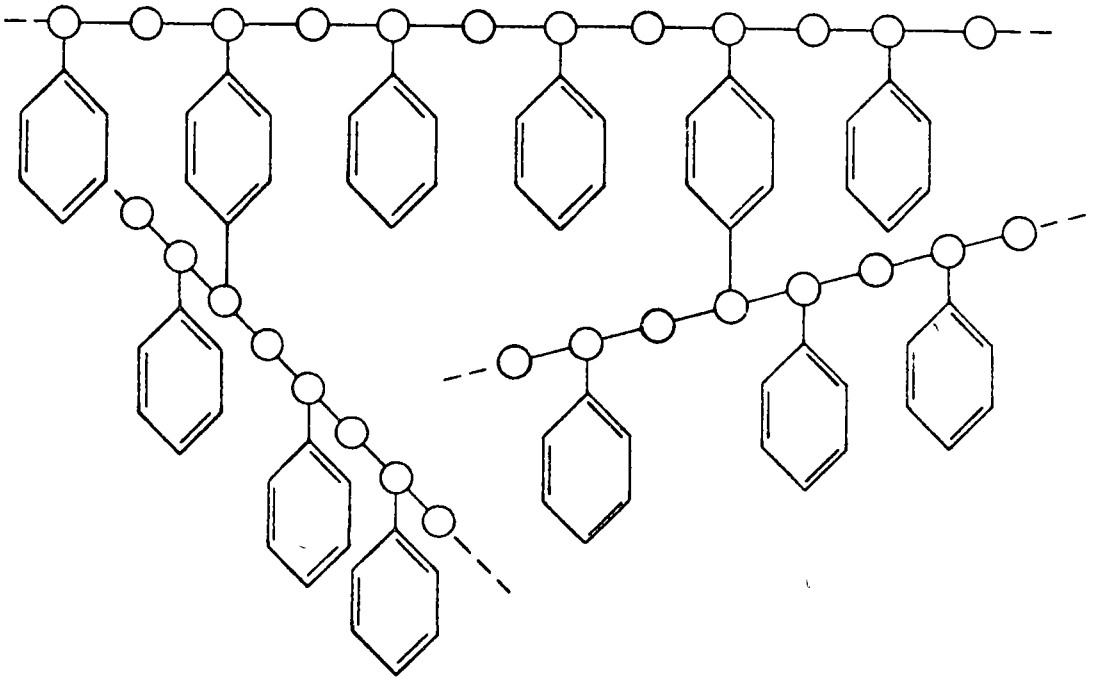
Divinyl Benzene



Polystyrene
a polymer of styrene



Cross Linked
Polystyrene



The production of a stable, rugged plastic by cross-linking polymer chains

Water Conditioning Processes

There are many ways to use cation exchangers, anion exchangers, or combinations of both, using different chemicals for their regeneration, to produce a variety of water treating processes (Figure 4). The simplest of these processes, serving as an excellent example of how ion exchange works, is water softening using only a cation exchanger, regenerated with brine.

Another important ion exchange process using cation exchangers is operated with acid regeneration. This makes it possible to remove sodium from raw water as well as calcium and magnesium. This is the only chemical treatment process which can remove sodium from water solutions economically.

The most significant process using anion exchange resins employs the strongly basic type exchanger regenerated with caustic soda for complete removal of all anions from water. If the water being treated has first been passed through an acid-regenerated cation exchanger, the finished water is essentially mineral-free. So little dissolved matter remains in this water that it may have an electrical resistance of over 1,000,000 ohms per cubic centimeter, as compared to a range of 1,000 - 5,000 for many natural water supplies.

Another important anion exchange process uses strongly basic resin regenerated with salt. Resin so treated is able to remove alkalinity from water for such uses as make-up to boilers or to cooling tower systems.

Softening Operations

The water softening process is typical of almost all ion exchange processes; it is a "batchwise" operation. A vessel containing a bed of resin, usually about 30" deep, serves as a water softener. As hard water percolates downward through the resin, the ion exchange beads are continually bombarded by the calcium and magnesium ions, which gradually replace the sodium on the resin skeleton (Figure 5).

The bed of ion exchange material is somewhat like a storage battery. It can continue to supply sodium ions only until its charge is exhausted. Then it must be regenerated. This is done by washing the resin bed with a relatively strong solution of ordinary salt. Excess salt is rinsed out, and the softener is then ready for another cycle of operation. There are various other steps in the regeneration process designed to improve performance and produce acceptable efficiency. Since the resin acts as a filter, an important step is an upflow wash to rid the bed of debris accumulated during the treating process.

Figure 6 illustrates the various stages of softener operation. The first panel shows the composition of the ion exchange bed at the completion of its softening duty — at "exhaustion." The upper layers have a high hardness content and very little sodium-form resin remains even at the bottom. In the second panel backwashing has redistributed the ionic matter through the bed, so that there is substantially the same composition at each bed level. In the third panel, brine has converted the upper layers completely to the sodium form, since all of the brine used for regeneration passes downwardly and the amount contacting the top few inches is enormously greater than is needed for regeneration. The contaminants from the upper layers are pushed downward, and at the end of the brine regeneration there is still hardness in

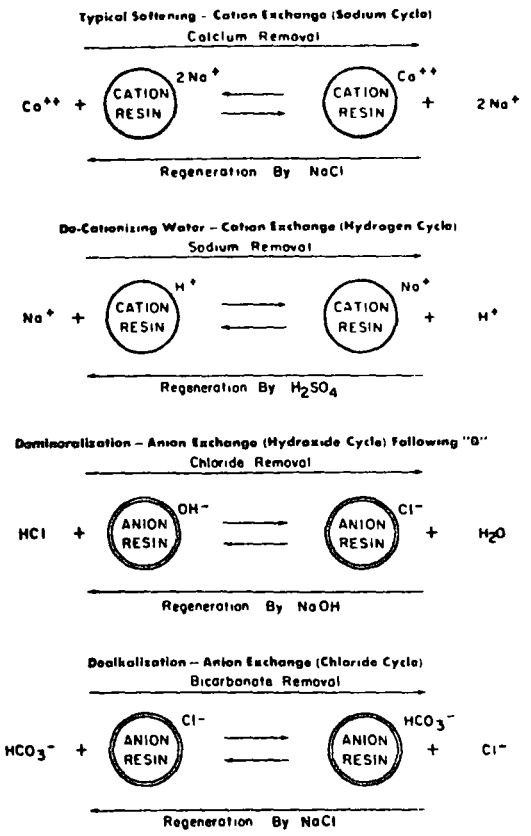
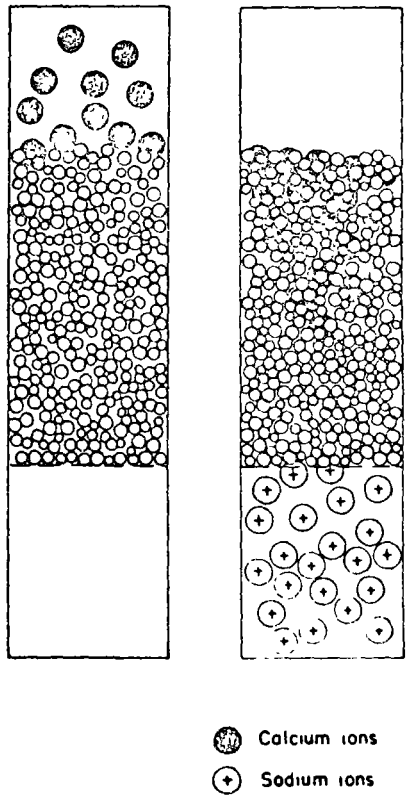
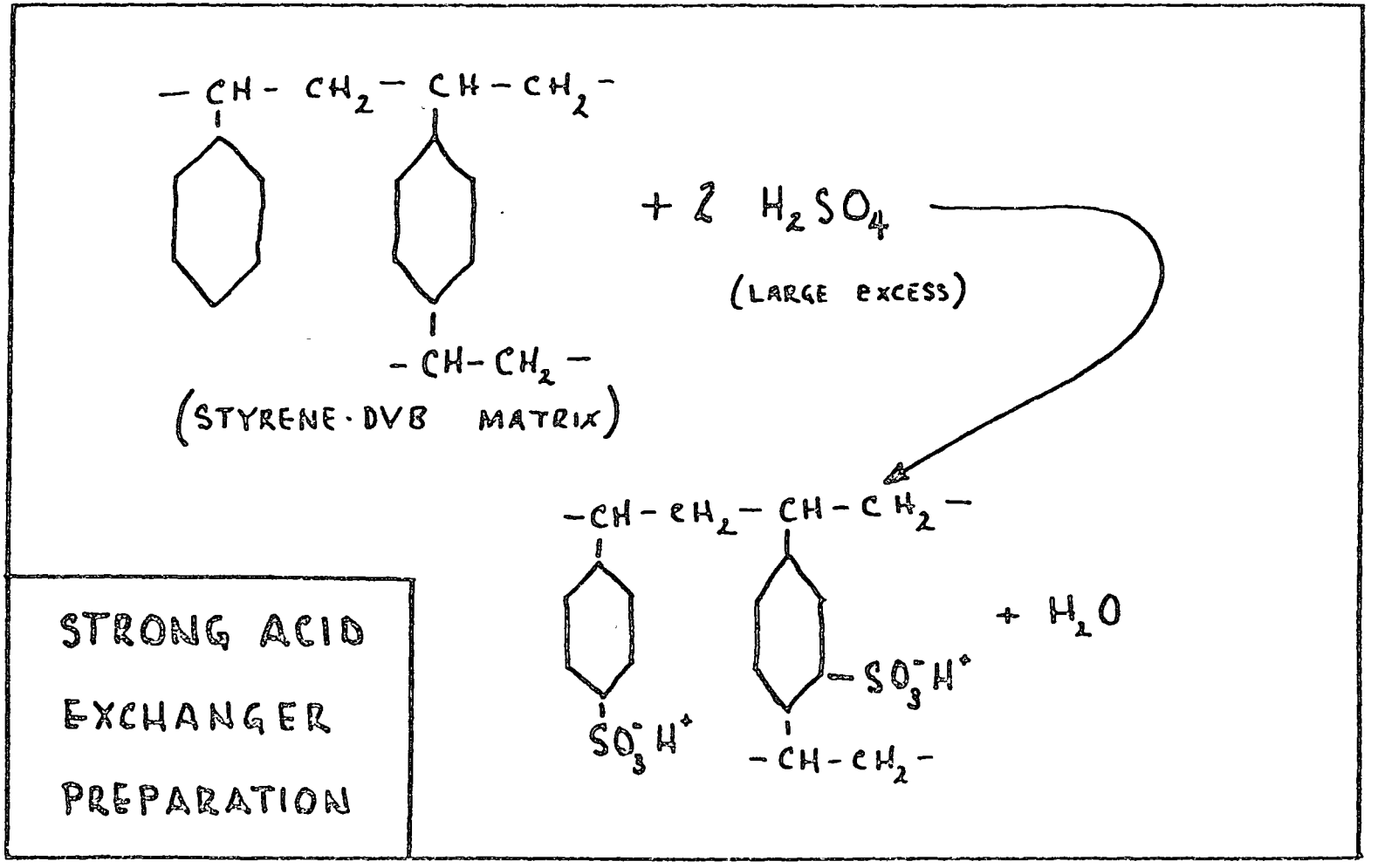


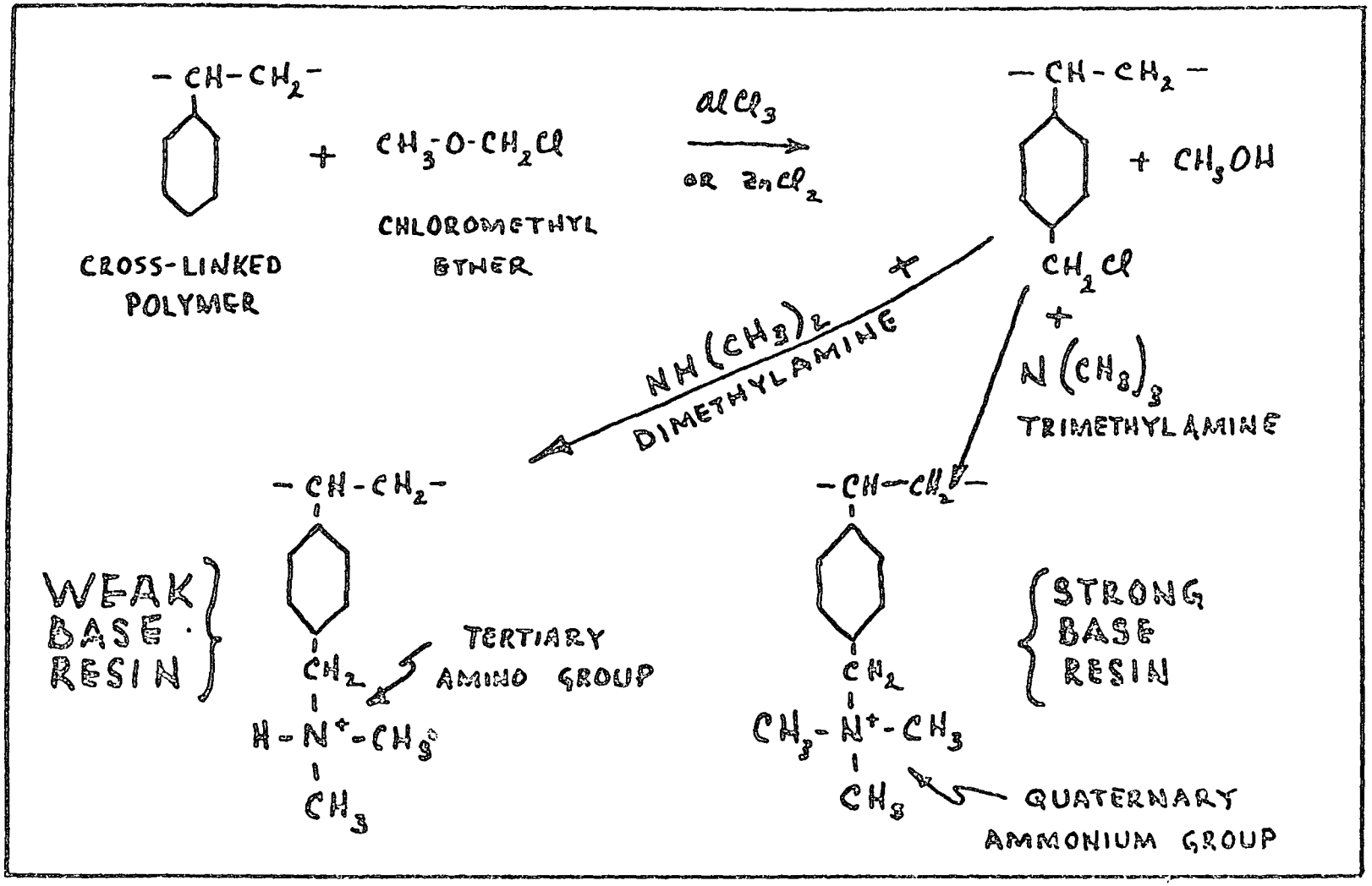
Figure 4 — Examples of ION exchange processes

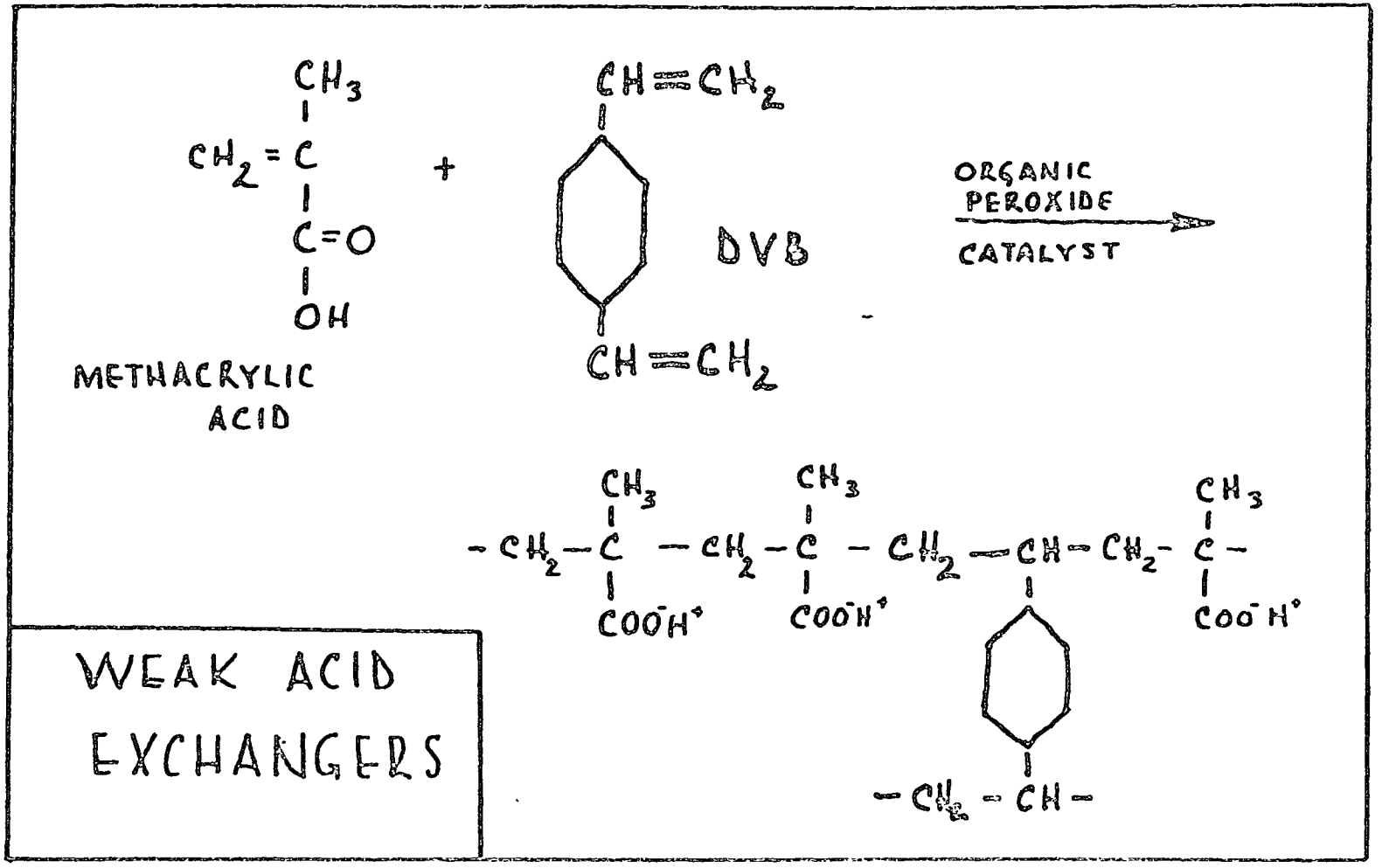


Calcium IONS in a hard water are captured by the cation exchanger, releasing "soft" sodium IONS.

Figure 5


+ 2 H_2SO_4
(LARGE EXCESS)
(STYRENE·DVB MATRIX)
+ H_2O
STRONG ACID
EXCHANGER
PREPARATION


CROSS-LINKED POLYMER
CHLOROMETHYL ETHER
$AlCl_3$ OR $ZnCl_2$
CH_3OH
CH_2Cl
$NH(CH_3)_2$
DIMETHYLAMINE
$N(CH_3)_3$
TRIMETHYLAMINE
WEAK BASE RESIN
TERTIARY AMINO GROUP
STRONG BASE RESIN
QUATERNARY AMMONIUM GROUP


METHACRYLIC ACID
DVB
ORGANIC PEROXIDE
CATALYST
WEAK ACID EXCHANGERS

RULE-OF-THUMB BEHAVIOR FOR ION EXCHANGE RESINS

1. EXCHANGE POTENTIAL $\propto$ CHARGE

$$Na^{+} < Ca^{++} < Al^{+3} < Th^{+4}$$

2. EXCHANGE POTENTIAL $\propto$ ATOMIC WEIGHT

$$Li^{+} < Na^{+} < K^{+} < Rb^{+} < Cs^{+}$$

$$Mg^{++} < Ca^{++} < Sr^{++} < Ba^{++}$$

3. HIGH ION CONCENTRATIONS REDUCE OR REVERSE THE EFFECT OF CHARGE

4. HIGH TEMPERATURE REDUCES THE EFFECT OF ATOMIC NUMBER

5. EXCHANGE POTENTIALS MAY BE APPROXIMATED BY THEIR ACTIVITY COEFFICIENTS

6. EXCHANGE POTENTIAL FOR H^+ AND OH^- VARIES WITH RESIN FUNCTIONALITY

   e.g. STRONG ACID AND BASE RESINS REQUIRE AN EXCESS DURING REGENERATION

7. ORGANIC IONS AND ANIONIC METALLIC COMPLEXES HAVE VERY HIGH EXCHANGE POTENTIALS

1. HIGH CAPACITY ~ 4.5 meq/g ≈ 2.0 meq/ml

2. RAPID EXCHANGE RATE

3. "SPLITS NEUTRAL SALTS" IN H-FORM

$$R\,SO_3^-\,H^+ + Na^+ + Cl^- = R\,SO_3^-\,H^+ + H^+ + Cl^-$$

4. VERY DURABLE - OPERATION POSSIBLE AT HIGH AND LOW pH AND SALT CONCENTRATION

5. DOES NOT HAVE A HIGH SPECIFICITY FOR DIFFERENT IONS

6. REQUIRES MORE THAN THE STOICHIOMETRIC AMOUNT OF ACID FOR COMPLETE REGENERATION IN THE H-FORM

PROPERTIES OF STRONG-ACID EXCHANGE RESINS

1. RAPID EXCHANGE RATE

2. REMOVES ANIONS AT ALL pH'S AND ION CONCENTRATIONS

   REVERSE DEIONIZATION ; SB $\longrightarrow$ SA

   MONOBED DEIONIZATION ; SB + WA

3. MORE UNSTABLE THAN STRONG ACID RESINS

4. POSSIBILITY OF ORGANIC FOULING - AVOID BY ENLARGED PORE SIZES

5. CAPACITY $\sim$ 3.5 meq/g $\approx$ 1.3 meq/ml

<u>PROPERTIES OF STRONG BASE EXCHANGE RESINS</u>

1. WEAKLY ACIDIC - WILL NOT REMOVE CATIONS AT NEUTRAL pH, REQUIRES pH 9 TO 10

2. VERY EFFICIENTLY REGENERATED WITH ACID

3. USUALLY NOT USED FOR WATER SOFTENING - HIGH AFFINITY FOR Ca^{++} OVER Na^{+}

4. SLOW EXCHANGE RATES

5. USES: MOSTLY IN OPTIMIZED DEMINERALIZATION PROCESSES

6. CAPACITY $\sim$ 10 meq/g $\approx$ 4 meq/ml

PROPERTIES OF WEAK ACID EXCHANGE RESINS

ION EXCHANGE EQUILIBRIUM

USE SELECTIVITY COEFFICIENTS :

e.g. $Na^+ + HR = NaR + H^+$

$$K_H^{Na} = \left(\frac{C_{H^+}}{C_{Na^+}}\right)\left(\frac{q_{Na}}{q_H}\right)$$

$q \equiv$ MATERIAL ON RESIN

$C \equiv$ MATERIAL IN SOLUTION

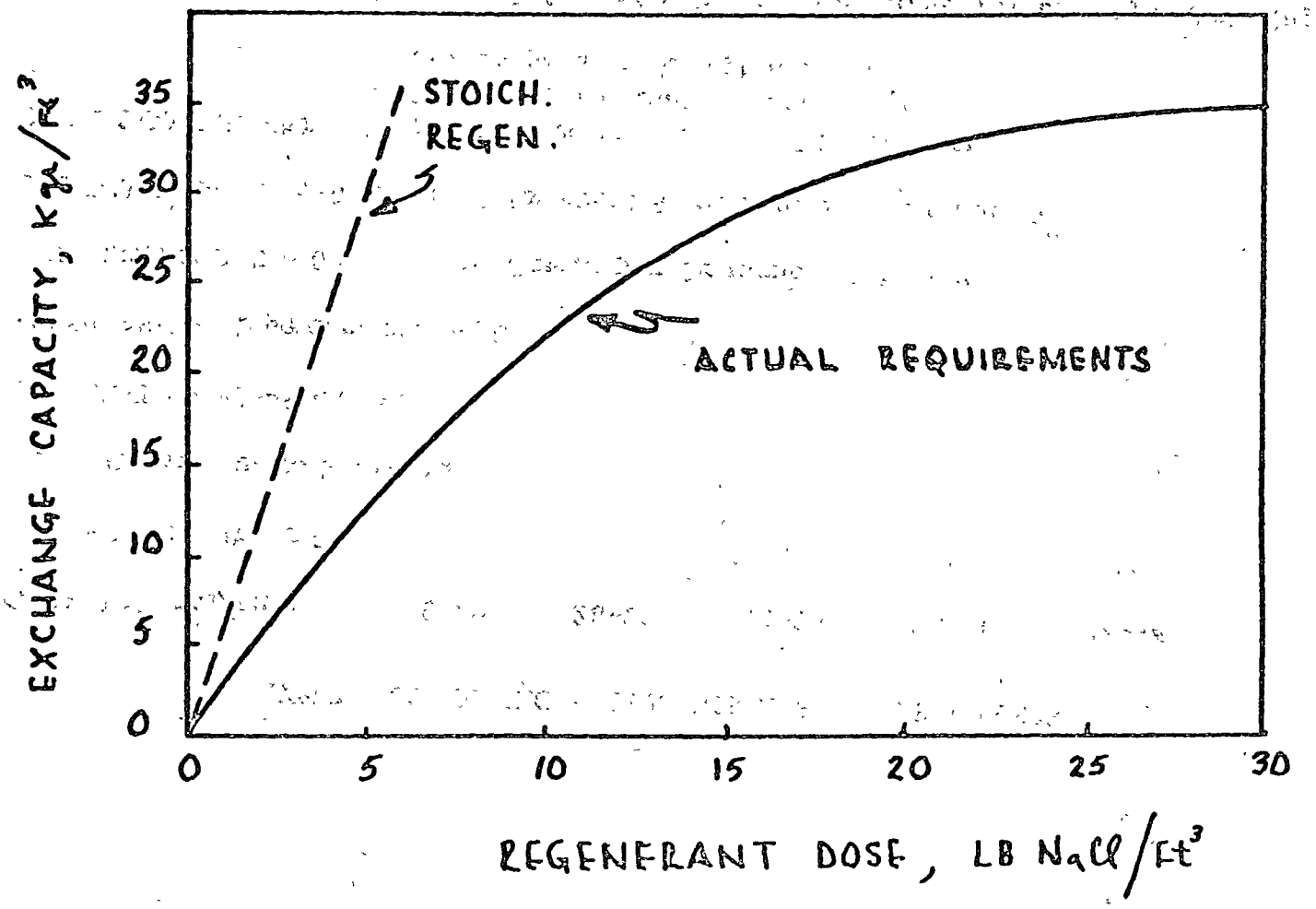
q & C IN CONCENTRATION UNITS

- EQUIVALENTS

PERCENT DIVINYL BENZENE	PERCENT MOISTURE	CAPACITY meq/g	CAPACITY meq/ml
4.0	62.6	4.81	1.27
8.5	48.6	4.79	1.87
10.0	43.1	5.07	2.30
12.5	40.8	5.12	2.47
15.0	35.4	4.81	2.65

CAPACITY AND POROSITY OF ION EXCHANGE RESINS AS A FUNCTION OF DIVINYL BENZENE CONTENT

TYPICAL REGENERATION BEHAVIOR



TYPICAL SOFTENING EXCHANGER DESIGN PARAMETERS

CAPACITY, Kgr/cu ft	18-20	20-22	24-26	28-30	32-34
SALT REQ'D., lb/cu ft	4	5	6	10	18

FLOW RATES - up to 5 gpm/cu ft

BED DEPTH - 30-48 inches

FREEBOARD - 50 percent bed depth

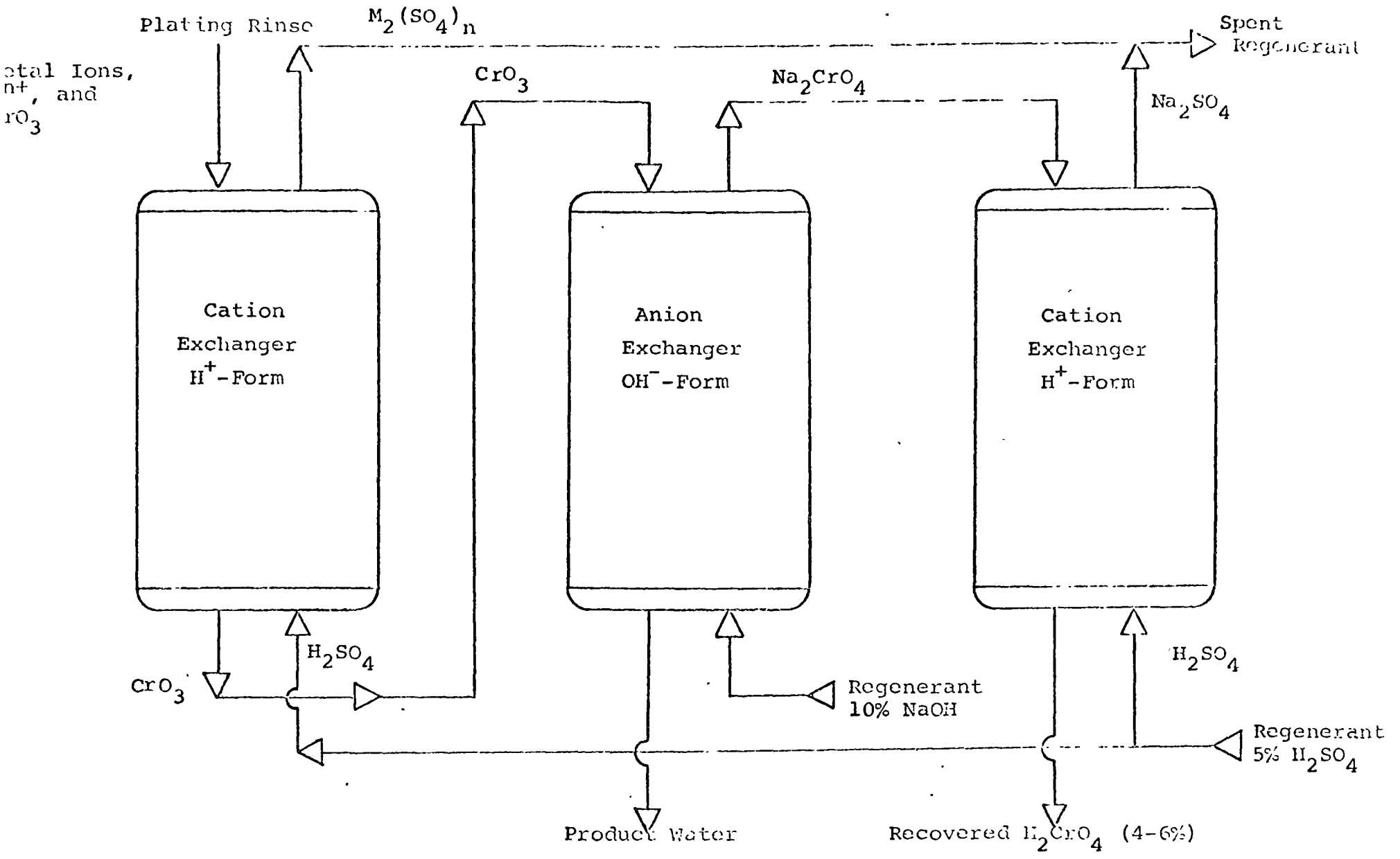
SUPPORTING BED - 6 inches low flow, up to 18 inches high flow

BACKWASH RATE - 5-6 gpm/sq ft for about 50 percent expansion at 65°F.

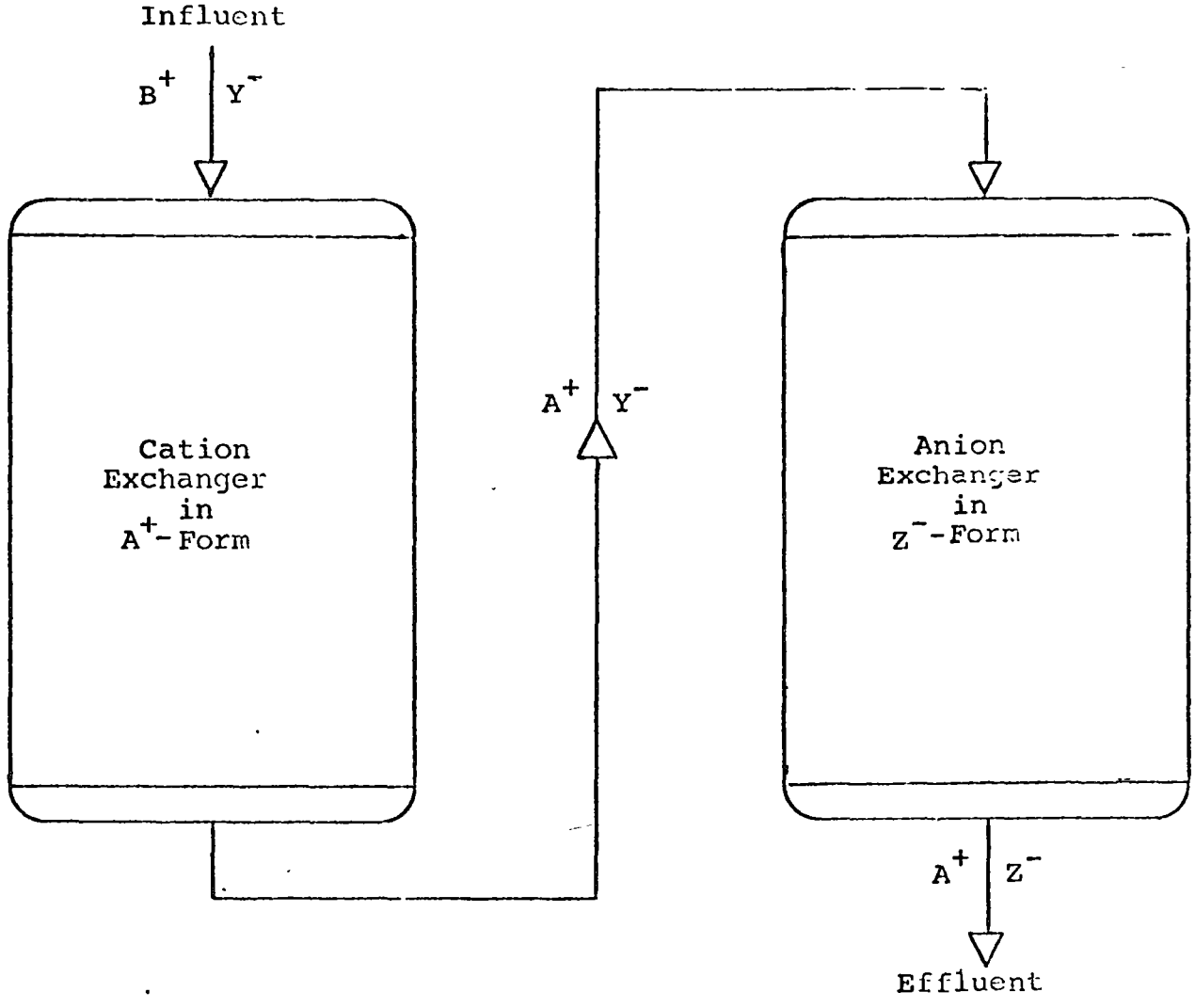
BRINE CONCENTRATION - about 10 wt percent Diluted from:
50% maximum solution, heat and mix
30% by passing through a salt bed

REGENERANT FLOW RATE - 0.25-1.0 gpm/cu ft for 40-60 minutes in brining and rinsing

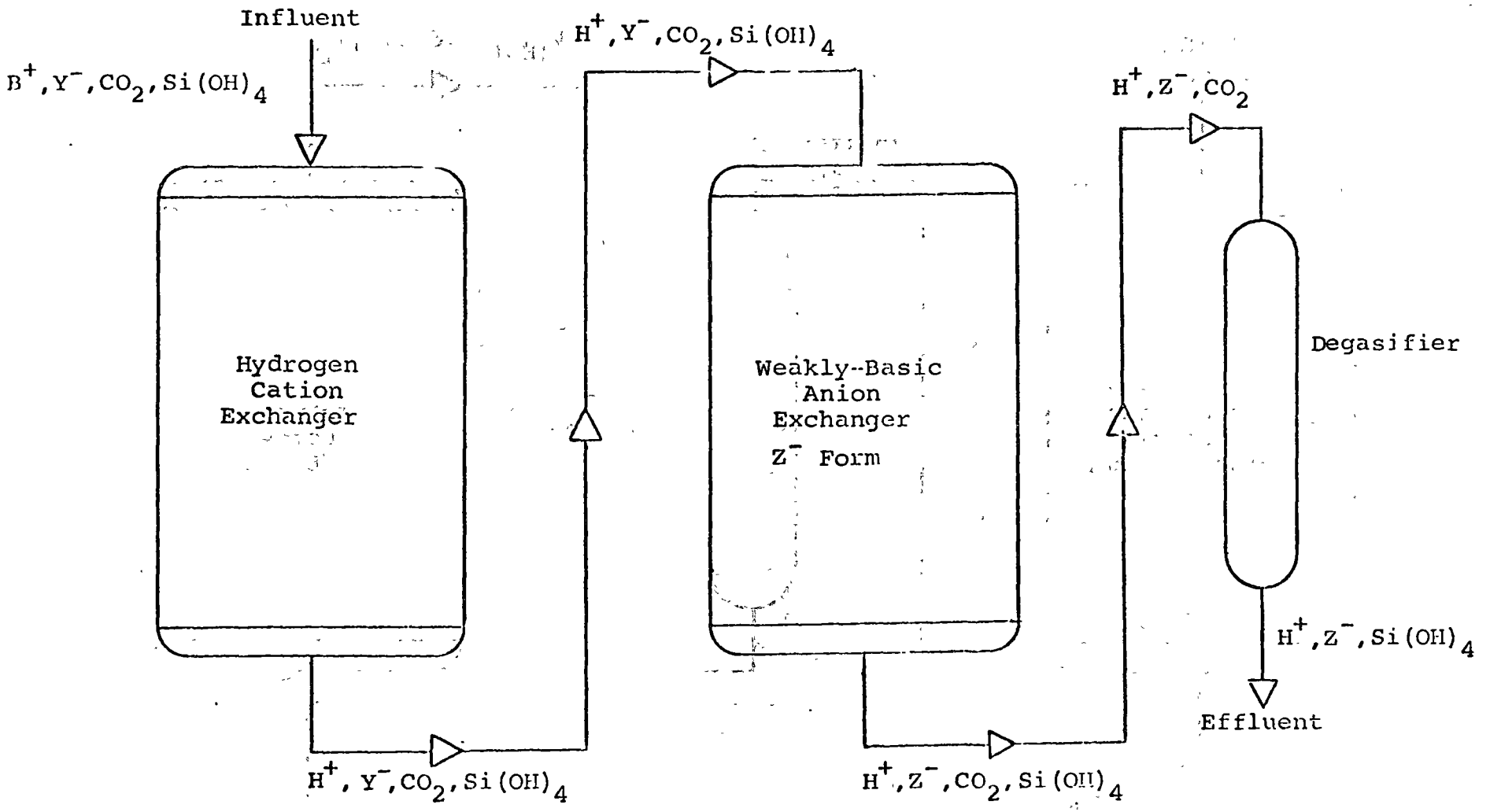
RINSE REQUIREMENTS - 20-35 gal/cu ft



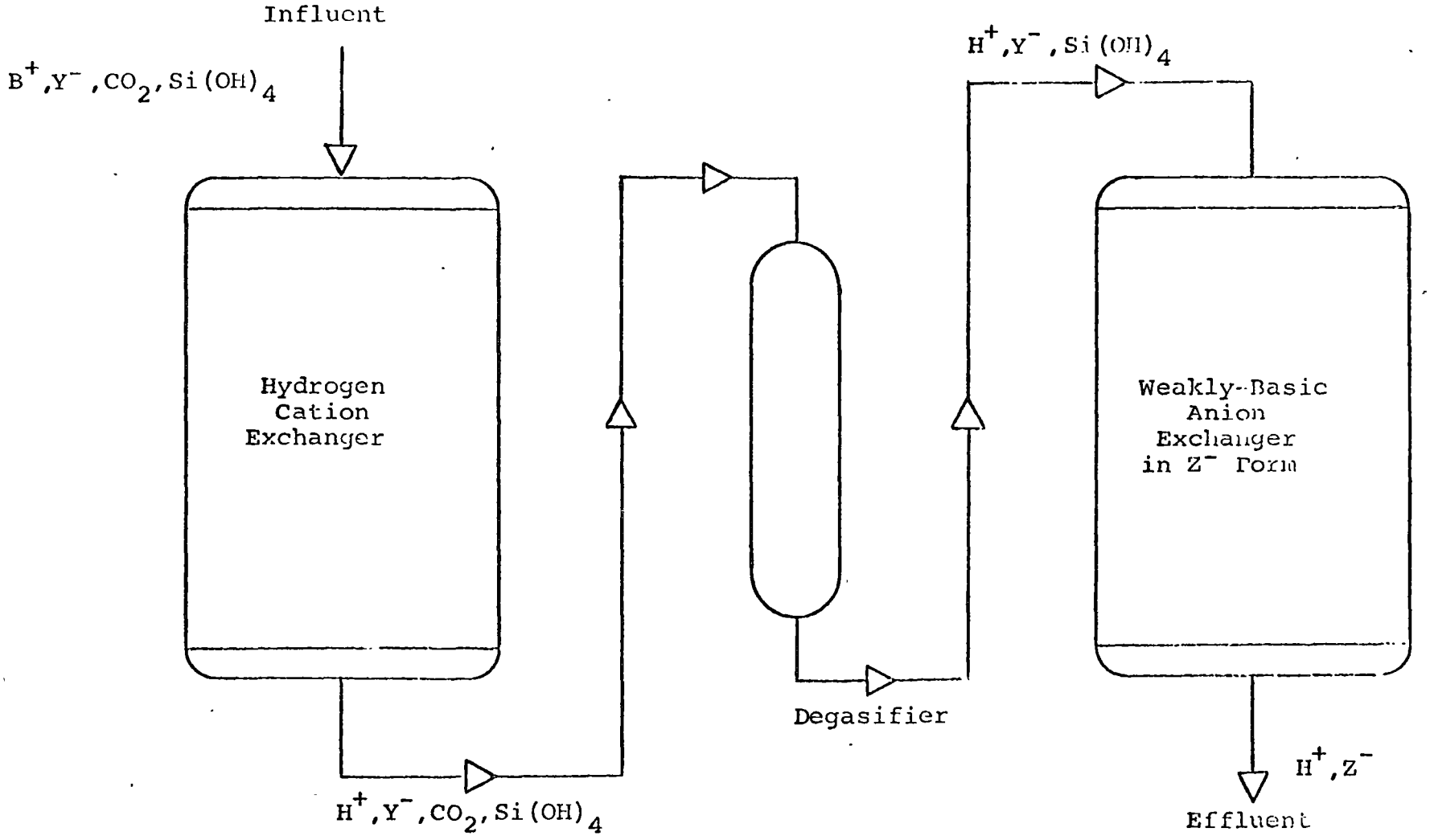
- Schematic Flow-Diagram for Treatment of Plating Wastes by Ion Exchange for Chromate Recovery and High Quality Product Water



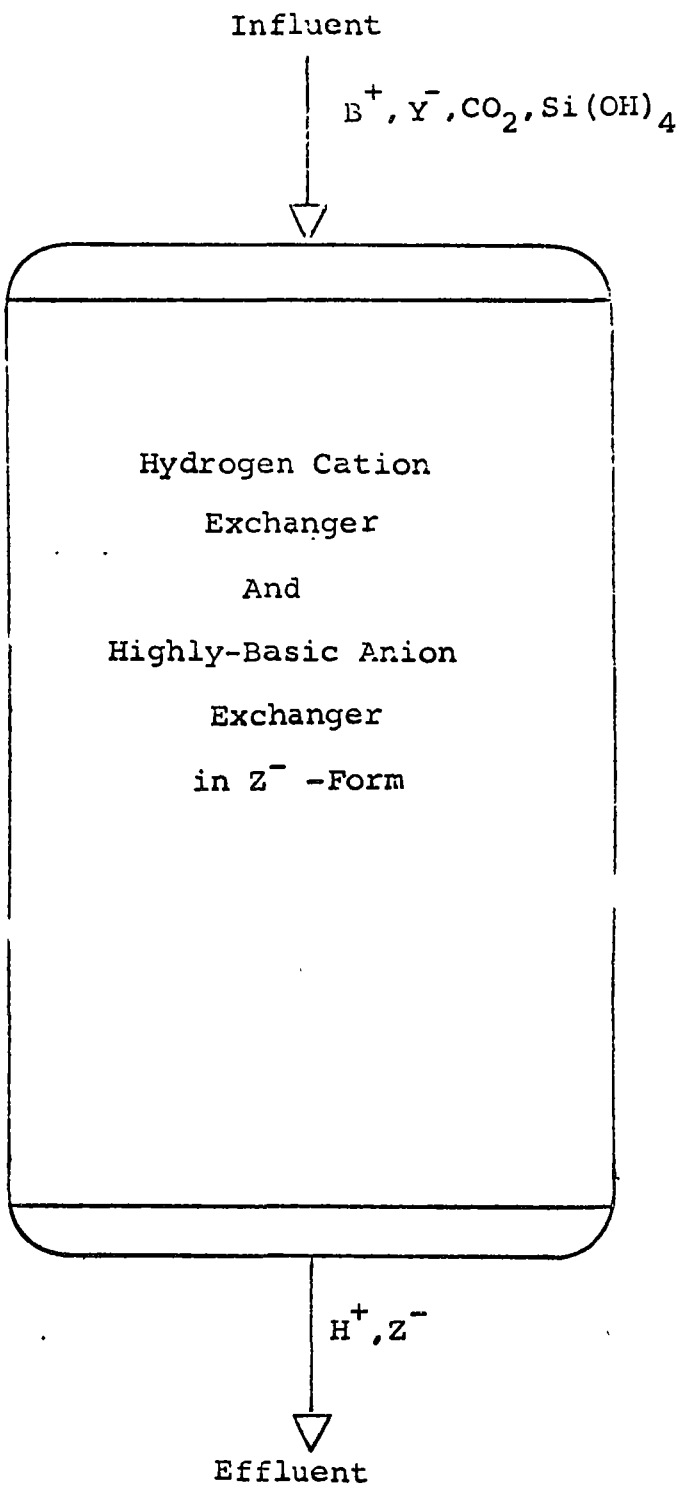
- Two-Stage Ion Exchange Operation



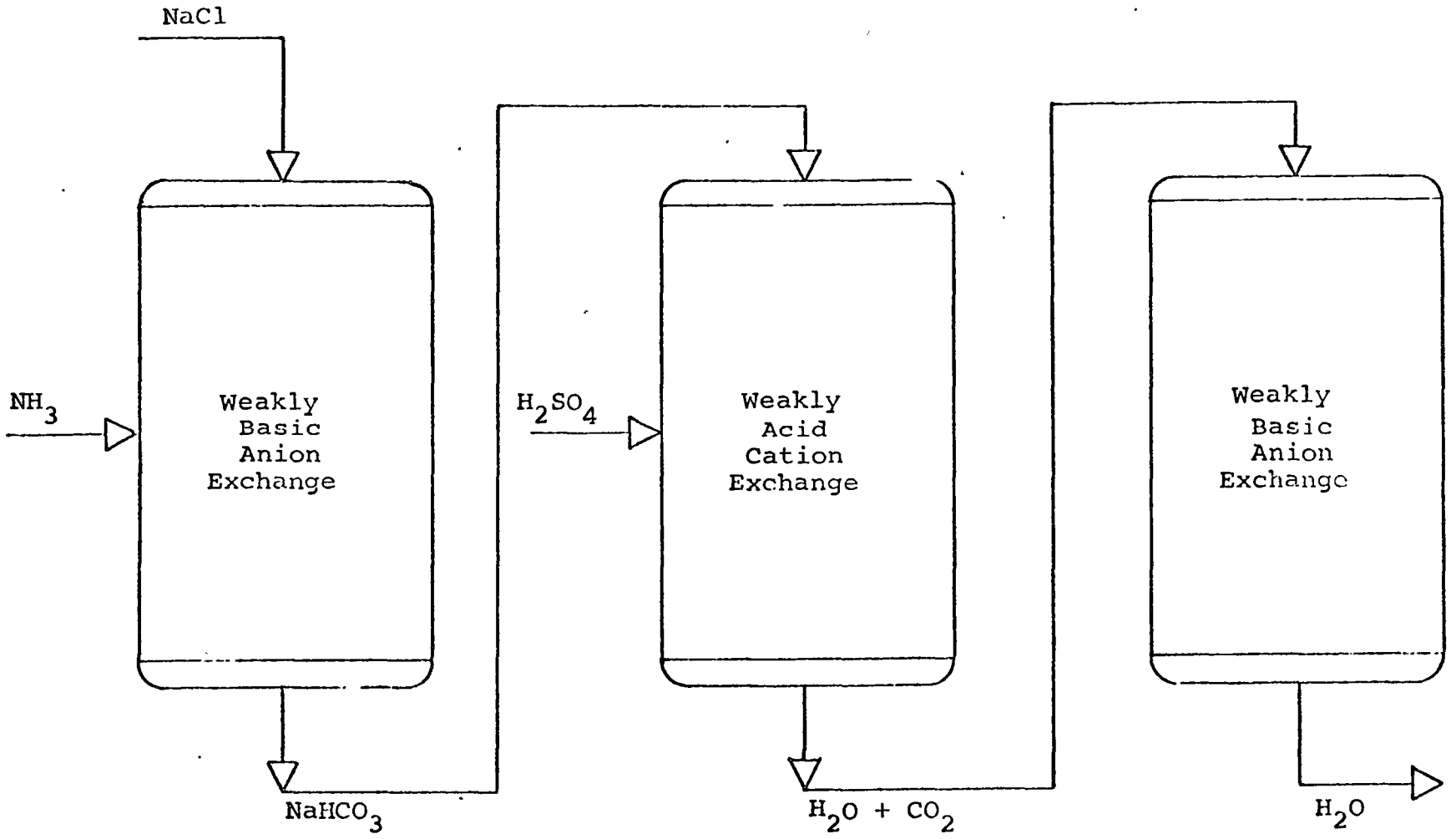
- Two-Stage Operation With Degasification for Removal of Carbon Dioxide



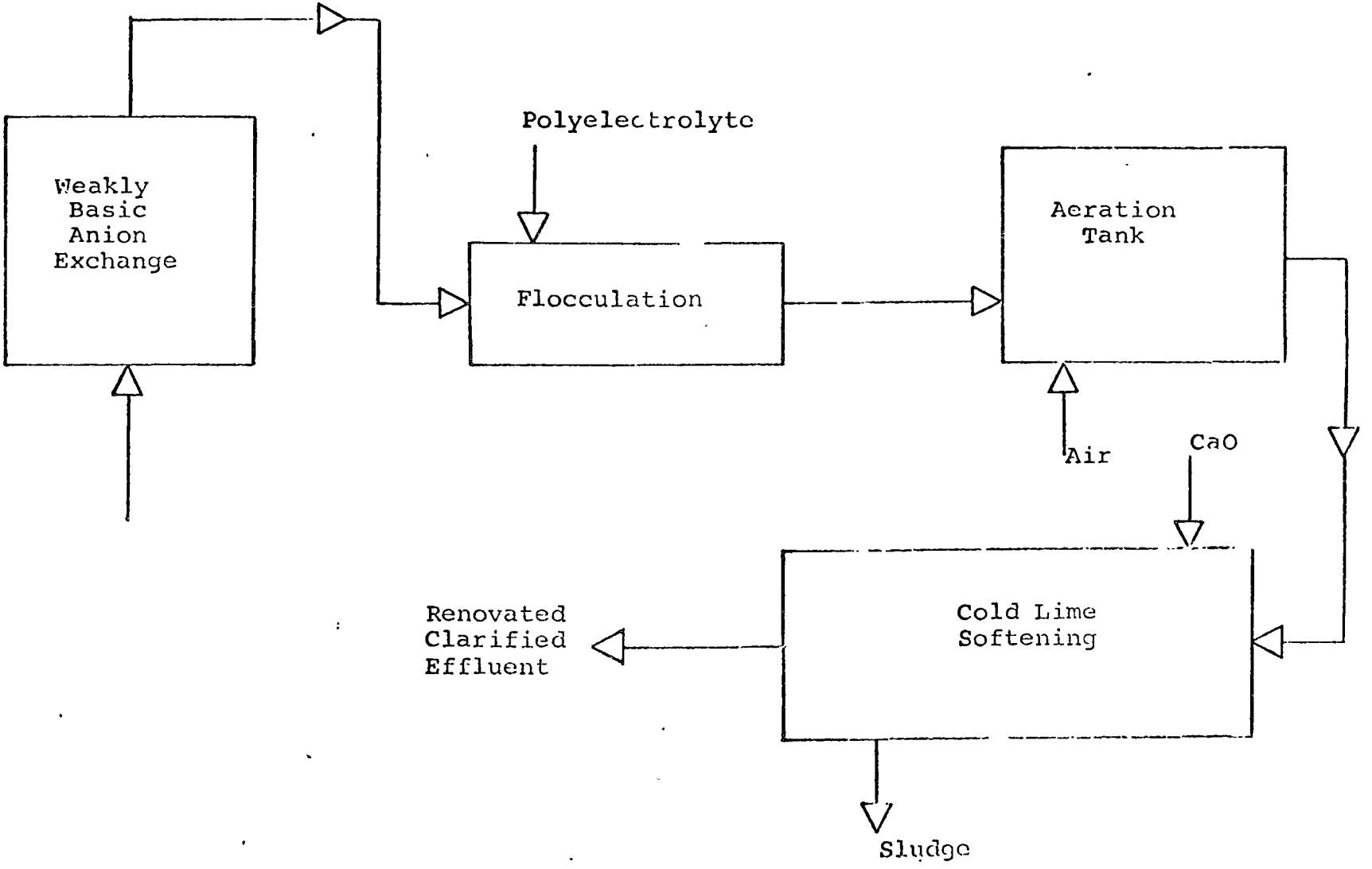
- Two-Stage Operation for Removal of Both Carbon Dioxide and Silica



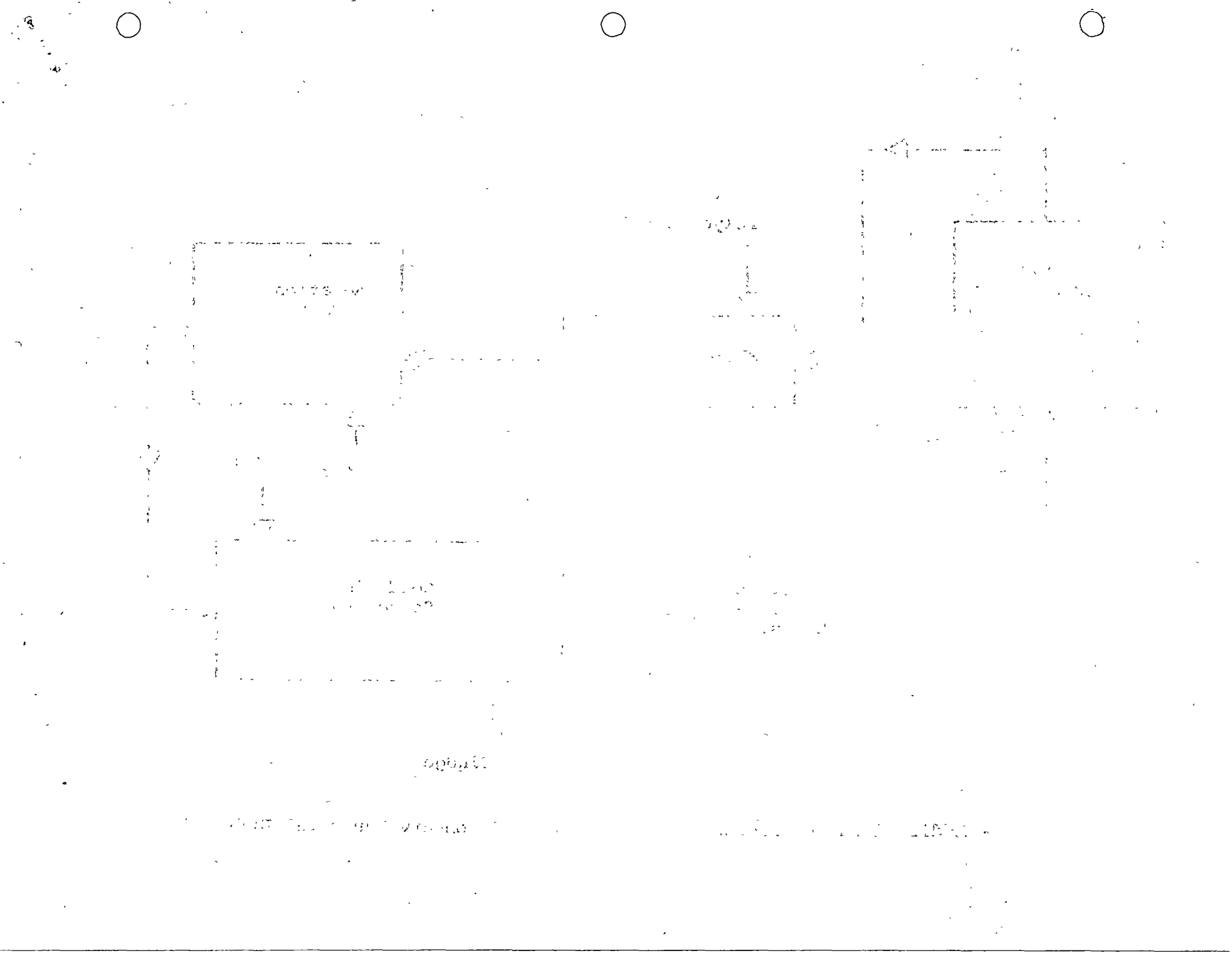
- Mixed-Resin Exchanger



- Schematic Diagram of the DESAL Ion Exchange Process



- Modified DESAL Process for Treatment of Secondary Municipal Effluent



centro de educación continua
facultad de ingeniería, unam

TRATAMIENTO DE AGUAS RESIDUALES

PARAMETROS DE POLUCION DEL AGUA

ING. PEDRO MARTINEZ PEREDA

Tacuba 5, primer piso. México 1, D.F.
Teléfonos: 521-30-95 y 513-27-95

PARAMETROS DE POLUCION DEL AGUA: DBO, DQO.

CARACTERIZACION DE LAS AGUAS RESIDUALES: FRACCION ORGANICA

El creciente interés en el aprovechamiento multiple de las aguas ha ocasionado la definición de un numero de parámetros de significado especial en las aguas residuales municipales e industriales. Entre estos destacan los encáminados a definir la fracción orgánica de estas aguas residuales: la demanda bioquimica de oxígeno y la demanda quimica de oxígeno.

Determinación del contenido orgánico de las aguas residuales

El contenido orgánico de una agua residual puede determinarse por medio de tres pruebas; sinembargo, la interpretación de los resultados requiere experiencia y buen juicio. La prueba de la Demanda Bioquimica de Oxígeno (DBO), nos proporciona información sobre la materia orgánica biodegradable principalmente. La prueba de la Demanda Química de Oxigeno (DQO) medirá el carbón orgánico total, con excepción de ciertos aromáticos como el benceno, que no se oxidan completamente en la reacción. Además, como es una reacción de oxidación-reducción, otras sustancias reducidas, como sulfuros, hierro ferroso y sulfitos, tambien se oxidarán y se incluirán en el valor de la prueba de DQO.

La prueba del Carbón Orgánico Total (COT) mide todo el carbon presente como CO_2, y por lo tanto debe

removerse de la muestra todo el carbón inorgánico (CO_2, HCO_3, etc.) antes del análisis de la muestra; o si no, hacer las correcciones pertinentes en el calculo final.

DEMANDA BIOQUIMICA DE OXIGENO

Definición. Cantidad de oxigeno requerida para estabilizar la materia orgánica biodegradable en una muestra de aguas residuales, por una población heterogénea de microorganismos, en condiciones aerobias. La prueba estándar implica la siembra con aguas residuales domésticas, agua de rio, o agua de la descarga industrial y la incubación a 20°C. Ver Standard Methods for the Analysis of Water and Wastewater (1).

Reacción en la botella de DBO

La reacción ocurre en dos etapas distintivas, segun se ilustra en la Fig. 1. Inicialmente los microorganismos sembrados utilizan la materia orgánica para obtener energía y para su crecimiento. El resultado es la utilización de oxígeno y el crecimiento de nuevos microorganismos.

Cuando se ha removido la materia orgánica inicialmente presente en las aguas residuales, los organismos (bacterias) continuan utilizando oxígeno para la autooxidación de su propia masa celular.

Al completarse la oxidación de la masa celular, solo queda un residuo celular no biodegradable, y la reacción es completa. Esto se define como la demanda bioquímica de oxígeno última (DBO_u).

El procedimiento para llevar a cabo la prueba de DBO se describe en "Standard Methods for the Examination of Water and Wastewater" (1). El período de incubación para la prueba estándar es de 5 días y los resultados usualmente se indican como DBO_5.

La remoción y oxidación de la materia orgánica presente en las aguas residuales se completa esencialmente en un período de 18 a 36 horas (fase 1, Eckenfelder, 1968). La oxidación total de toda la masa celular o la DBO_u tomará mas de 20 días, según la naturaleza de las aguas residuales (fase 2). La tasa de reacción en la fase de asimilación (fase 1) es de 10 a 20 veces la tasa de respiración endógena, Fig. 1.

Formulación de la curva de DBO

La tasa de oxidación de muchas sustancias químicas inestables puede estimarse a partir de una reacción de primer orden. Una reacción de primer orden es aquella que está caracterizada por una tasa

ó velocidad directamente proporcional a la concentración de la sustancia que reacciona. En el caso de aguas residuales municipales e industriales parece ser que una reacción de primer orden define razonablemente bien la oxidación de la materia orgánica de la primera etapa. La ecuación puede expresarse como sigue:

$$\frac{dL}{dt} = -K_1 L \qquad \text{Ec. 1}$$

donde,

L = concentración de la sustancia que reacciona (materia organica)

K_1 = constante de reacción

De la integración de la Ec. 1, se obtiene:

$$\ln \frac{L_t}{L_o} = -K_1 t \quad ; \quad \log_{10} \frac{L_t}{L_o} = -k_1 t \qquad \text{Ec. 2}$$

donde,

L_o = concentración inicial de materia orgánica o demanda ultima de oxígeno.

L_t = concentración de materia organica despues de un tiempo t.

K_1 = coeficiente (tasa) de reacción en base e.

k_1 = coeficiente (tasa) de reacción en base 10.

Las ecuaciones anteriores se refieren a la materia orgánica medida en terminos del oxigeno remanente al final de un período de tiempo. La materia orgánica oxidada, o el oxigeno utilizado es:

$$y = L_o - L_t \qquad \text{Ec. 3}$$

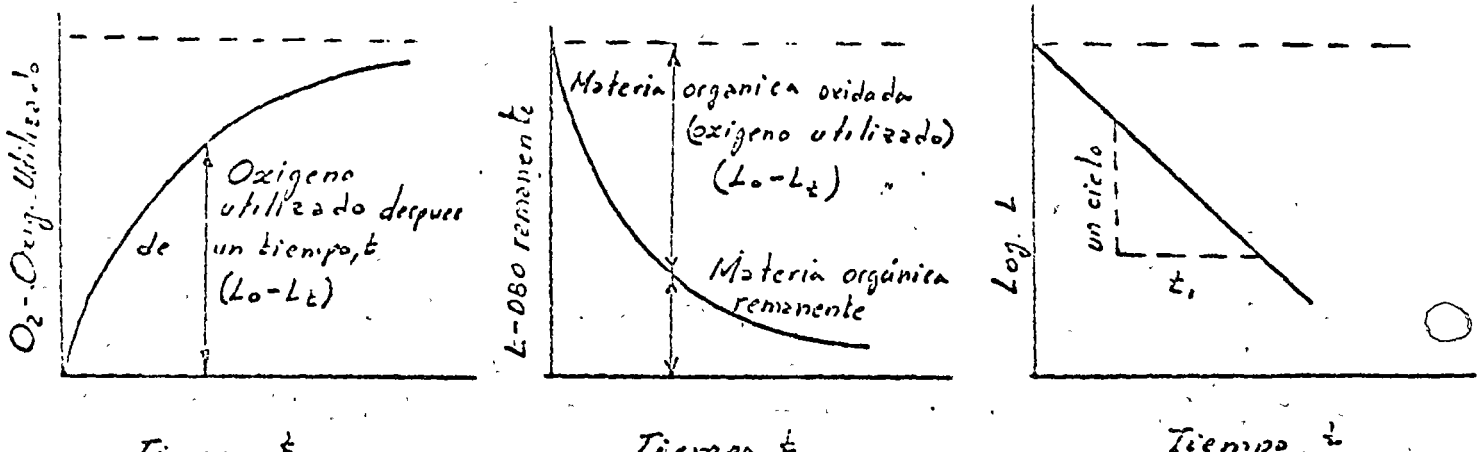
Sustituyendo la Ec. 3 en la Ec. 2 y haciendo los arreglos necesarios resulta:

$$\underline{y = L_o\ (1 - 10^{-k_1 t})} \qquad \text{Ec. 4}$$

donde,

y = DBO ejercida en el tiempo, t.

Estas ecuaciones pueden representarse gráficamente:



Como la DBO es en realidad la suma de dos tasas diferentes (síntesis y respiración endógena) la ecuación monomolecular es solo una aproximación.

Debido a que tanto k_1 como L_o son desconocidos, es necesario emplear el calculo indirecto. Se han desarrollado varios procedimientos para estos calculos, tres de ellos se presentan en forma resumida a continuación:

1. Método de los momentos (Moore y colaboradores): partiendo de una curva continua a través de los datos experimentales del laboratorio (prueba de DBO), se tabulan t, y, y ty para una cierta secuencia de días (por ejemplo 1, 2 y 3 días). De las gráficas expresamente preparadas Figs. 2,3,4 que se anexan se obtiene k a partir de la relación $\Sigma y / \Sigma ty$, y L_o partiendo de $\Sigma y / L_o$.

   En este método, los datos se ajustan a una curva de primer orden que tiene sus dos primeros momentos Σy y Σty iguales a los de los puntos experimentales.

2. Método de las diferencias logaritmicas ("log-difference").

   La ecuación de la DBO se expresa como:

$$y = L_o (1 - 10^{-k_1 t})$$

   Diferenciando la ecuación anterior

$$\frac{dy}{dt} = r = L_o k e^{-k_1 t}$$

donde,

T = tasa de consumo de oxígeno con el tiempo

Esta ecuación es una gráfica semilogarítmica de la forma

$$\ln T = \ln L_o k_1 - k_1 t$$

Partiendo de los valores corregidos de y, se calculan y tabulan las diferencias para días consecutivos. Las diferencias se tabulan contra el tiempo en papel semilogarítmico. De la gráfica se calculan k_1 y L_o.

3. Método gráfico (Thomas). Se hace una gráfica de $(\frac{1}{t}y)^{1/3}$ como ordenadas contra t, como abscisa. De esta gráfica,

$$k_1 = 2.61 \frac{b}{a}, \quad L_o = \frac{1}{2.3} k_1 a^3$$

donde, b, es la pendiente de la línea y, a, la intersección con el eje de las ordenadas. Fig. 5

Ejemplo. Evaluación de k_1 por el método de las diferencias

a. Grafique y vs. t en papel de coordenadas cartesianas. Dibújese una curva de mejor aproximación a través de los puntos observados, para indicar la forma de la deoxigenación.

b. Grafíquese la diferencia diaria, corregida si es necesario.

en papel semilogaritmico poniendo el tiempo en la escala lineal y las diferencias diarias en la escala logaritmica

c. De la Figura 6, el valor correspondiente a la intercepcion cero de la pendiente es igual a $L_o k$. El numero que representa a $L_o k$ para $t=0$ es igual a 8.3.

$$k_{10} = \frac{\log (8.3/1.3)}{7} = 0.115$$

La intercepción $= L_o k$

$$8.3 = 2.3 \times 0.115 \times L_o$$

$$L_o = 31 \text{ mg/l}$$

t	y	Diferencias diarias
0	0	—
1	7.3	7.3
2	12.8	5.5
3	16	3.3
4	20.1	4.3
5	22.5	2.4
6	23.8	1.3
7	25.3	1.5

Factores que afectan la DBO

Temperatura. La constante de rapidez de reacción de la DBO, k_1, es afectada directamente por la temperatura. La relación, derivada de la ley de Vant Hoff, es como sigue:

$$k_t = k_{20}\,\theta^{(T-20)}$$

$\theta = 1.047$ (Phelps) inexacta a bajas temperaturas

$= 1.056$ (20-30°C) Schroepfer

$= 1.135$ (4-20°C)

Siembra. Los microorganismos aclimatados aguas abajo de las descargas industriales proporcionan una buena fuente de siembra para la prueba de DBO. La siembra tomada de las aguas receptoras proporciona los mayores valores de DBO.

Para aguas residuales municipales y derechos similares pueden utilizarse las aguas residuales municipales almacenadas 24 hrs. a 20°C.

En ocasiones se necesita desarrollar artificialmente un cultivo microbiano que oxide el derecho industrial. Esto se logra con aguas residuales domésticas sedimentadas que contengan una gran variedad de microorganismos. A estas se les agrega una pequeña cantidad del efluente industrial. La cantidad de

derecho agregado se incrementa hasta que se desarrolle un cultivo adaptado al derecho. La mezcla de aguas residuales domesticas e industriales se aerea burbujeando aire continuamente en el liquido. El incremento notable de la turbiedad de la mezcla bajo aeración indica, en general, un cultivo aclimatado. En la Figura 7, se indica el efecto de la aclimatación.

La cantidad de siembra que se requiere para producir una tasa normal de oxidación debe determinarse experimentalmente. En la Figura 8, se muestra el efecto de la concentración de siembra en la DBO.

Toxicidad. Varios compuestos quimicos son tóxicos para los microorganismos. En concentraciones altas estas sustancias pueden matar a los microorganismos, y en concentraciones subletales se reduce su actividad. En la Figura 9, se ilustra el efecto de los metales pesados en la DBO.

Nitrificación. El proceso de oxidación descrito por la ecuación de la DBO: $y = L_o(1-10^{-k_1 t})$ representa la oxidación de la materia carbonosa:

$$C_x H_y O_z \longrightarrow CO_2 + H_2O$$

La oxidación de la materia nitrogenada se puede indicar como

$$NH_3 \xrightarrow[\text{Nitroromonas}]{O_2} NO_2 \xrightarrow[\text{Nitrobacter}]{O_2} NO_3$$

La constante de reacción generalmente es menor que en el caso de la materia carbonosa. Normalmente, la nitrificación no comenzará hasta que la demanda carbonacea haya sido satisfecha parcialmente, proporcionando una curva similar a la de la Figura 10.

La ecuación puede describirse:

$$y = L_o (1-10^{-k_1 t}) + L_N (1-10^{-k_2 t})$$

donde;

L_o = demanda carbonosa última

L_N = demanda nitrogenada última

k_1 = constante de reacción para la demanda carbonosa

k_2 = constante de rapidez para la demanda nitrogenada

La nitrificación representa una demanda de los recursos de oxigeno de las aguas receptoras, por lo tanto debe incluirse como parte de la demanda total del derecho.

La nitrificación se puede eliminar por medio de una pasteurización con resiembra o agregando azul de metileno o figurea.

DEMANDA QUÍMICA DE OXÍGENO

La demanda química de oxígeno (DQO) es una medida del equivalente de oxígeno de la fracción orgánica en la muestra que puede ser oxidada con permanganato o dicromato en solución ácida.

El procedimiento para determinar la demanda química de oxígeno se describe en (1), utiliza dicromato de potasio con reflujo. Se agrega sulfato de plata como catalizador y cuando hay cloruros se puede agregar Hg_2SO_4 para formar un complejo con los cloruros.

No todos los compuestos orgánicos son químicamente oxidables por el procedimiento del dicromato, como por ejemplo el benceno, el tolueno y la piridina.

La demanda química de oxígeno teórica de compuestos orgánicos puede calcularse si se conoce la reacción. La oxidación de 1000 mg de fenol resulta en:

$$C_6H_5OH + 7O_2 \longrightarrow 6CO_2 + 3H_2O$$

$$DQO_{teórica} = \frac{(1000)(224)}{94} = 2383\ mg$$

En general, se podría esperar que la DBO_u de las aguas residuales fuese aproximadamente igual a la DQO. Esto no ocurre, especialmente cuando se trata de aguas residuales industriales. Lo anterior se debe:

1. Muchos compuestos que se oxidan con el dicromato no son biologicamente oxidables.
2. Ciertas sustancias inorganicas, tales como los sulfuros, sulfitos, tiosulfatos, nitritos y el hierro ferroso, ocasionan demanda quimica de oxígeno.
3. Los resultados de la DBO pueden ser afectados por falta de siembra aclimatada, produciendo resultados bajos
4. Los cloruros interfieren con el análisis de la DQO. Al oxidarse los cloruros por el dicromato, se producen resultados elevados:

$$6\,Cl^- + Cr_2O_7^{=} \longrightarrow 3\,Cl_2 + 2\,Cr^{+++} + 7\,H_2O$$

Esta interferencia puede eliminarse agregando $HgSO_4$ a la mezcla:

$$Hg^{++} + 2\,Cl^- \longrightarrow HgCl_2$$

Si no se tiene suficiente cantidad de $HgSO_4$, el exceso de Cl^- precipitará el catalizador de plata

c. $Ag^+ + Cl^- \longrightarrow AgCl \downarrow$

Como la presencia del catalizador es esencial para la oxidación de ácidos y alcoholes de cadena abierta, pueden esperarse resultados muy bajos.

Hay varios métodos para determinar la DQO. La oxidación con dicromato produce los mejores resultados. El método se describe en Standard Methods for the Examination of Water and Wastewater (1971).

El método utiliza dicromato de potasio como oxidante. Se utiliza un catalizador de plata y se agrega $HgSO_4$ para formar un complejo con los cloruros. La muestra y el oxidante se digieren en una solución de ácido sulfúrico utilizando un tiempo de reflujo de aproximadamente 2 horas.

Carbono organico total

Durante mucho tiempo el método empleado para determinar el nivel contaminante de una corriente de aguas residuales ha sido el de la determinacion del Carbono Organico Total (COT). Hay varios métodos para determinar el contenido de carbono orgánico en una muestra acuosa. Estas pruebas implican la oxidación de la materia orgánica a dioxido de carbono y agua, y la medición por medio de una titulación del gas generado y atrapado en una solución cáustica stándar.

Recientemente se ha desarrollado el analizador de carbono, que utiliza el concepto de la combustion de toda la materia orgánica a dioxido de carbono y agua en un tubo de combustión catalítica. El dioxido de carbono y el vapor generados en el tubo de combustión se transportan, por medio de una corriente de gas, a través de un condensador que remueve el vapor, y el CO_2 pasa por un analizador infrarojo sensibilizado para detectar dioxido de carbono. Como la cantidad de dioxido de carbono es proporcional a la concentración inicial en la muestra, la respuesta puede compararse a una curva de calibración para determinar el carbono orgánico total. El carbono inorganico debe removerse acidulando antes de proceder al analisis. En la Fig. 11 se muestra el diagrama de un analizador de carbo... Se inyecta una micromuestra en el tubo de combustion catalítica,

el cual se mantiene a una temperatura de 900 a 1000 °C. La muestra se vaporiza y el material carbonoso se oxida completamente en presencia de un catalizador de cobalto y de oxigeno puro, que es el gas que transporta la muestra. Los pasos subsecuentes son los que se explicaron anteriormente.

El carbono orgánico determinado por este método está libre de las muchas variables que afectan tanto a la prueba de OA como a la de DBO

RELACIONES ENTRE DBO, DQO.

Cuando se trata de programas de investigación y de control rutinario, la DBO no es una prueba muy util debido al tiempo que toma su determinación. Es importante por lo tanto desarrollar correlaciones entre DBO, DQO.

Consideremos una sustancia completamente biodegradable como la glucosa. La DBO_u medirá aproximadamente el 90 porciento de la demanda teórica de oxigeno. La DQO medirá la demanda teórica de oxígeno. Por lo tanto, para este sustrato tendremos:

$$DQO = \frac{DBO_u}{0.9}$$

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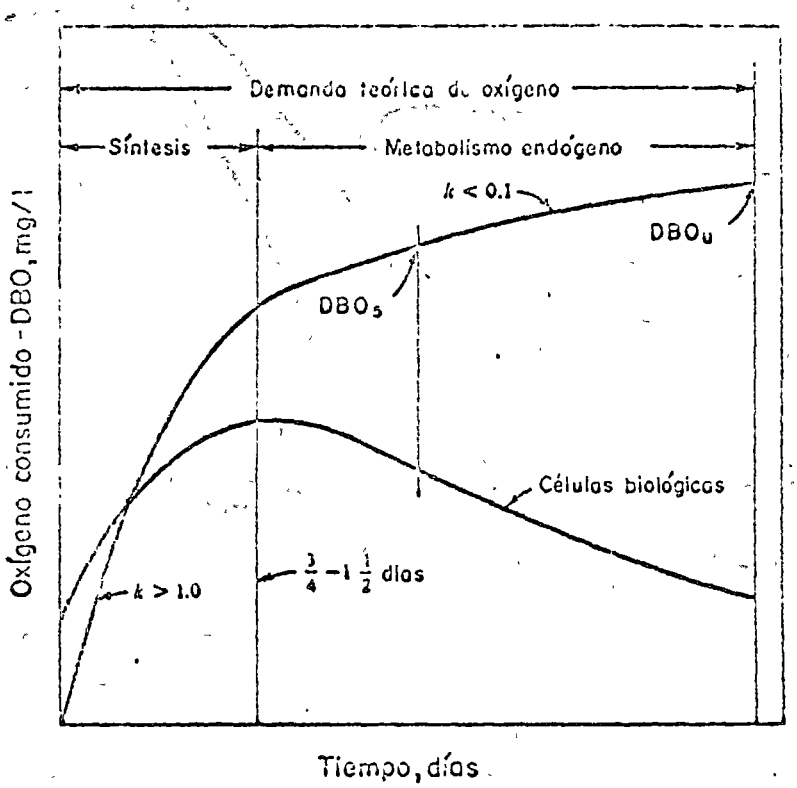
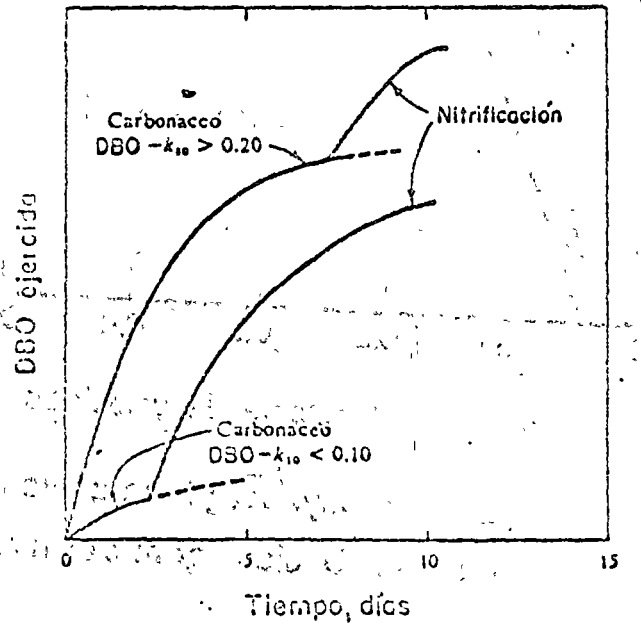


Fig. 1 Reaciones que ocurren en la botella de DBO



Comparación de curvas de DBO para aguas residuales crudas y tratadas

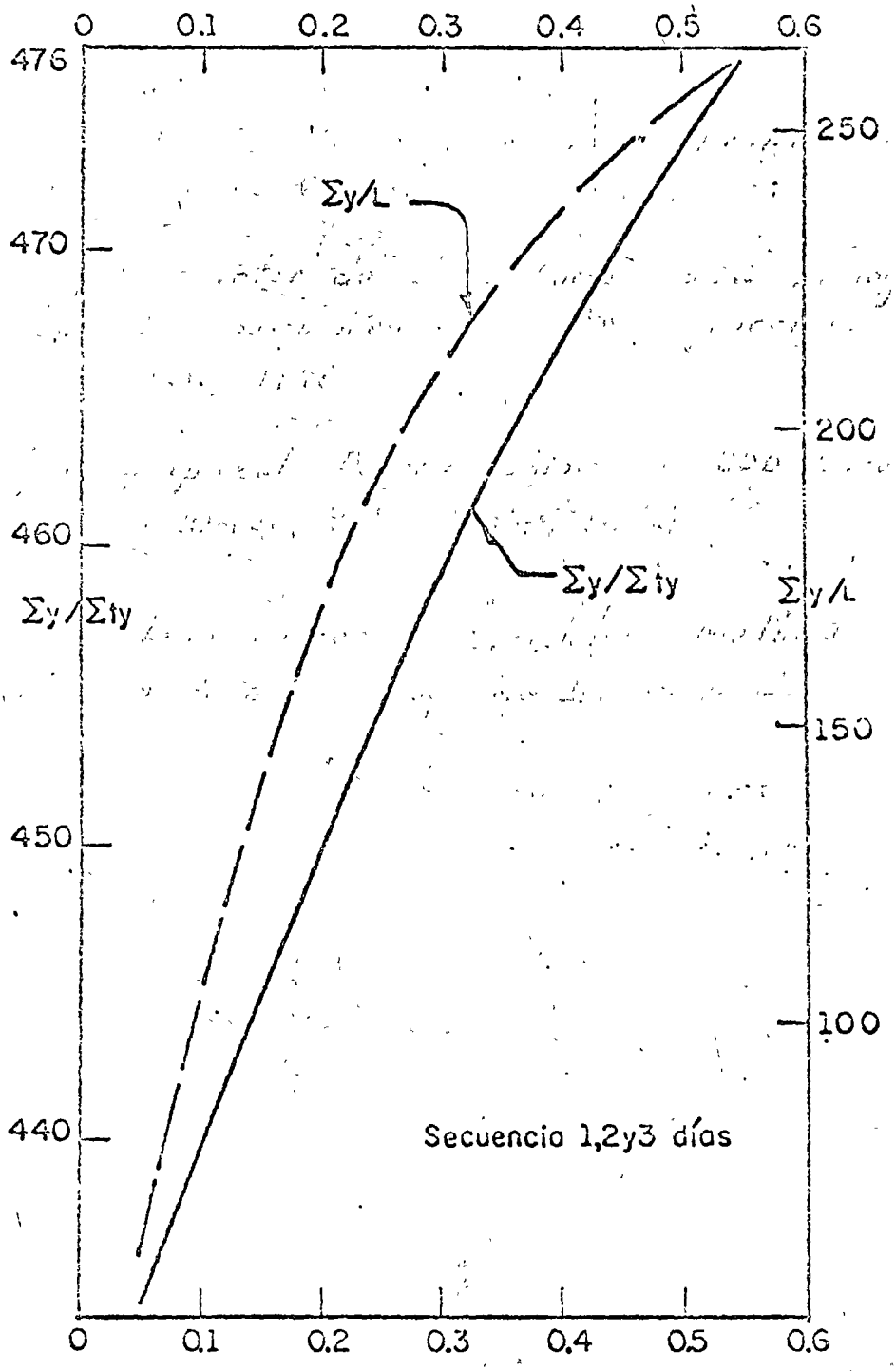


Fig. 2 Constante de velocidad de reacción, k

$\Sigma y/L$ y $\Sigma y/\Sigma(ty)$ para varios valores de k en 3 días consecutivos

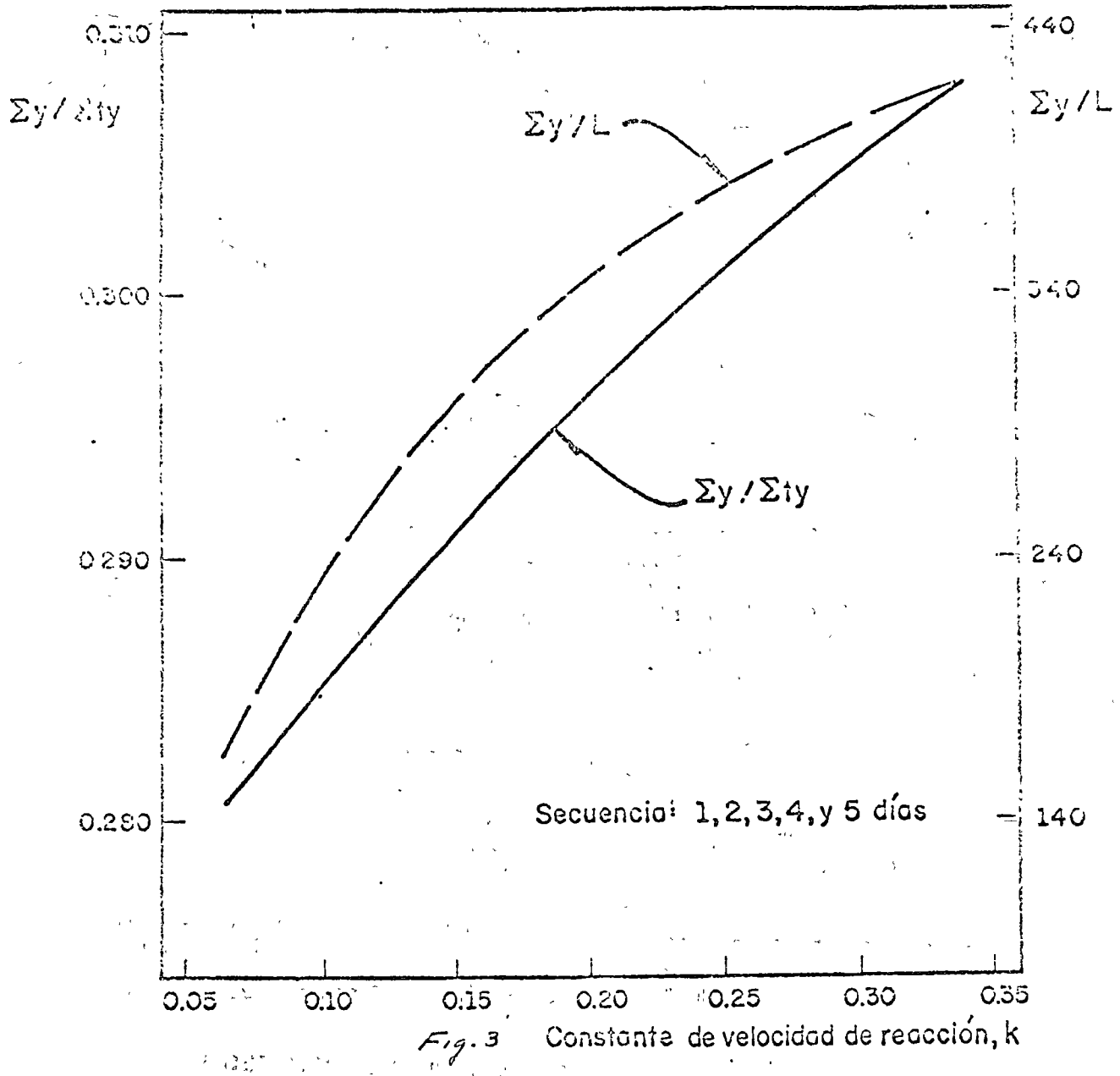


Fig. 3

$\Sigma y / L$ y $\Sigma y / \Sigma ty$ para varios valores de k en 5 días consecutivos

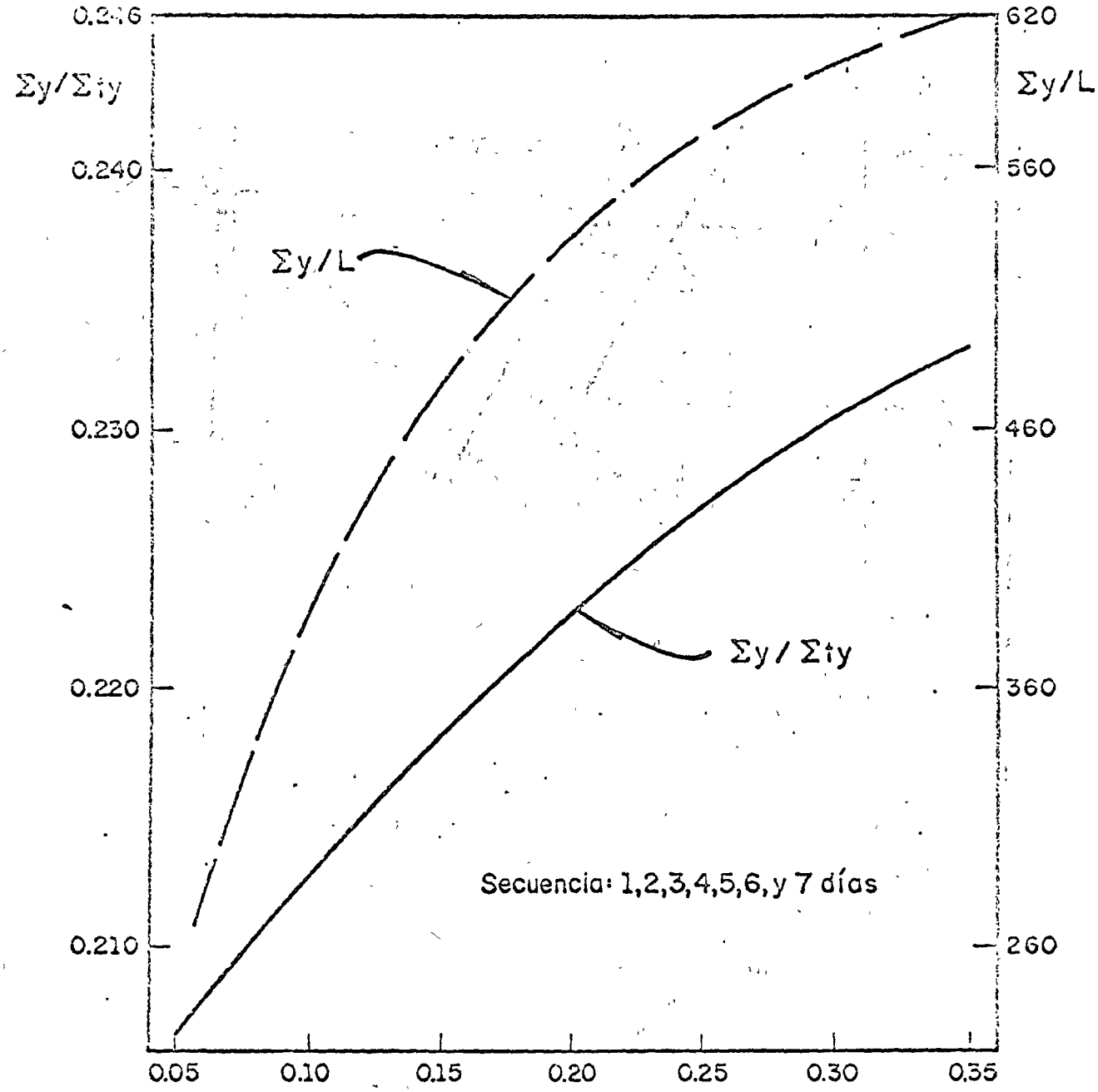


Fig. 4 Constante de velocidad de reacción, k

$\Sigma y/L$ y $\Sigma y/\Sigma ty$ para varios valores de k en 7 días consecutivos

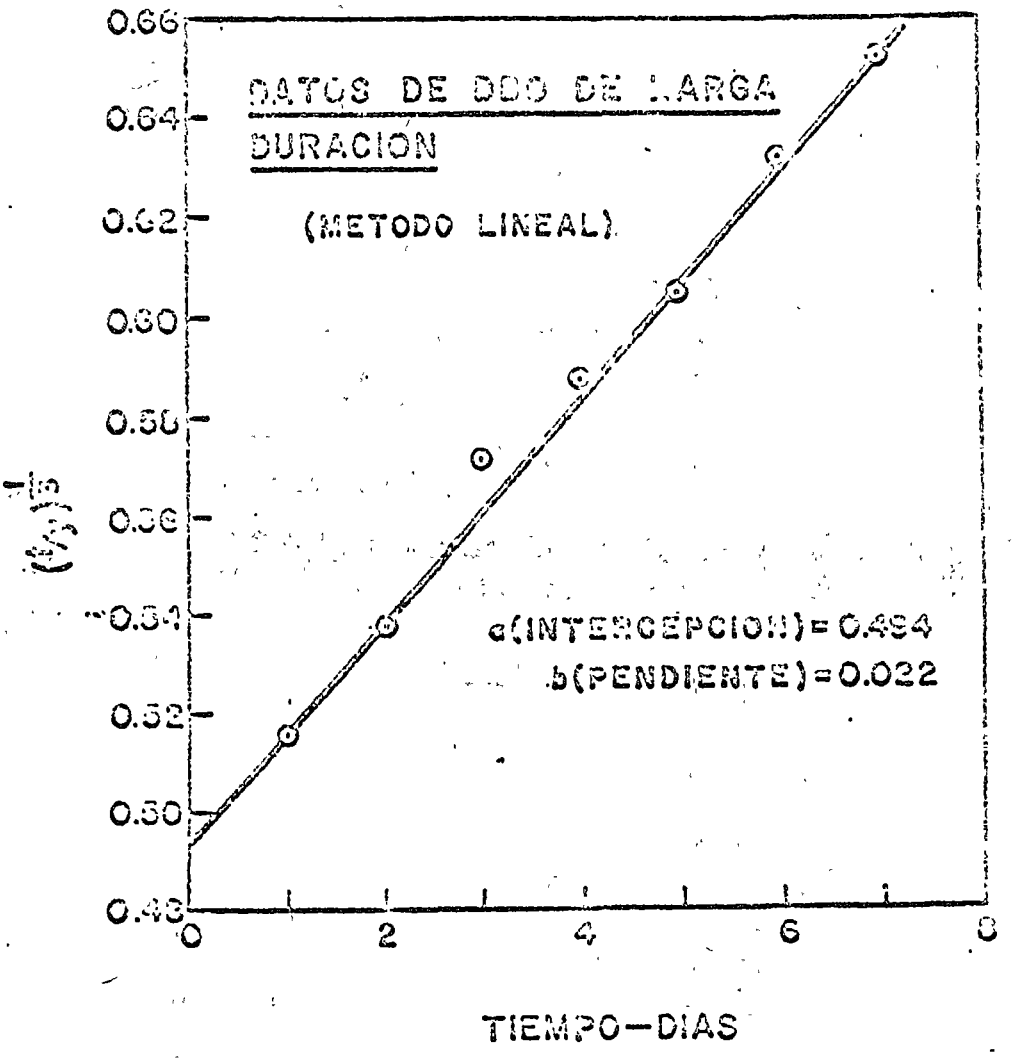


Fig. 5 Cálculo de k y Lo por el método gráfico

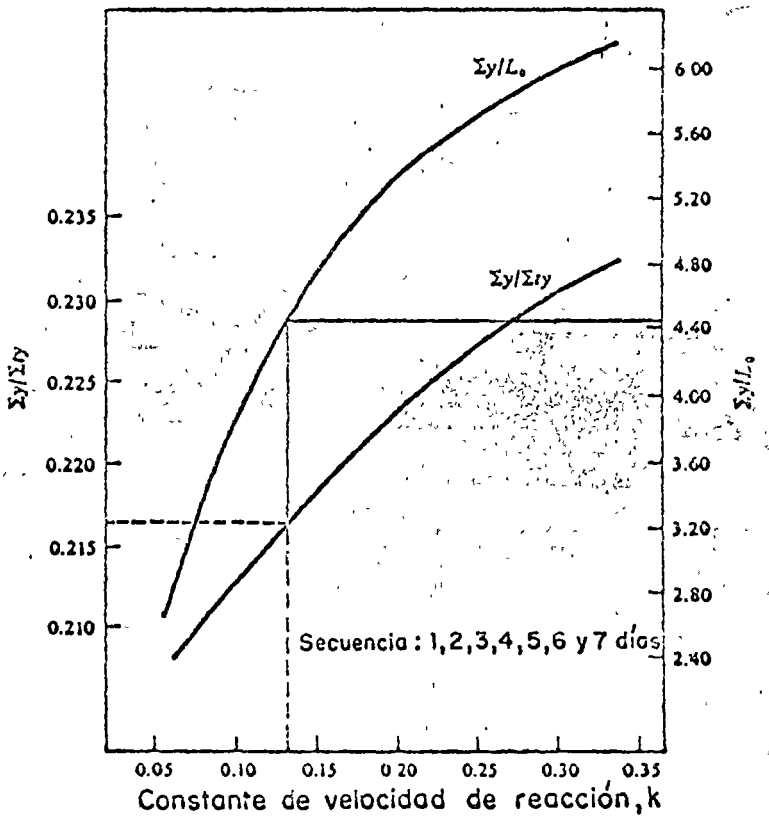


Fig. 4 bis. Cálculo de las constantes de la DBO por el método de los momentos

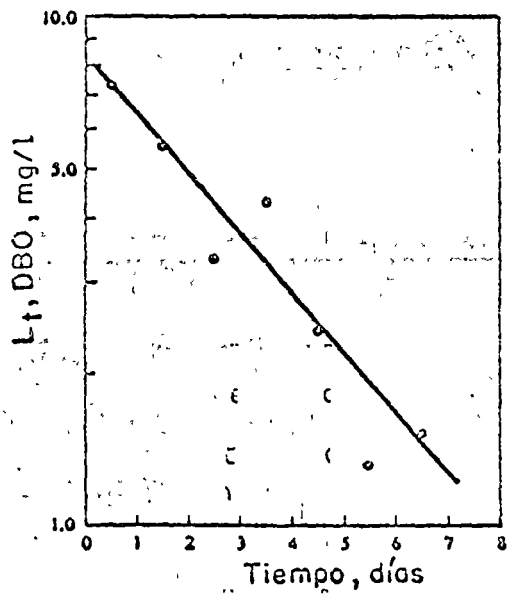


Fig. 6 Cálculo de k y L_o por el método de las diferencias

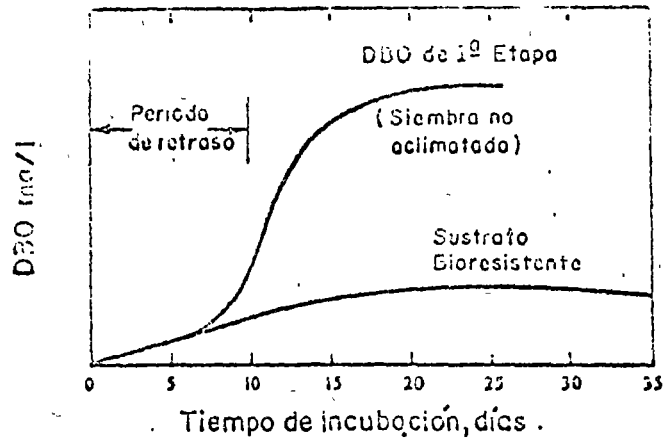


Fig. 7, Efecto de la aclimatación en la DBO

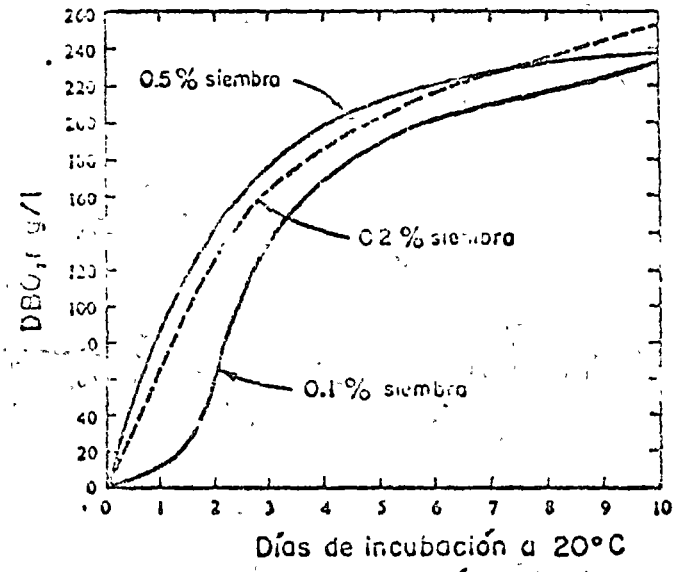


Fig. 8 Efecto de la concentración de la siembra en la DBO

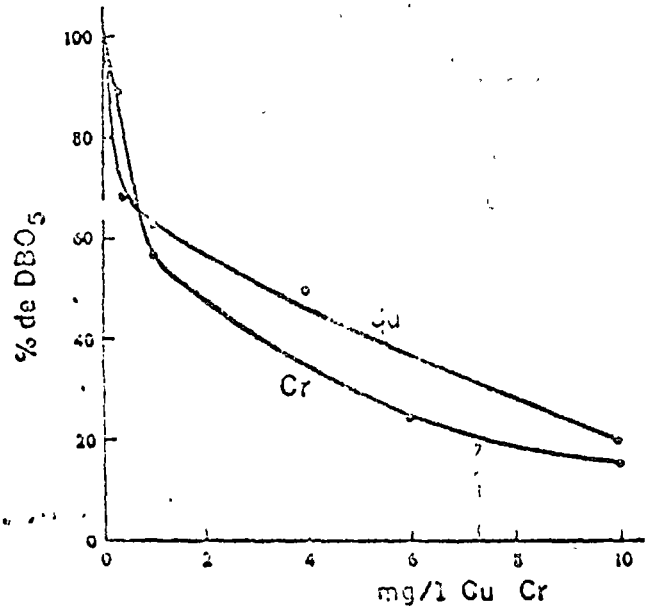


Fig. 9 Efecto de la concentración de iones metálicos en

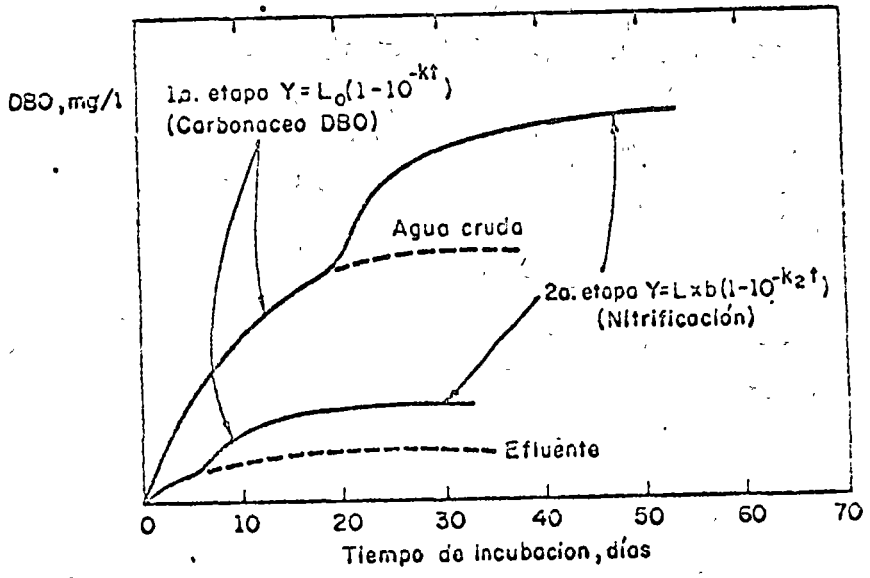


Fig. 10 Primera y segunda etapas de la DBO en aguas residuales, crudas y tratadas

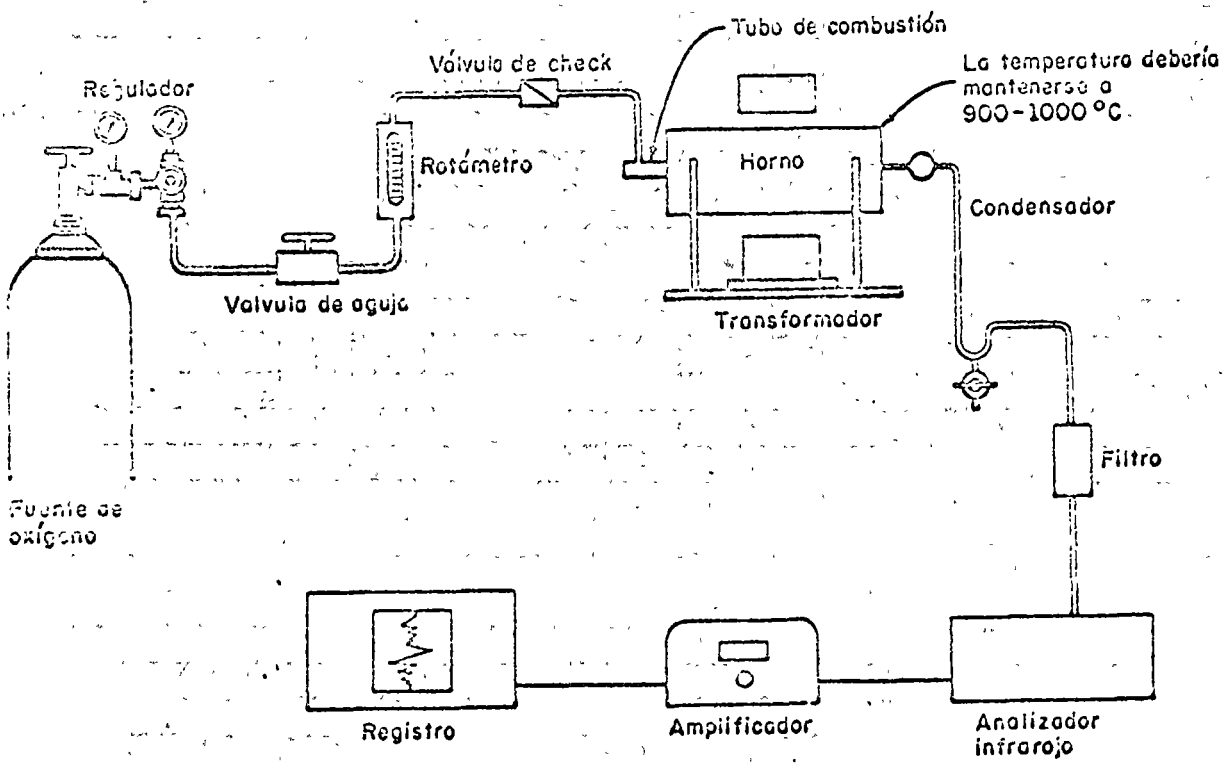


Fig. 11 Diagrama de un analizador de carbono.

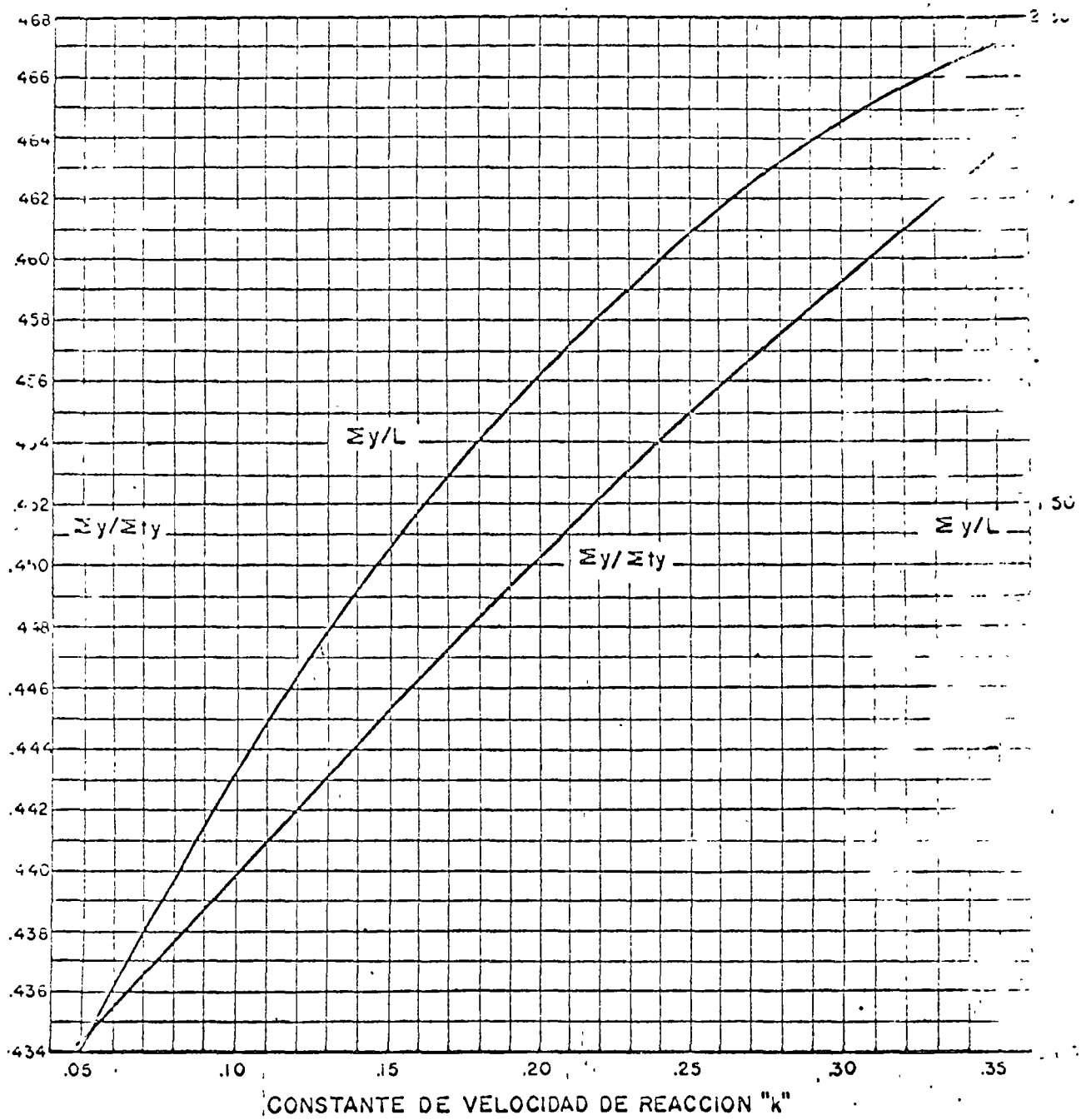


FIG. Valores de "k" y de la DBO última para series de pruebas de la DBO por 1, 2 y 3 dias (según Moore, Thomas y Snow).

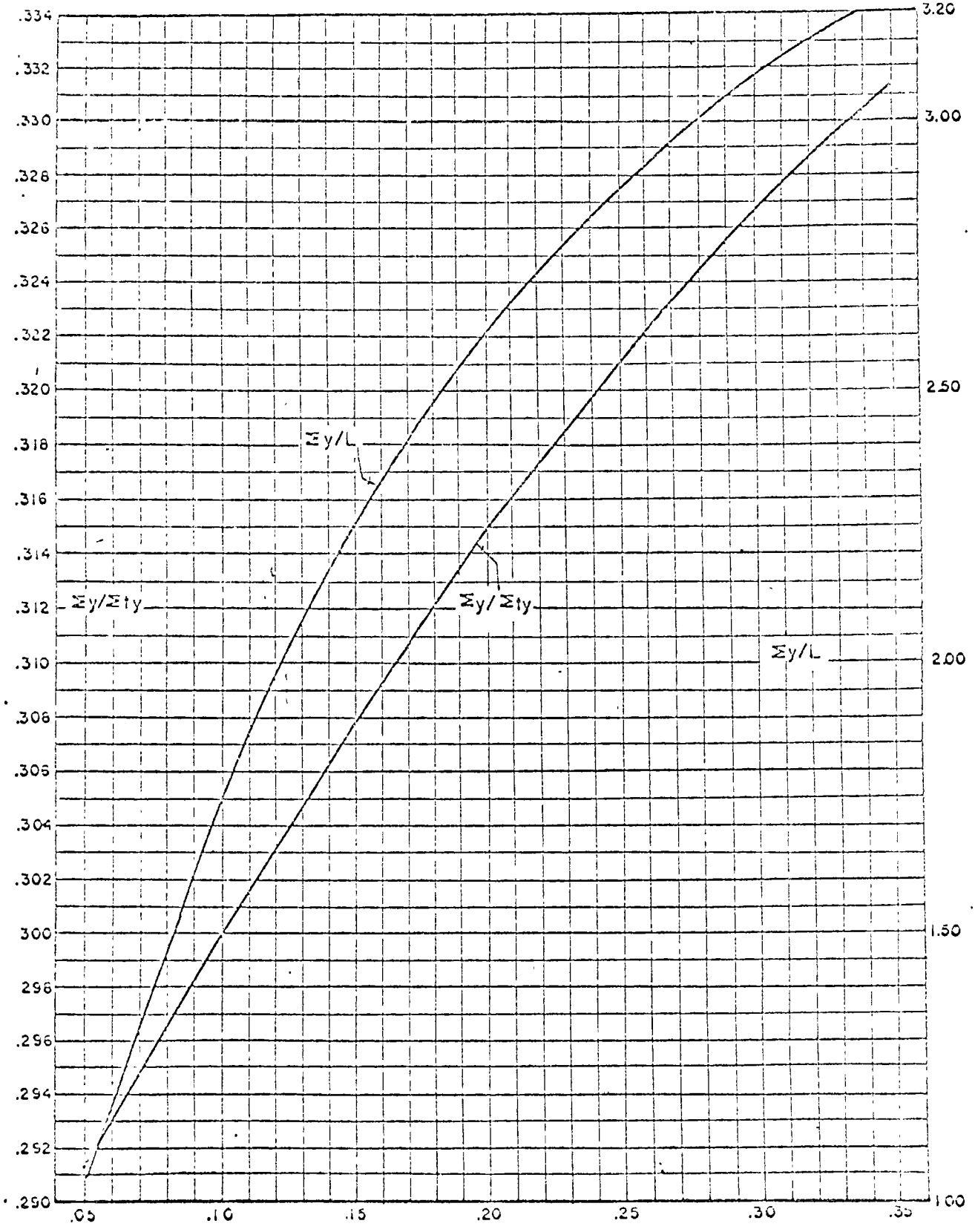


FIG. Valores de "k" y de la DBO última para series de pruebas de la DBO por 1,2,3 y 5 días. (según Moore, Thomas y Snow)

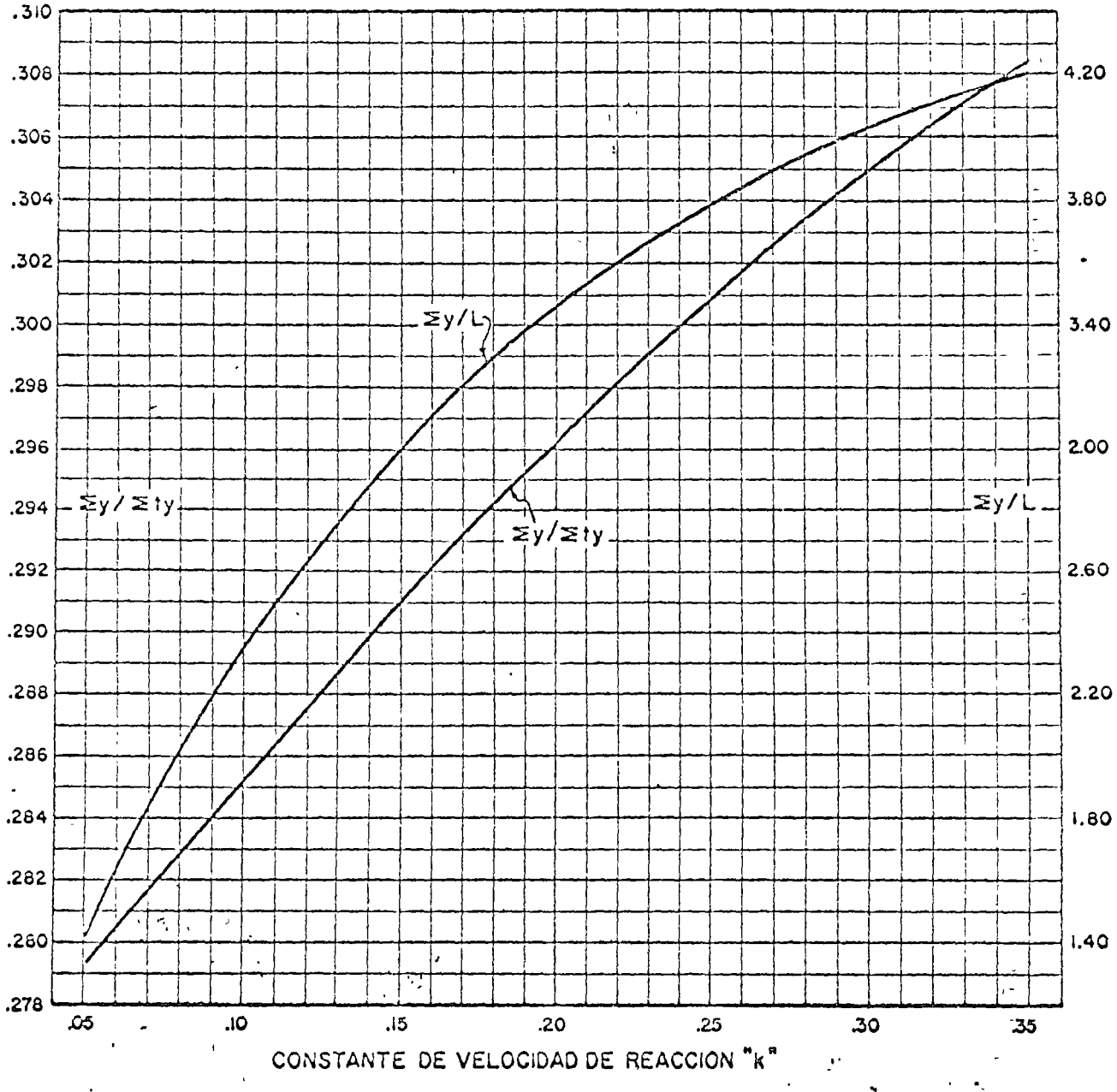


FIG. ____ Valores de "k" y de la DBO última para series de pruebas de la DBO por 1, 2, 3, 4 y 5 días, (según Moore, Thomas y Snow).

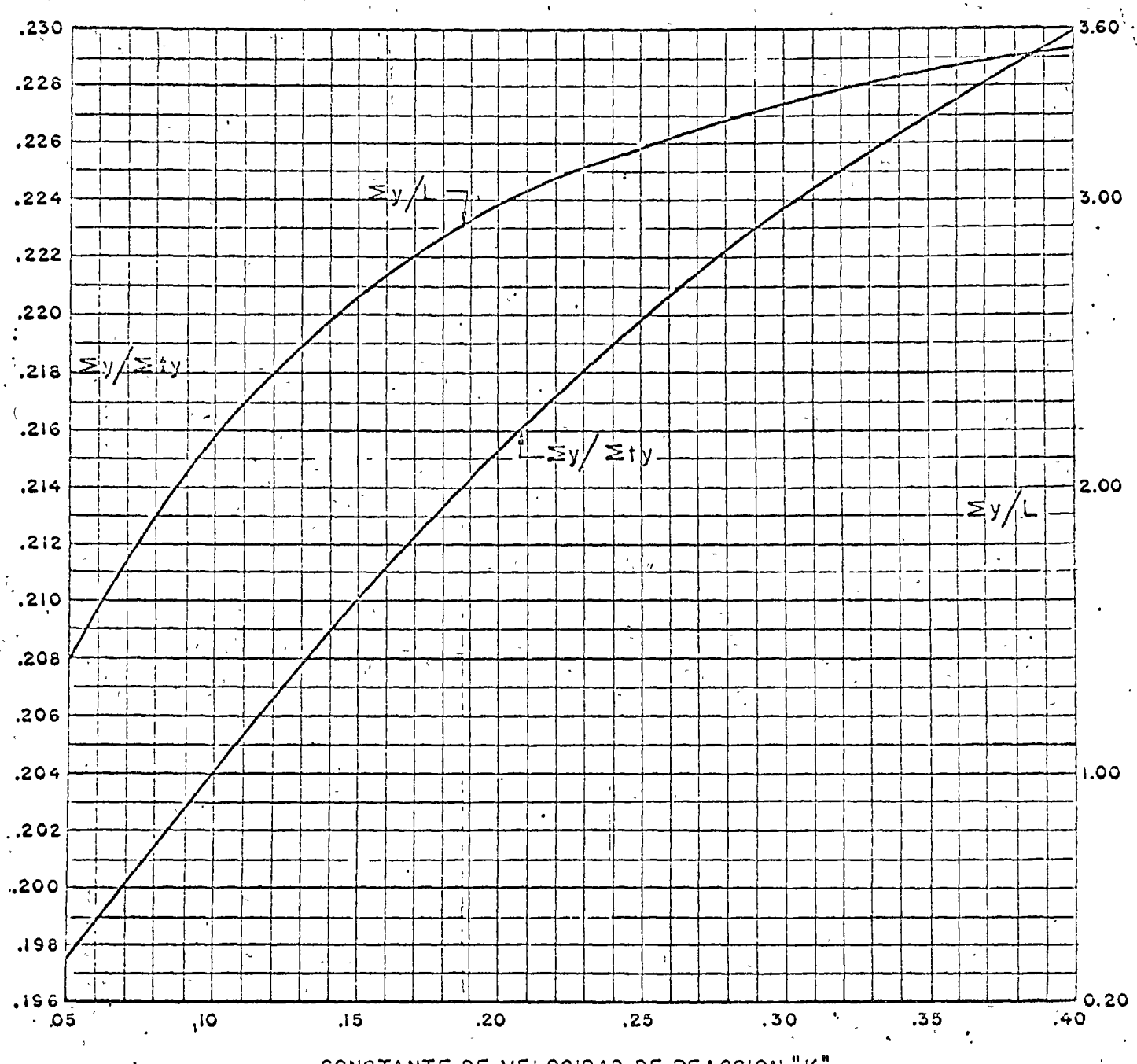


FIG. Valores de "K" y de la DBO última para series de pruebas de la DBO por 1, 3, 5 y 7 dias (según -- Moore, Thomas y Snow).

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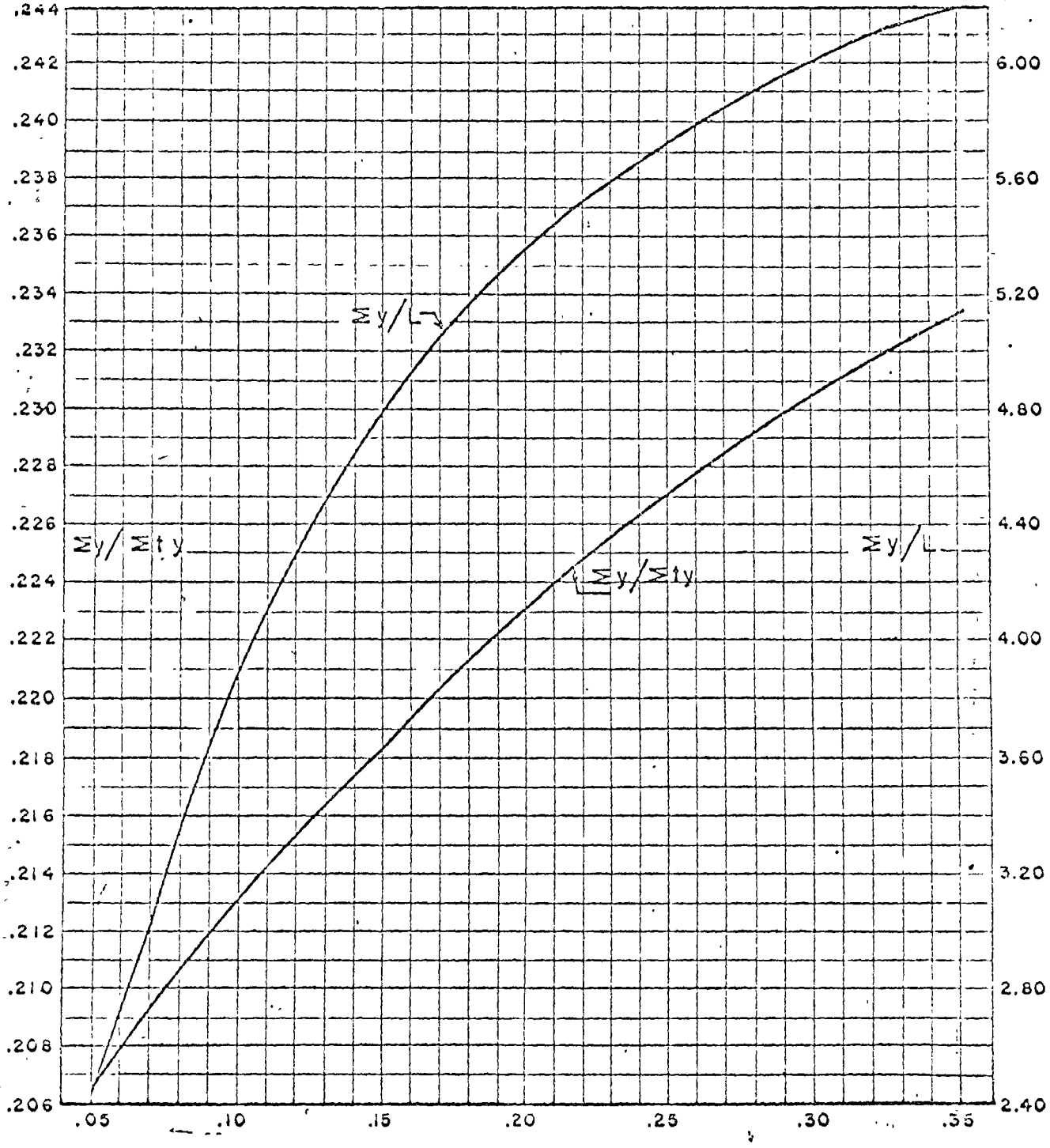

FIG. Valores de "K" y de la DBO última para series de pruebas de la DBO por 1,2,3,4,5,6 y 7 dias (según Moore, Thomas y Snow).

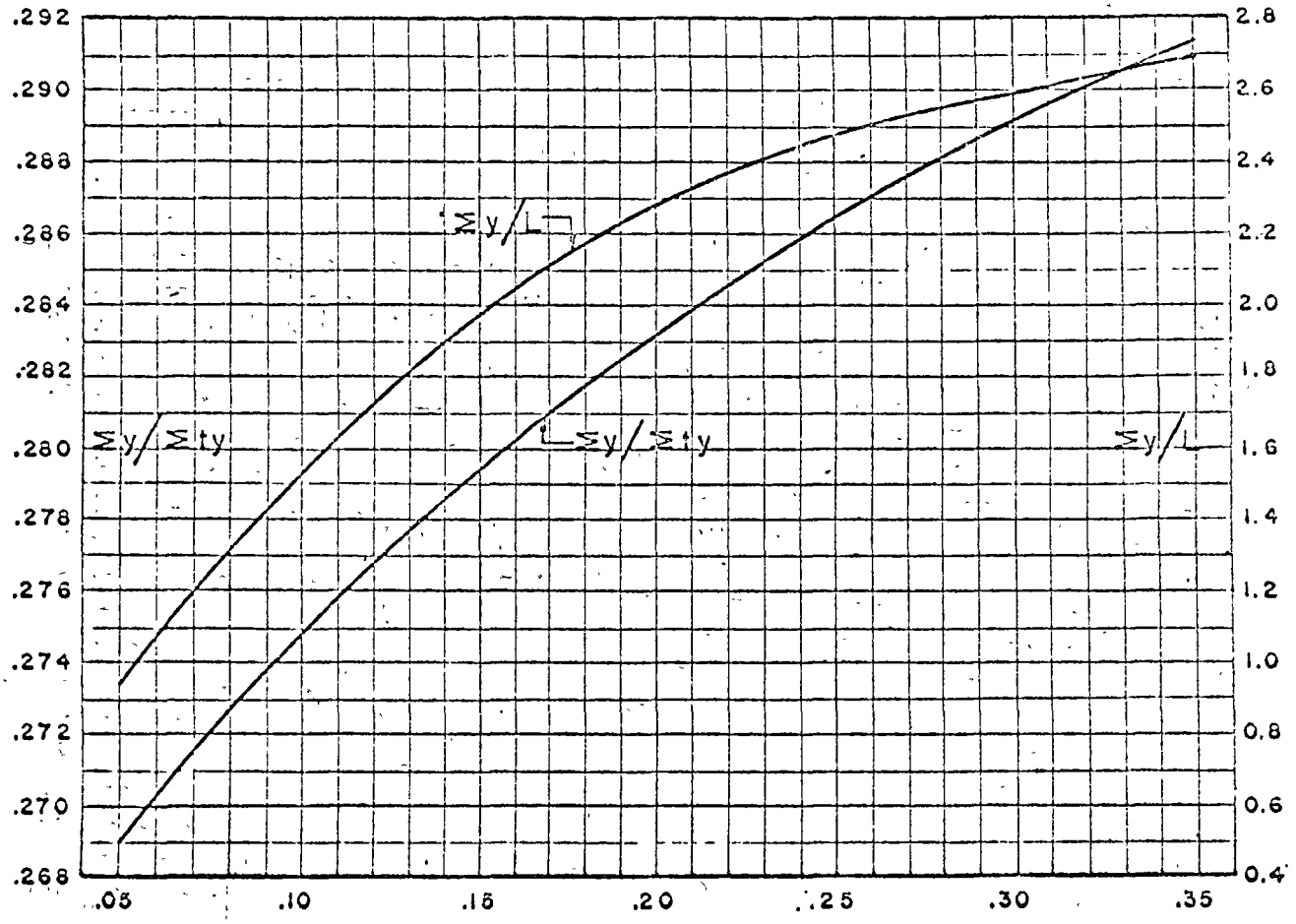

FIG. Valores de "K" y de la DBO última para series de pruebas de la DBO por 2, 3 y 5 dias (según Moore, Thomas y Snow).

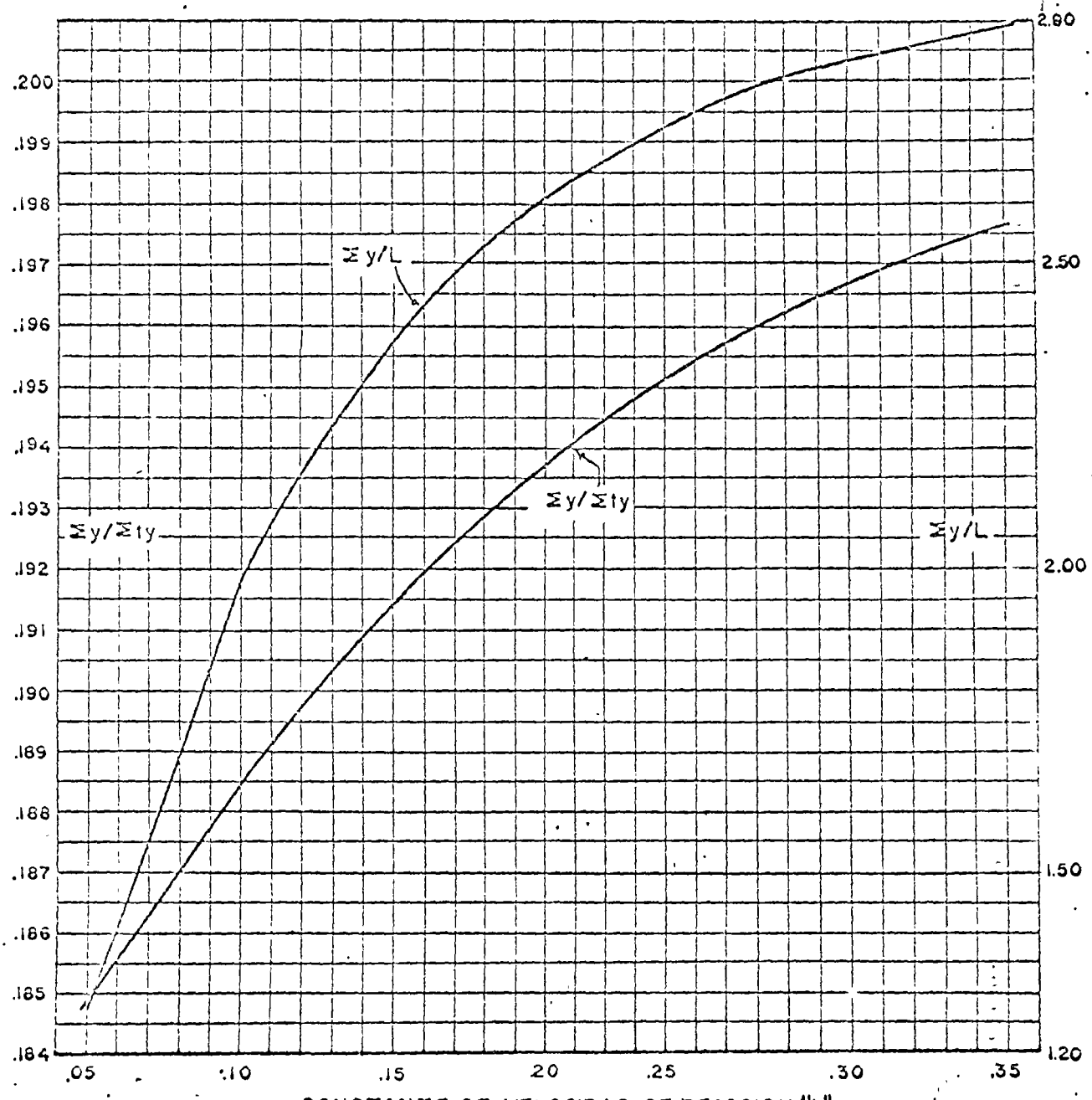

FIG. Valores de "k" y de la DBO última para series de pruebas de la DBO por 3,5 y 7 días (según Moore Thomas y Snow).

ION EXCHANGE*

I. Introduction

Ion exchange is an exchange adsorption process in which ions associated with the solid adsorbent are exchanged for ions in solution. The phenomenon of ion exchange occurs in many natural solids, such as, soils, humus cellulose, wool, protein, carbon, aluminum oxide, lignin, and living cells. Synthetic ion exchange resins also exhibit ion exchange capabilities.

The ion exchange process can be employed to remove undesirable anions and cations from wastewaters. Generally, hydroxyl ions are exchanged for the anions removed from solution while hydrogen or sodium ions are replaced by the cations which are taken up by the exchange solid.

A synthetic ion-exchange resin generally consists of a network of hydrocarbon molecules which contain soluble ionic functional groups. The overall insolubility and toughness of a synthetic resin are the result of the three-dimensional matrix form by the crosslinked hydrocarbon molecules. This crosslinking establishes the internal pore structure of the resin. The pore size must be large enough to permit the free movement of the exchanging ions which must diffuse into and out of the resin for exchange to take place. By proper selection of the degree of crosslinking in a resin, ions larger than the predetermined size may be excluded from reaction.

The behavior of the resin is determined to a large extent by the nature of the ionic groups associated with the hydrocarbon molecules. The exchange capacity of the resin is controlled by the total number of ionic functional groups per unit weight of resin. The type of ionic group affects the ion selectivity and ion-exchange equilibria. Anion exchangers primarily contain such functional groups as the strong-base quaternary ammonium group ($- \overset{|}{N} -^{+}$), the weak-base amino groups ($- NH_3^{+}$, $= NH_2^{+}$). On the other hand the cation exchangers primarily contain such functional groups as the strong-acid sulfonic group ($- SO_3 -$) and the weak-acid carboxylic group ($- COO -$).

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*Joseph F. Malina, Jr.

II. Kinetics

The rates at which ions are exchanged by porous synthetic resins are controlled by transport forces which cause intraparticle diffusion rather than by chemical forces. However, mathematical formulations of exchange kinetics have not been successful. In general, the principles of diffusion processes apply to the kinetics of ion exchange.

Consider an exchange reaction proceeding toward equilibrium. In order for an exchange to occur, ion (A) in solution must travel through the bulk of the solution, through the stagnate film surrounding the resin, and through the pore spaces of the resin particle. Similarly, exchanging ion (B) must undergo the reverse process. In the usual operation, rate of flow of the solution phase is sufficient to effectively carry ions up to and away from the film layer. The rate of exchange, therefore, depends upon ion diffusion rates through the film and within the particle. The two rates are seldom equal and one or the other is rate limiting. The rate of diffusion through the resin is proportional to the concentration of fixed charges and the effective particle-diffusion coefficient of the ions (the latter decreases with greater crosslinking), and is inversely proportional to the volume of the particle. However, the rate of diffusion through the film is proportional to the solution concentration and the effective film-diffusion coefficient of the ions, and is inversely proportional to film thickness.

The exchange reaction is stoichiometric, and since electroneutrality must always be maintained, the reaction can proceed no faster than the transport of the slowest ion. In reactions involving the exchange of two or more ions from solution phase, it is possible for the exchanger to temporarily overshoot equilibrium with respect to one of the competing ions. The exchanging ion with the greatest rate of movement in solution initially displaces the ions of the resin, only to be replaced later with a more strongly preferred, but more slowly diffusing, ion.

III. Ion Exchange Reactions

The four fundamental types of synthetic ion exchange undergo similar reactions which are analagous to common acids and bases. The major difference, however, is that the resins are insoluble and actually remove constituents from solution by forming resin salts. Typical reactions are shown below. Note that R represents the non-mobile part of the ion exchange resin.

Strongly Acidic Cation Exchangers--analogous to sulfuric acid

$$RSO_3H + NaOH \rightleftharpoons RSO_3Na + H_2O$$
$$RSO_3H + NaCl \rightleftharpoons RSO_3Na + HCl$$
$$2RSO_3Na + CaCl_2 \rightleftharpoons (RSO_3)_2Ca + 2NaCl$$

Weakly Acidic Cation Exchange Resin--analogous to acetic acid

$$RCO_2H + NaOH \rightleftharpoons RCO_2Na + H_2O$$
$$2RCO_2Na + CaCl_2 \rightleftharpoons (RCO_2)_2Ca + 2NaCl$$

Strongly Basic Anion Exchange Resin--analogous to sodium hydroxide

$$RNR'_3OH + HCl \rightleftharpoons RNR_3Cl + H_2O$$
$$RNR'_3OH + NaCl \rightleftharpoons RNR_3Cl + NaOH$$
$$2RNR'_3Cl + H_2SO_4 \rightleftharpoons (RNR_3)_2SO_4 + 2HCl$$

Weakly Basic Anion Exchange Resin--analogous to ammonium hydroxide

$$RNH_2 + HCl \rightleftharpoons RNH_3Cl$$

or

$$RNH_3OH + HCl \rightleftharpoons RNH_3Cl + H_2O$$
$$2RNH_3Cl + H_2SO_4 \rightleftharpoons (RNH_3)_2SO_4 + 2HCl$$

When all the ions at the exchange sites in the resin have been substantially replaced by the ions from solution, the resin may be regenerated and the exchange capacity restored. Regenerants are usually used at a 1N concentration or percentagewise in solutions of about 2 to 10 percent by weight. Table 1 lists some of the regenerants that may be used with each of the different types of ion exchange resins.

TABLE 1

Ion Exchange Resin	Ionic Form	Regenerant
Strong Acid Cation	H^+	HCl or H_2SO_4
	Na^+	NaCl
Weak Acid Cation	H^+	HCl or H_2SO_4
	Na^+	NaOH
Strong Base Anion	OH^-	NaOH
	Cl^-	NaCl or HCl
	$SO_4^=$	Na_2SO_4 or H_2SO_4
Weak Base Anion	Free Base	NaOH or NH_4OH or Na_2CO_3
	Cl^-	HCl
	$SO_4^=$	H_2SO_4

IV. Selection of Ion Exchange Resin

An ion exchange resin should be chosen based on (a) required functionality, (b) proper porosity or degree of crosslinkage, and (c) particle size. Generally sulfonic acid cation exchange resins and quaternary ammonium anion exchange resins can be used for the removal of almost all ionic species. The porosity of a resin decreases as the degree of crosslinking increases. For general application, medium porosity resins are used for low molecular weight ionic species, and high porosity resins are usually reserved for high molecular weight species. The degree of crosslinkage also affects the selectivity pattern for various cations and anions. The particle size of resin most frequently used in separation of anions and cations from nonionic species ranges between 16 and 50 mesh.

V. Ion Exchange Selectivity

Some empirical rules which could be used as a guide in understanding the relative selectivity patterns are presented below. These relationships cannot be interpreted strictly for all cases.

1. At low aqueous concentrations and ordinary temperatures, the extent of exchange or the exchange potential increases with increasing valence of the exchanging ion.

   $(Na^+ < Ca^{++} < Al^{+++})$

2. At low aqueous concentrations, ordinary temperatures, and constant valence, the exchange potential increases with increasing atomic number.

   $(Li < Na < K;\ Mg < Ca < Sr < Ba;$
   $F < Cl < Br < I)$

3. At high concentrations, the differences in exchange potentials of ions of different valence diminish and, in some cases, the ion of lower valence has the higher exchange potential.

   $(Na^+ \text{ vs } Ca^{++})$

4. The exchange potentials of various ions may be approximated from their activity coefficient--the higher the activity coefficient the greater the potential.

5. The exchange potential of the hydrogen ion or the hydroxyl ion depends upon the strength of the acid or base formed between the functional group and the hydrogen or hydroxyl ion. The stronger the acid or base formed, the lower is the potential.

6. As the degree of crosslinking or the fixed ion concentration of any ion exchanger is lowered, the exchange equilibrium or selectivity coefficient approaches unity.

TABLE 2

Relative Selectivity Coefficients of Sulfonic Cation Exchange Resins

	% Divinylbenzene (crosslink)		
Cation	4	8	10
Li	1.00	1.00	1.00
H	1.30	1.26	1.45
Na	1.49	1.88	2.23
NH_4	1.75	2.22	3.07
K	2.09	2.63	4.15
Cs	2.37	2.91	4.15
Ag	4.00	7.36	19.4

TABLE 3

Relative Selectivity Coefficients of Quaternary Ammonium Anion Exchange Resins

Anion	Coefficient
F	0.09
OH	0.09
Cl	1.0
Br	2.8
NO_3	3.8
I	8.7
ClO_4	10.0

VI. Applications

One of the first practical applications of ion exchange materials was in the field of water softening, and their application in this field is among their major use today. The basic principles of ion exchange for softening of water have not changed, but the exchange materials have been vastly improved. At the present time styrene base cation resins with sulfonic acid functional groups are the most widely used exchange materials for water softening. This type of resin has high capacity, excellent stability, and no adverse selectivity for ions normally associated with natural waters.

Nearly all cation exchangers used in practical water and waste treatment operations are strongly acidic, that is, they contain strongly ionized groups and are thus capable of exchanging all cations. Two general types of anion exchangers are employed, however; strong basic anion resins are capable of exchanging all anions including such weakly ionized materials as silica and carbon dioxide, while weakly basic resins will exchange only strongly ionized anions such as chlorides and sulfates.

For water softening, as for most practical ion exchange process operations, columnar operation is employed. The installation is similar to that for a pressure sand filter. The exchanger is most commonly in the sodium form initially, that is, it contains the sodium ion as the exchangeable ion. As raw water comes in contact with the resin the cations in the water are replaced with the non-hardness sodium ion. Eventually the majority of the sodium ions are displaced by other cations from solution and the resin becomes inefficient as an exchanger. The exchanger must then be removed from service, backwashed to loosen the bed and remove accumulated dirt, and regenerated to the sodium form by passing a concentrated solution of sodium chloride through the bed. After rinsing to remove excess regenerant solution, the bed is again ready for service.

In order to obtain reasonable and practical rates of soft water production, applied feed rates, usually in the range from 2 to 8 gallons per minute per cubic foot of resin, are in excess of those which would permit equilibrium contact between resin and solution. This condition, however, is operationally favorable in that the resin is subjected to a continuously high concentration of exchanging ions, thus forcing the resin to more rapid and complete utilization of capacity. The result is that the most active exchange occurs within a particular longitudinal zone of the bed. The active zone moves progressively down the column as the reaction proceeds. On the influent side of the reaction zone, the resin has attained equilibrium with the feed and the released ions of the exchanger flow through the lower part of the bed without further change. In the upstream portion of the zone the resin is very nearly exhausted. However, in its relative position within the reaction zone it is subjected

to the highest concentration of exchanging ions, and is thus yet capable of participating in the exchange reaction. The middle portion of the zone contains a relatively large quantity of unspent resin and also a relatively high concentration of exchanging ions remaining in solution phase. In this portion of the bed, the exchange reaction is most rapid. Near the downstream edge of the reaction zone, the solution contains a low concentration of ions to be removed, but also in this area the resin is highest in exchangeable counter ions. Below the zone of exchange, the resin is essentially in the sodium form and the passing solution contains only sodium ions. As the forward edge of the zone reaches the bottom of the column, hardness ions appear in the effluent. When their concentration becomes unacceptably high, the exchanger must be regenerated.

The design of an ion exchange unit requires knowledge of the capacity of the resin bed and of the efficiency of the process. The "theoretical" capacity of a resin is the number of ionic groups (equivalent number of exchangeable ions) contained per unit weight or unit volume of resin. This capacity is generally expressed as equivalents per gram dry hydrogen-form resin, but may also be expressed as kilograins $CaCO_3/ft^3$ resin bed, pounds $CaCO_3/ft^3$ resin bed, etc. In practice, however, an exchanger is generally operated at a level considerably below its theoretical capacity. The softening exchange reactions,

$$2RNa^+ + Ca^{+2} \rightleftharpoons R_2Ca^{+2} + 2Na^+$$

and

$$2RNa^+ + Mg^{+2} \rightleftharpoons R_2Mg^{+2} + 2Na^+$$

are equilibrium reactions, and an impractically large quantity of regenerant would be required to drive the reactions completely to the left. Although increasing the quantity of salt per unit volume of resin in regeneration increases the operational capacity of the exchanger, the resulting bed capacity is not directly proportional to the increase in regenerant required. In other words, doubling the quantity of salt increases the bed capacity but by less than a factor of two. The degree of theoretical capacity attained in an operation is termed the "degree of column utilization"; the ratio of the operating to the theoretical exchanger capacity. The term "efficiency" is used to designate the degree of utilization of the regenerant. Column efficiency is the ratio of the operating exchange capacity of a unit to the exchange that theoretically could be derived from a specific weight of applied regenerant. In this term it is important to note that the "theoretical capacity" of the exchanger is not a factor. Efficiency refers only to the output of an exchanger relative to the input of regenerant, on an equivalent basis.

The characteristics of an exchanger, therefore, are such that higher efficiencies are achieved with lower levels of regeneration. However, low bed capacities also result at low regeneration levels. In practice some efficiency is generally sacrificed to obtain a reasonable column utilization.

storage. Since the maximum concentration of CrO_3 which can be passed through some resins to avoid deterioration is 14 - 16 oz/gal as CrO_3 the bath may require dilution and the recovered solution may require make-up to strength.

The rinse waters are first passed through a cation exchanger to remove metal ions. The effluent from this unit is passed through an anion exchanger to remove chromate and to obtain demineralized makeup water. It is desirable to pass the rinse water through the cation unit first to avoid precipitation of metal hydroxides on the exchange resin. The anion exchanger is regenerated with sodium hydroxide resulting in a mixture of Na_2CrO_4 and NaOH in the spent regenerant. This is then passed through the cation exchanger to recover H_2CrO_4 which is returned to the plating bath. The recovered chromic acid from the spent regenerant will average 4 - 6 % concentration. The spent regenerant from the cation exchanger will require neutralization and possibly precipitation of metallic ions prior to discharge to the sewer. Since most of the metal ions are eluted in the first 70% of the regenerant volume, neutralization requirements can be reduced by reusing the last portion of the acid regenerant for the subsequent regeneration. In like manner the last portion of the caustic regeneration can be used for neutralization of the spent cation regenerant.

In cation units, the regeneration requirements are higher than those employed in water purification because of the competition with the H^+ present in the waste solution. For water reuse, 4 - 5 lbs H_2SO_4/ft^3 may be required for regeneration while for recovery of H_2CrO_4 as high as 25 lbs H_2SO_4/ft^3 may be required to reduce leakage of sodium ions.

VII. Modes of Operation

Complete demineralization operations generally involve a cation exchanger followed by a weakly basic anion exchanger. If the cation resin is on the hydrogen-ion cycle and the anion resin on the hydroxide-ion cycle, the series exchangers successively convert salt impurities into acids and then into water, and remove all ionic materials except carbon dioxide and silica.

If it is desired to remove carbon dioxide, a degasifier, decarbonation tank, or vacuum deaerator may be installed following the anion exchanger. If both carbon dioxide and silica are objectionable, the decarbonation unit preceeds the highly basic anion exchanger in the flow sequence. The reason for this arrangement is the highly basic resins will remove carbon dioxide, as well as silica, and it is generally less expensive to save the capacity of the resin by removing carbon dioxide in advance. The power required for a degasification unit is relatively inexpensive compared to costs of resin regeneration.

Mixed-resin exchangers use a cation resin which is intimately mixed

with a highly basic anion resin. A conventional two-stage exchanger will accomplish 90-99% total dissolved solids reduction; however, a mixed bed exchanger will remove all but a fraction of a percent of the ionic impurities. Mixed-bed exchangers must of course be separated for regeneration. This poses no serious problems since resins of such respective densities as will result in separation upon backwashing may be selected. It is of course necessary to remix the resins after regeneration. This is generally accomplished by blowing air through the expanded bed while drawing it down.

In most instances in which two-stage operation is employed it is advantageous to use a four-bed system with two two-stage units in series. Such an arrangement allows operation of the first two units to a higher solids endpoint, yielding more complete removal at lower costs.

In addition to the arrangements previously cited, various combinations of units for specific purposes are possible. For example, an installation may include a series arrangement of a cation resin, a degasifier, a weakly basic anion resin, and a strongly basic anion resin. In such an installation, the weakly basic anion resin, which is relatively inexpensive to regenerate, absorbs the major anion lead, thus preventing the capacity of the strongly basic resin. Also, units may be devised in which countercurrent operation may be practiced if desirable.

VIII. Equipment and Operation Details

Because strong acid and alkali solution are used for exchanger regeneration, it is essential that all tanks and internal parts be of resistant materials or be lined or coated with resistant materials. Large units are usually lined with phenolic or vinyl chloride type materials. These coatings are generally about 0.01 inches in thickness for the plastic materials and about 0.2 inches for hard rubber.

It is important for good operation that flow through an exchanger be uniformly distributed. In general, exchangers are vertical and constructed with provisions for leveling adjustments, and the flow is from top to bottom to avoid channeling and uneven distribution. Depths of exchangers usually range from a minimum of two feet to a maximum of about six feet. Depending upon resin type, 50 to 100 per cent of packed column height is provided for expansion during backwashing.

Exchangers are normally operated under pressure, and pressure losses generally approximate a few pounds per square inch, of which the bed contributes in the neighborhood of one or two feet head loss. For highly turbid waters or wastes it is often desirable to pretreat by coagulation or filtration so as to minimize head loss through the exchanger itself.

Design criteria for ion exchange systems are summarized in Table 4.

TABLE 4

Design Criteria for Ion Exchange Systems

Minimum bed depth	24-30"	60-70 cm
Treatment flow rate	2-5 gpm/ft^3	3.5-9.0 liter/sec-m^3
Regeneration	0.5-1.5 gpm/ft^3	1-3 liter/sec-m^3
Reuse water volume	30-150 gas/ft^3	3500-17,000 liter/m^3
Rinse flow rate	6 gpm/ft^2	4 liter/sec-m^2
Backwash flow rate (anion unit)	3 gpm/ft^2	2 liter/sec-m^2
Backwash flow rate (cation unit)	6 gpm/ft^2	4 liter/sec-m^2
Backwash time	15 minutes	
Regenerant concentration (H_2SO_4)	2-5%	
Regenerant concentration (NaCl)	10-20%	
Regenerant concentration (NaOH)	4%	
Treatment flow rate	5gpm/ft^2	

IX. Economic Considerations

There is a considerable literature on the economics of ion exchange for different types of applications, and Smith has presented a rather good bibliography on this literature. The principal operating cost factor is regeneration and regenerants, and this varies with raw water quality and operating arrangement.

Exchangers employing highly basic resins, which are regenerated with sodium hydroxide, involve higher operating costs than those employing weakly basic resins. Additionally, regeneration of the former is a less efficient process than that for the weakly basic resins. For weak-base exchangers, costs usually are in the neighborhood of one cent per thousand gallons per grain per gallon, depending on the raw water quality.

The cost of ion exchange equipment will vary with the total volume of exchange resin required as well as on the number of units which will be used to house the resin. Cost data developed by the Rohm and Haas Company indicate that the cost per single ion exchange column of a given volume (V) may be calculated from the following equations:

Cost ($ US) $1208\ V^{0.55}$ (acid & alkaline resistant)

Cost ($ US) $906\ V^{0.55}$ (salt resistant)

where: V = cubic feet of resin required per unit.

These equations are applicable for volumes of resin per unit of one to one thousand cubic feet (.028 to 28 m^3). These estimated costs include the cost of the ion exchange unit, the cost of automatic controls, and the installation costs. These costs are summarized for various volumes of resin in Table 5.

TABLE 5

Equipment Costs For Ion Exchange

Volume of Resin (V) Cu. Feet	$V^{0.55}$	Rubber-lined Acid Resistant $1208\ V^{0.55}$ ($ US)	Steel, not Acid Resistant $906\ V^{0.55}$ ($ US)
1	1.00	1,208	906
10	3.55	4,290	3,220
350	8.60	10,400	7,790
100	12.60	15,220	11,420
750	38.10	46,000	34,500
1000	44.70	54,500	40,500

Although the equations are applicable, only up to a volume of 1000 cubic feet (28 m^3) ; larger units may be designed, but special construction considerations are required. Therefore, the standard costs cannot be used.

The cost of resin is at times included as part of the equipment costs and at other times as part of the operating costs. Typical resin costs are about $20 US per cubic foot ($706 US for m^3) for cation exchange resins while the cost of anion exchange resins is approximately $60 US per cubic foot ($2118 US per m^3).

X. Experimental Procedure

It is frequently necessary to operate a laboratory ion exchange column to develop the necessary design criteria for the removal of ions from complex industrial wastes. A suggested procedure is outlined below.

1. Rinse the column for 10 minutes at a flow rate of 50 ml/min with deionized water.
2. Adjust flow rate to column to 50 ml/min of solution containing the waste to be treated.
3. Measure initial volume of solution to be treated.
4. Start treatment cycle. Develop the breakthrough curve until the ion concentration reaches the maximum effluent limit.
5. Back wash to 25% bed expansion for 5-10 minutes. (Use distilled water for backwash operation).
6. Regenerate at a flow rate of 6 ml/min using the concentration and volume recommended for the resin. Collect spent regenerant and measure the recovered ions.
7. Rinse column with distilled water.

By making several runs it should be possible to develop a relationship between resin utilization and regenerant efficiency and to select the optimum operating level for the system.

XI. Example

A general plating plant operates 16 hours/day, 5 days/week. The total discharge of rinse waters has the following characteristics:

Copper	22 mg/l as Cu
Zinc	10 mg/l as Zn
Nickel	15 mg/l as Ni
Chromium	130 mg/l as CrO_3

The rate of flow is 50 gpm and inplant separation is not feasible. Design an exchanger system to include water and chromium recovery. The operating characteristics of the cation exchanger are as follows:

Cation Exchanger

Regenerant	H_2SO_4
Dosage lbs/ft^3	12
Concentration	5%
Flow rate	0.5 gpm/ft^3
Operating Capacity	1.5 eq/l

Anion Exchanger

Regenerant	NaOH
Dosage lbs/ft^3	4.8
Concentration	10%
Operating Capacity	3.8 lbs CrO_3/ft^3

A. Cation Exchanger

The cations removed include:

Zn	= 10mg/l =	0.306 meq/l
Cu	= 22mg/l =	0.693 meq/l
Ni	= 15mg/l =	0.511 meq/l
	Total	1.510 meq/l

1.51 meq/l (10^{-3})(50 gal/min)(3.785 liter/gal)(60 min/hr)(16 hr/day) = 274 eq/day

At an operating capacity of 1.5 eq/l the volume of resin required for regeneration every 2 days is

$$\frac{274 \text{ eq/day (2 days)}}{1.5 \text{ eq/l } (28.3 \text{ l/ft}^3)} = 12.9 \text{ cubic feet}$$

Use a diameter = 2.0 ft
Total depth = 4.1 ft.

For flexibility in operation use 2 units which are 2 ft. in diameter and 36 inches deep to allow for 50% bed expansion.

B. Regeneration of Cation Exchanger

Regeneration is accomplished by using 5% H_2SO_4 at a rate of 12 lb/ft^3. The required H_2SO_4 is

$$12 \text{ lb/ft}^3 \ (12.9 \text{ ft}^3) = 155 \text{ lbs}$$

Volume of H_2SO_4 storage tank is

$$155 \text{ lb} \left(\frac{1}{0.05 \ (1.038) \ 8.34} \right) = 358 \text{ gal}$$

Rinse requirements are

$$120 \text{ gal/ft}^3 \ (12.9 \text{ ft}^3) = 1550 \text{ gal}$$

The waste resulting from regeneration of the cation exchanger contains metal sulfates and some free sulfuric acid and must be neutralized to precipitate the metals prior to disposal.

C. Anion Exchanger

The CrO_3 in the effluent of the cation exchanger is removed from the rinse water on the anionic resin and replaced by OH^-.

The weight of CrO_3 in the waste is 130 mg/l (50)(60)(16) (8.34×10^{-6}) = 52 lb/day.

At an operating capacity of 3.8 lb CrO_3/ft^3 the required volume for daily regeneration $\frac{52}{3.8} = 13.7 \text{ ft}^3$.

Use a diameter of = 2.0 ft.
Required depth of resin = 4.35 ft.

For flexibility in operation use 2 units which are 2 feet in diameter and 36 inches deep to allow for approximately 50% bed expansion.

D. Regeneration of Anion Exchanger

Regeneration is accomplished by using 10% NaOH at a rate of 4.8 lb/ft^3. The NaOH required is

$$4.8 \text{ lb/ft}^3 \ (13.7 \text{ ft}^3) = 65.8 \text{ lb}$$

The volume of the NaOH storage tank is

$$65.8 \left(\frac{1}{(0.10)(1.15)\ 8.34}\right) = 68.8 \text{ gal}$$

Rinse requirements are

$$13.7 \text{ ft}^3 \ (100 \text{ gal/ft}^3) = 1370 \text{ gal.}$$

E. Recovery of Chromic Acid

The spent regenerant from the anion exchanger contains Na_2CrO_4 and NaOH. Chromic acid may be recovered by passing the spent regenerant through a hydrogen cation exchanger.

The sodium in the spent is:

$$65.8 \text{ lb NaOH } (454 \text{ gm/lb})(\text{eq}/40 \text{ gm}) = 745 \text{ eq}$$

If the cation exchange is regenerated once daily, the volume of cation resin with an operating capacity of 1.5 eq/l is

$$\frac{745 \text{ eq}}{(1.5 \text{ eq/l})(28.3)} = 17.6 \text{ ft}^3$$

Use a diameter = 2.0 ft
The required depth is 5.6 ft.

Therefore, for flexibility of operation use 2 units which are 2.0 ft in diameter and 50 inches deep to allow for 50% bed expansion.

F. Regeneration of Cation Exchanger Used for Chromic Acid Recovery

Regenerant used is 5% H_2SO_4 at a rate of 12 lb/ft^3. The required H_2SO_4 is:

$$12 \text{ lb/ft}^3 \ (17.6 \text{ ft}^3) = 210.5 \text{ lb}$$

Volume of H_2SO_4 storage tank is

$$210.5 \ \left(\frac{1}{0.05 \ (1.038)8.34}\right) = 490 \text{ gal.}$$

Rinse water requirements are

$$120 \text{ gal/ft}^3 \ (17.6 \text{ ft}^3) = 2105 \text{ gal.}$$

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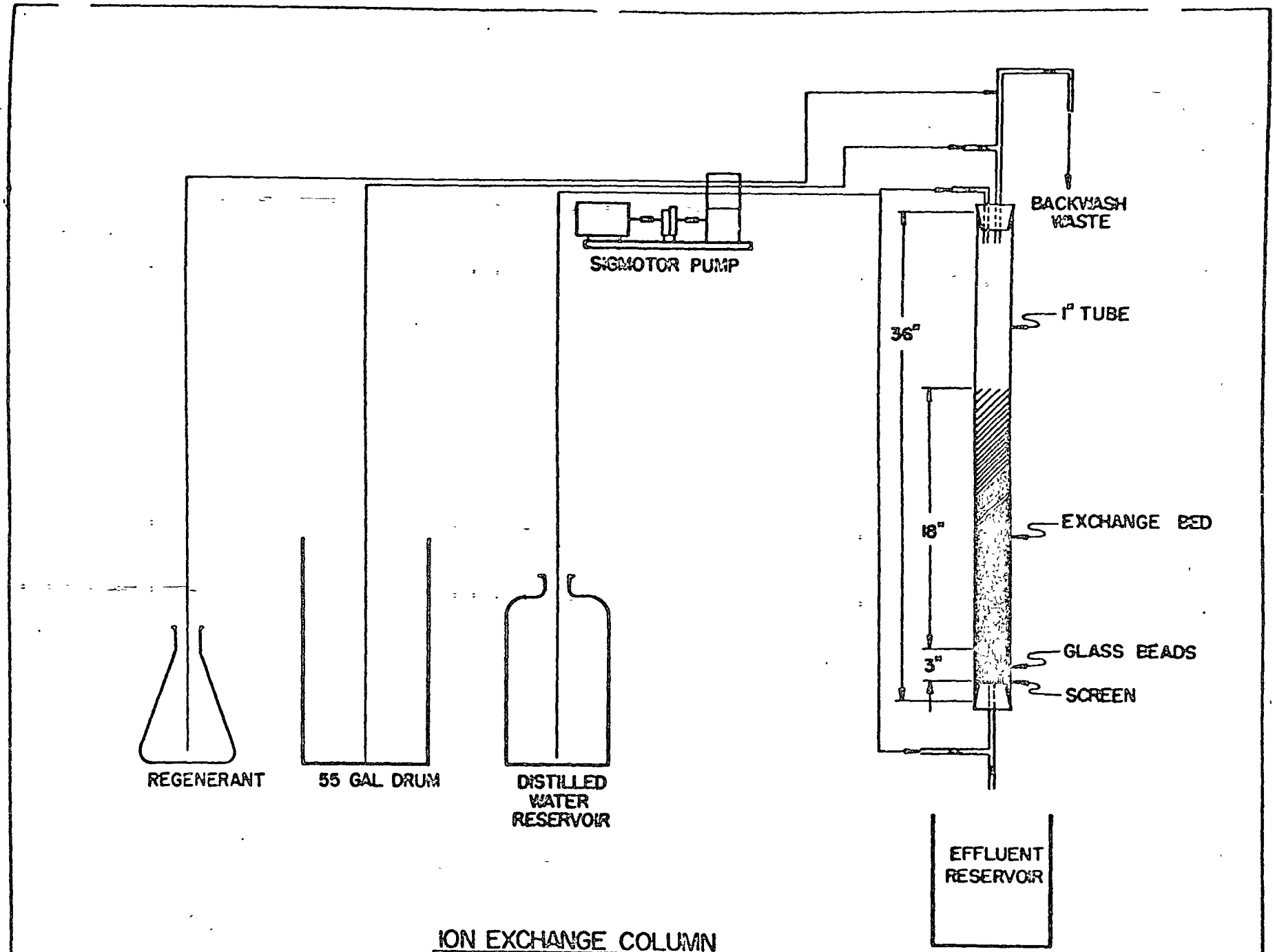
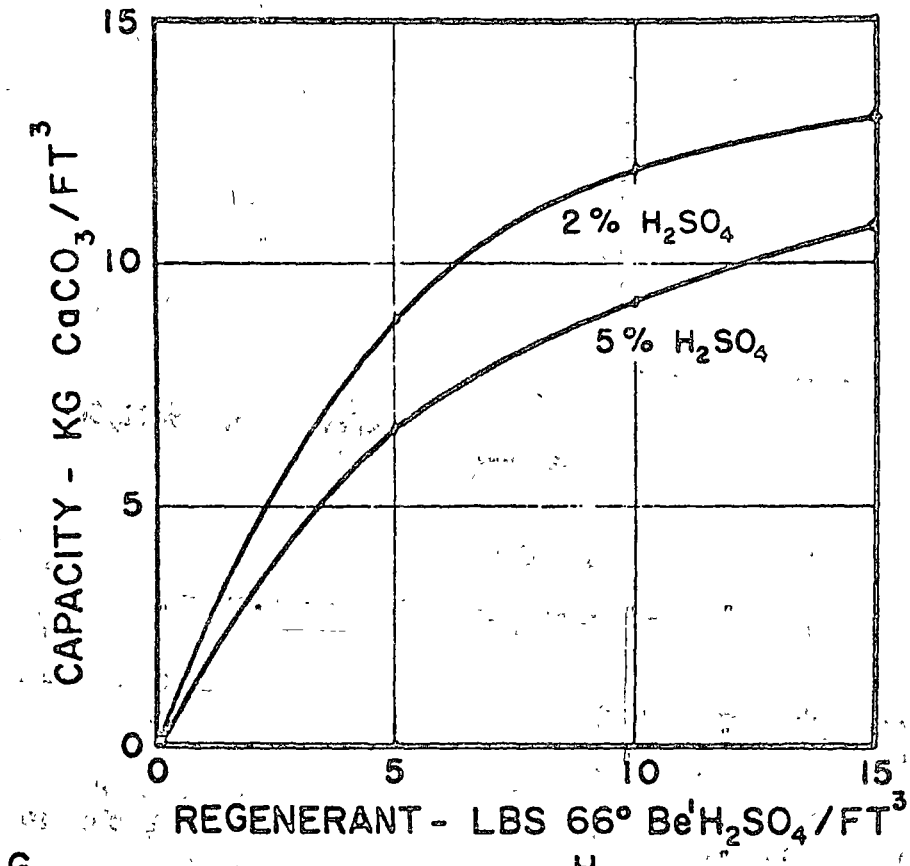


ION EXCHANGE COLUMN

FIGURE 1



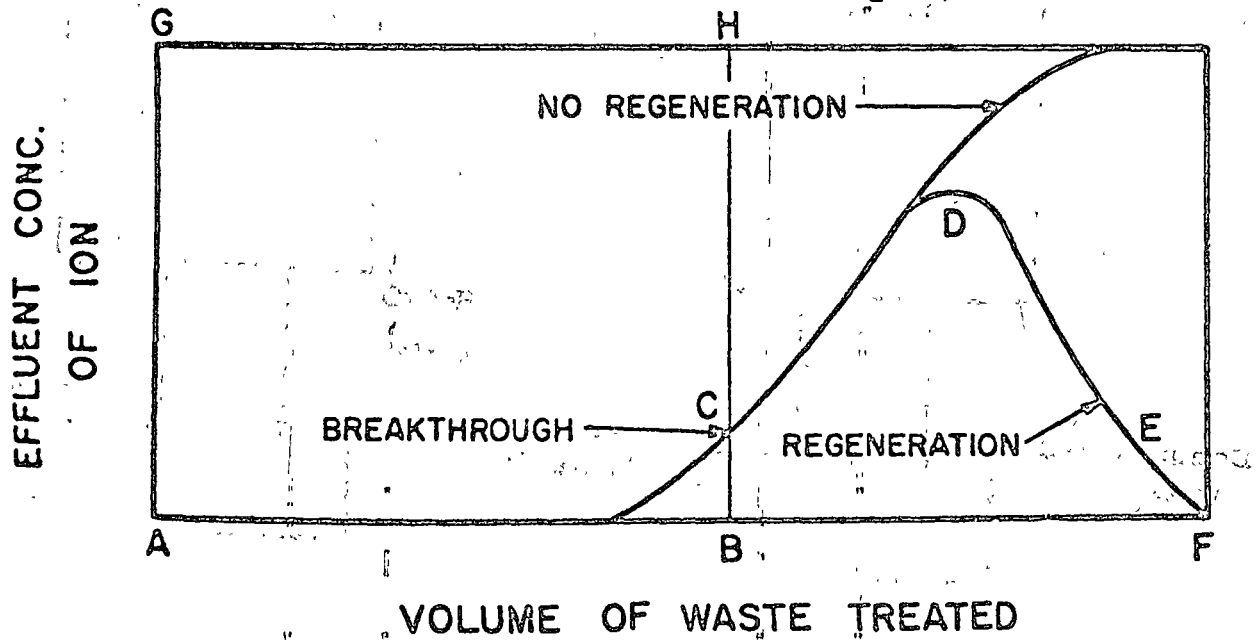


FIGURE 2

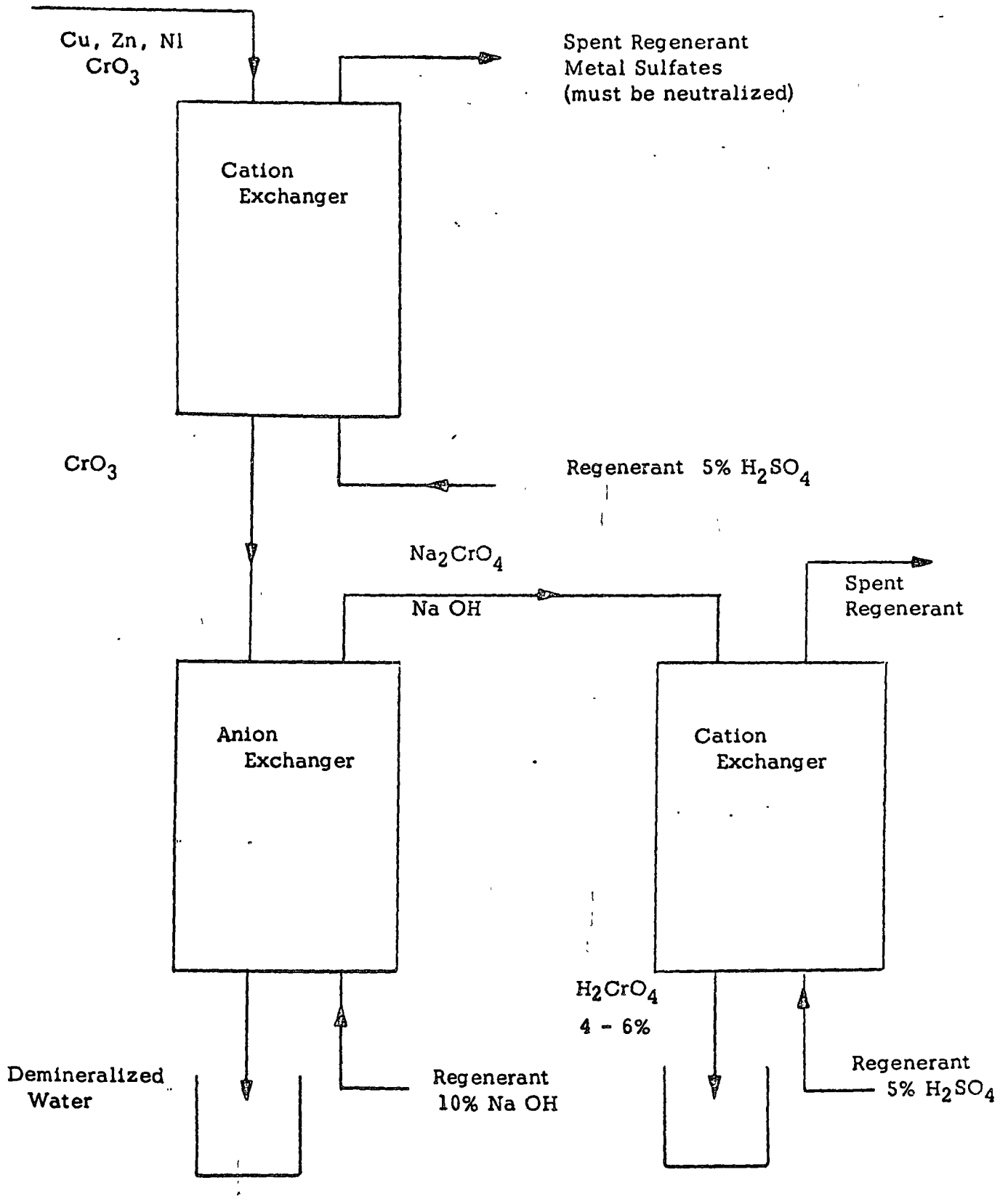


Figure 3 Schematic of ion exchange for chromate and water recovery.

NOTES ON EQUALIZATION*

The diurnal variability of flow entering wastewater treatment facilities has important ramifications in the design and operation of both conventional and advanced waste treatment plants. Conventional treatment plants are necessarily designed hydraulically to handle peak flows. Savings in capital investment would be realized if one could plan for peak daily rather than peak hourly flow. This point is especially significant in the case of either small or combined systems.

The operation of existing plants is affected by variable flow. Plants capable of handling daily average flow may be overloaded with respect to hourly flows. Plants are typically designed on the basis of this daily average, and as such do not meet the demands of the incoming waste. Temporary overloading has a deleterious impact on treatment efficiency and hence on receiving waters. For instance, the efficiency of a biological unit in secondary plants can be severely impaired by shock hydraulic loads. This is well established in a number of existing plants where by-passes are incorporated around the biological units.

Many advanced waste treatment schemes are adversely affected by the flow variation. For example, the solids-contact process utilized for chemical precipitation of solids and phosphorus removal, is extremely sensitive to a variable flow. A constant feed of chemicals would improve the efficiency of precipitation and coagulation processes. Carbon adsorption is more effective if hydraulic loadings are more uniform. With diurnal flow variation, design and operation are rendered more costly, and some advanced treatment methods become infeasible.

The central assumption underlying this session is that a potential solution to these problems is equalization of wastewater flows and/or concentration. Flow or concentration is said to be equalized if it is more or less constant with time. Thus, in its simplest form, equalization is often conceived to be attainable by use of a properly designed holding tank, from which wastewater is pumped to the treatment facilities at a constant rate. The actual situation is complicated by the variation in flow from day-to-day. This operational problem may be overcome by appropriate flow adjustment. A predictive model for flow forecasting provides the best basis for adjustment. Failsafe design of the facility is also advisable (i.e. provision for low level and high level conditions).

Waste Generation Survey

1. Most important aspect of entire plant design

*By Michael J. Humenick, Jr.

2. Requirements
   a) Flow and concentration as a function of time
   b) Length of record should be statistically adequate

3. Data analysis
   a) Statistical analysis. Plot a percent of time less than.
   b) Periodicity of flow and concentration. In phase, out of phase, or random fluctuations.

4. Design Decision
   a) Flow equalization?
   b) Concentration equalization?
   c) Flow and concentration equalization?

Design Methods

A. Flow equalization

1. Example: Small industrial waste problem
   a) Waste generation - Figure
   b) Mass Diagram - Figure
   c) Physical Design - Figure

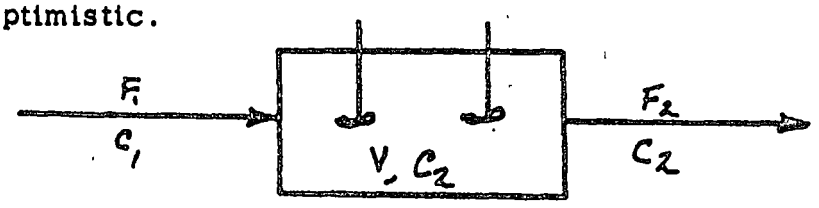
Example calculation for volume:

From the Mass Diagram, minimum volume required below and above mid-day level is 13,000 and 11,000 gallons, respectively. Choose a rectangular shape 15x15 feet = 225 sq ft. Working depth = 24,000 gal/ 225 sq ft x 7.48 = 14 ft. Add 2 feet for minimum level and 2 feet for the distance from maximum level to the safety overflow. Total depth = 18 feet.

2. Example: Combined equalization and tertiary treatment of municipal wastewater.
   a) Use variable level equalization basin
   b) Develop activated sludge with floating aerators.
   c) Provide supplemental mixing to avoid solids deposition.
   d) Basin is sized by Mass Diagram method as above.

Concentration Equalization, Flow relatively Constant.

A. Process to be modeled: Completely mixed tank. Deviation from complete mixing yields poorer equalization. Thus, calculations based upon complete mixing are optimistic.



B. Applicable Mass Balance:

Assumptions: Flows in and out are equal and constant ($F_1 = F_2$), volume, V, is constant, concentration of component C is conservative and addative, and that the equalization basin is completely mixed.

Mass balance equation:

rate of accumulation = rate in - rate out

$$V \frac{dC_2}{dt} = F_1 C_1 - F_2 C_2 \qquad (1)$$

or

$$\tau \frac{dC_2}{dt} = C_1 - C_2, \text{ where } \tau = \frac{V}{F} = \text{const.} \qquad (1a)$$

To solve Equation 1, various methods may be used depending on the accuracy needed, the type of expression describing C_1, and the availability of computer use. Several methods follow.

1. Analytical Expression for C_1. Periodic, repeating functions such as sine or sawtooth functions may be represented by mathematical expressions and allow exact solution of Equation 1. It is instructive to examine a simple case.

Let $C_1 = \bar{C}_1 + k\bar{C}_1 \sin wt$ which is an expression for C_1 where $\bar{C}_1$ is the mean value of C_1 and C_2, $k\bar{C}_1$ being the minimum and maximum deviation from $\bar{C}_1$, $w = 2\pi/T$ where T = period for one cycle of the sine function, and t = time.

Solution of the differential equation with boundary conditions $C_2 = \bar{C}$ at t = 0 which then yields:

$$\frac{C_2}{\bar{C}_1} = 1 + \frac{k\tau w}{(1+\tau^2 w^2)} e^{-t/\tau} + \frac{k \sin (wt-y)}{(1+\tau^2 w^2)^{1/2}} \qquad (2)$$

where

$$y = \tan^{-1} w\tau$$

After the transient portion of Equation 2 has died out (t becomes large), a regular output continues with C_2 lagging behind C_1 and having amplitude $k\bar{C}_1/(1+\tau^2 w^2)^{1/2}$ thus,

$$C_2 = \bar{C}_1 + \frac{k\,\bar{C}_1 \sin(wt-y)}{(1+\tau^2 w^2)^{1/2}} \qquad (3)$$

and

$$C_{2,\max} = \bar{C}_1 \left[1 \pm k/(1+\tau^2 w^2)^{1/2}\right] \qquad (4)$$

Attached figures show the results of the above relationships for various values of τ, k, and T.

2. Finite Difference Solutions Suitable for Desk Calculation.

If rather wide increments of time (say 10 minutes) are considered as having the influent concentration remaining constant at some average value, the solution of Reynolds, et al.(1) may be used. The equation to be solved is:

$$C_{2_{t+\Delta t}} = C_{1_t} \cdot \left[1 - e^{-t/\tau}\right] + C_{2_t} \cdot e^{-t/\tau} \qquad (5)$$

where:

$C_{2_{t+\Delta t}}$ = basin concentration after addition of the increment of flow at concentration C_{1_t}

C_{1_t} = input concentration averaged over Δt.

The solution simply involves a numberical evaluation of the integrated form of the differential equation, Equation 5, of the differential material balance for the system using actual data. The attached Figure illustrates the results of the above method for selected values of τ.

Another method utilizing statistical analysis of data was developed by Danckwerts and Sellers (2). The method is particularly useful if input concentration, C_1, fluctuates rapidly and randomly. The equation to be determined by graphical integration is:

$$\frac{\sigma_2^2}{\sigma_1^2} = \frac{1}{\tau} \int_0^\infty e^{-r/\tau} \cdot R(r) \cdot dr \qquad (6)$$

where

σ_2^2 = the variance in output concentration

σ_1^2 = the variance in input concentration

R(r) = the autocorrelation coefficient defined as:

$$R(r) = \frac{\overline{(C_1 - \bar{C}_1)_t \cdot (C_1 - \bar{C}_1)_{t+r}}}{\sigma_1^2}$$

where the numerator is the average value taken over all values of t. To calculate R(r) as a function of r, the following method is useful.

a) Tabulate the values of $(C_1 - \bar{C}_1)$ at uniform intervals of time, Δt. Let us call these values δ_1, δ_2, etc., numbered in the order in which they occur.

b) Find the differences, D_1, of $(\delta_1 - \delta_2)$, the difference of D_2 or $(\delta_2 - \delta_3)$, and so on. Square each difference and add giving ΣD^2.

c) Find the sum, S_1, of $(\delta_1 + \delta_2)$; the sum, S_2, of $(\delta_2 + \delta_3)$, etc. Square each sum and add the squares, giving ΣS^2.

d) Then,

$$R(r) \doteq \frac{\Sigma S^2 - \Sigma D^2}{\Sigma S^2 + \Sigma D^2} \qquad (7)$$

r being equal, in this case to Δt.

e) Find the sums $(\delta_1 + \delta_3)$; $(\delta_2 + \delta_4)$, etc., and the differences $(\delta_1 - \delta_3)$, $(\delta_2 - \delta_4)$, etc. Repeat the above process for $r = 2\Delta t$.

f) Repeat for other values of r.

When R(r) has been found for a sufficient range of r, Equation 6 can be integrated graphically or otherwise to give the ratio of the standard deviations for any assigned value of τ. The range of r must be such that $R(r) \cdot e^{-t/\tau}$ becomes much less than unity for the largest value of r. Use of the method has been illustrated by Wallace (3), and the results of one such calculation are attached.

3. Computer Calculations. Actual past data may be used to evaluate the effectiveness of various detention periods. Equation 1 is converted to finite differences:

$$\Delta C_{2_{t+\Delta t}} = \frac{1}{\tau} [C_{1_t} - C_{2_t}] \Delta t \qquad (8)$$

The computer is programmed to calculate C_2 for a given time increment, Δt. Past records are used as input for C_1. Concentration, C_2, at other times are simply calculated by:

$$C_{2_{t+\Delta t}} = C_{2_t} + \Delta C_{2_t} \qquad (9)$$

where ΔC_2 is obtained from the solution of Equation 8. Iteration is performed by the computer and the output concentration is calculated as a function of time for any input and detention period, τ.

It should be emphasized that simple solution of Equation 8 can be improved (error in the estimate of ΔC_2) by several computer subroutines such as the Runga - Kutta method or Euler's formulas.

Equalization of Flow and Concentration

If both flow and concentrations are to be equalized, the practical solution becomes rather involved because of the complexities of calculation. However, with the use of modern electronic computers, the problem is greatly simplified. Because level continues to vary within the equalization basin, volume changes as a function of changing influent rates. Thus the mass balance on the conservative material requires that this factor be accounted for.

In the real case, influent will not usually follow a regular, analytical expression, and exact solutions to the output concentration as a function of time would rarely be found. An answer to the problem is possible through the use of many, finite difference calculations of the mass balance equations. An outline follows.

1. From the record of past waste characteristics, size the equalization basin based upon the Mass Diagram method discussed previously. Several other basin volumes may be evaluated if outlet concentrations are calculated to be unacceptable.

2. Three equations are now used to calculate the outlet concentration C_2. They are:

$$V_{t+\Delta t} = V_t + [F_{1_t} - F_{1_{t+\Delta t}}] \cdot \Delta t \qquad (10)$$

$$\Delta C_{2_{t+\Delta t}} = \left[\frac{(F_1 C_1)_t}{V_t} - \frac{(F_2 C_2)_t}{V_t} \right] \cdot \Delta t \qquad (11)$$

and

$$C_{2_{t+\Delta t}} = C_{2_t} + \Delta C_{2_{t+\Delta t}} \qquad (12)$$

Iterative calculations are performed on Equation 11 with new values of V determined from Equation 10 for each iteration. Again, better estimates of ΔC_2 are obtained with the use of subroutines designed to minimize the calculation error in $C_{2_{t+\Delta t}}$.

Large Scale Plant Results of Equalization

The attached Figures show the results of a study (one of the very few) by LaGrega and Keenan (4).

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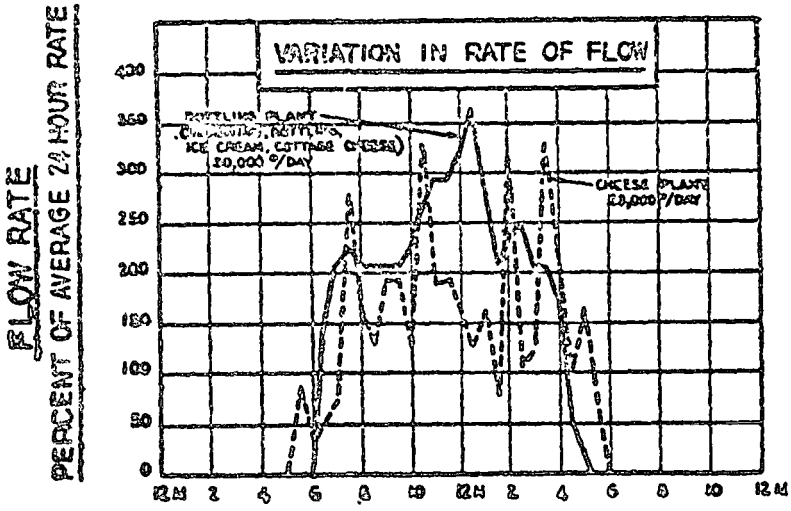
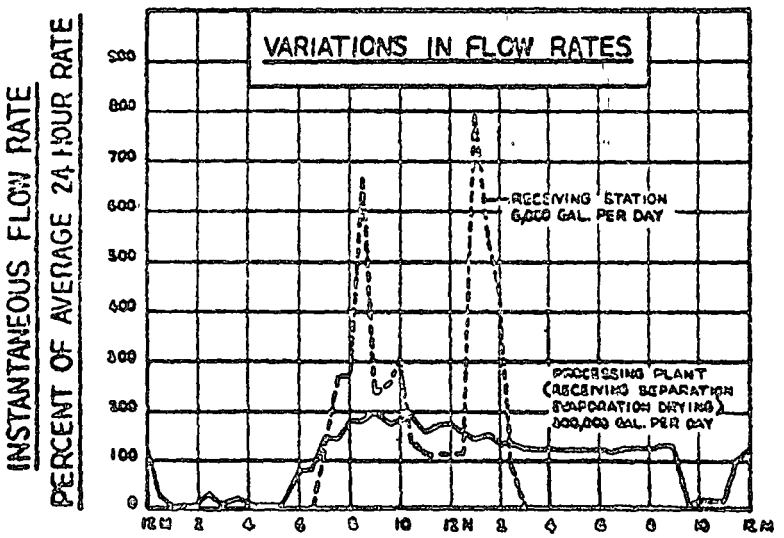
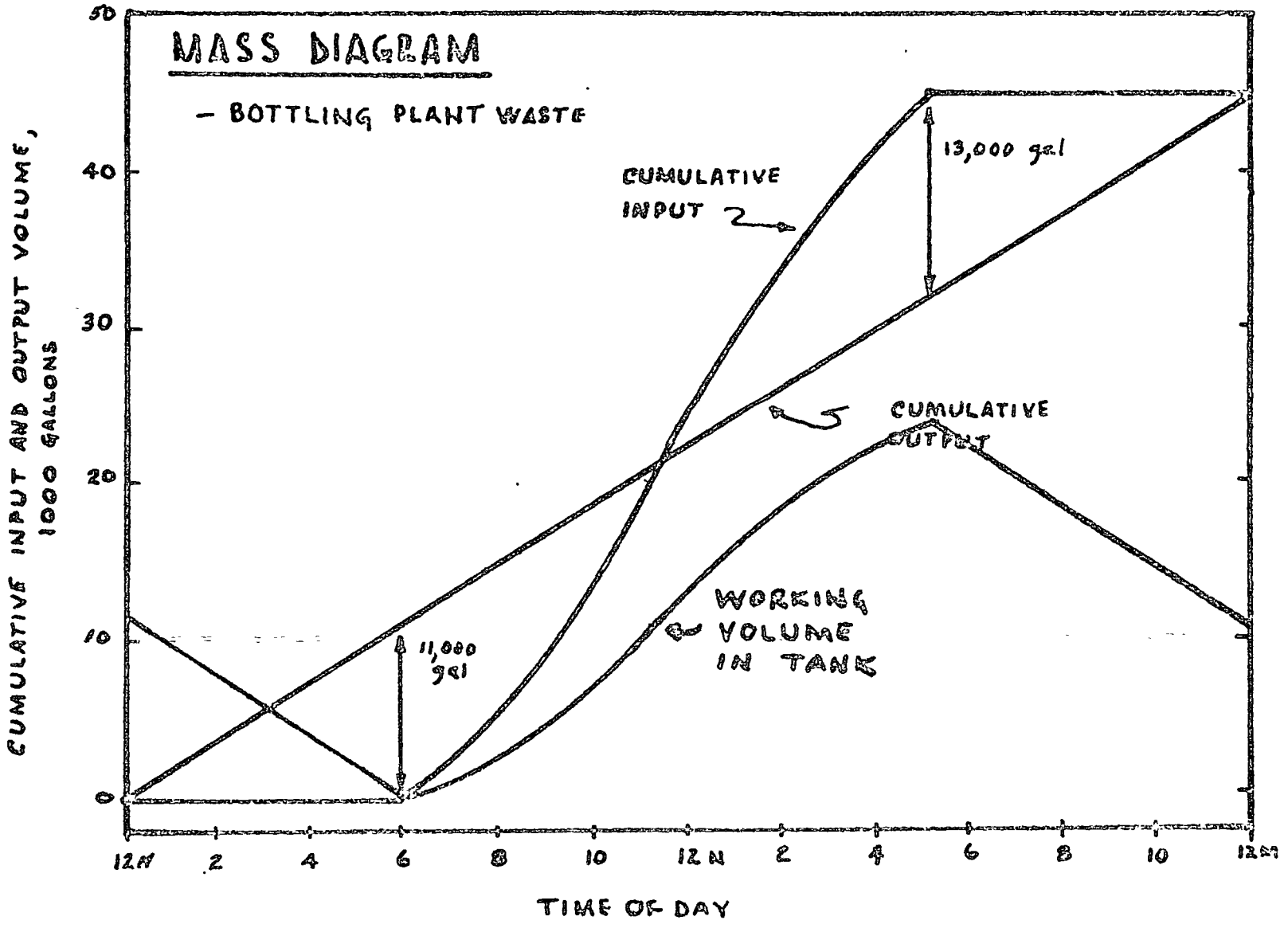


Variations in rate of milk waste discharge, bottling and cheese plants.



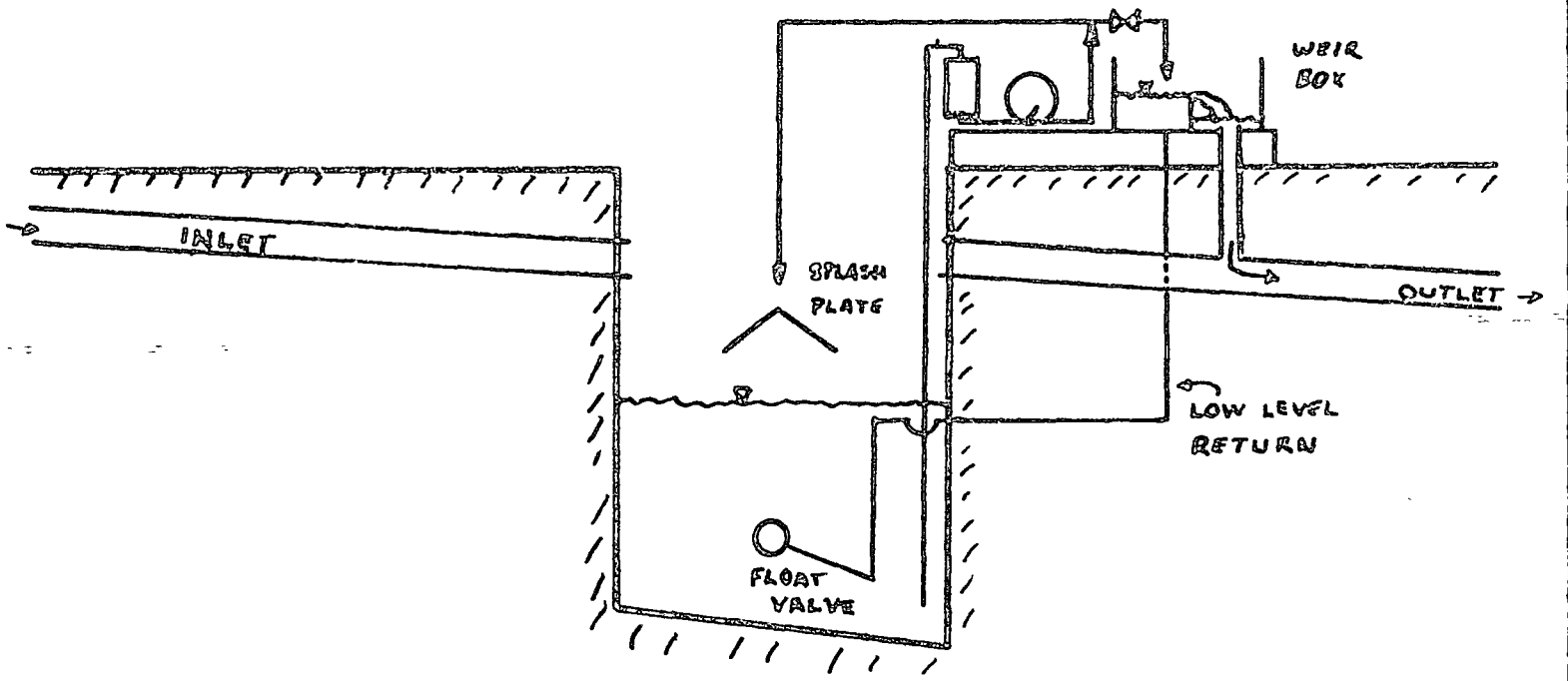
Variations in rate of milk waste discharge, processing plant and receiving station.

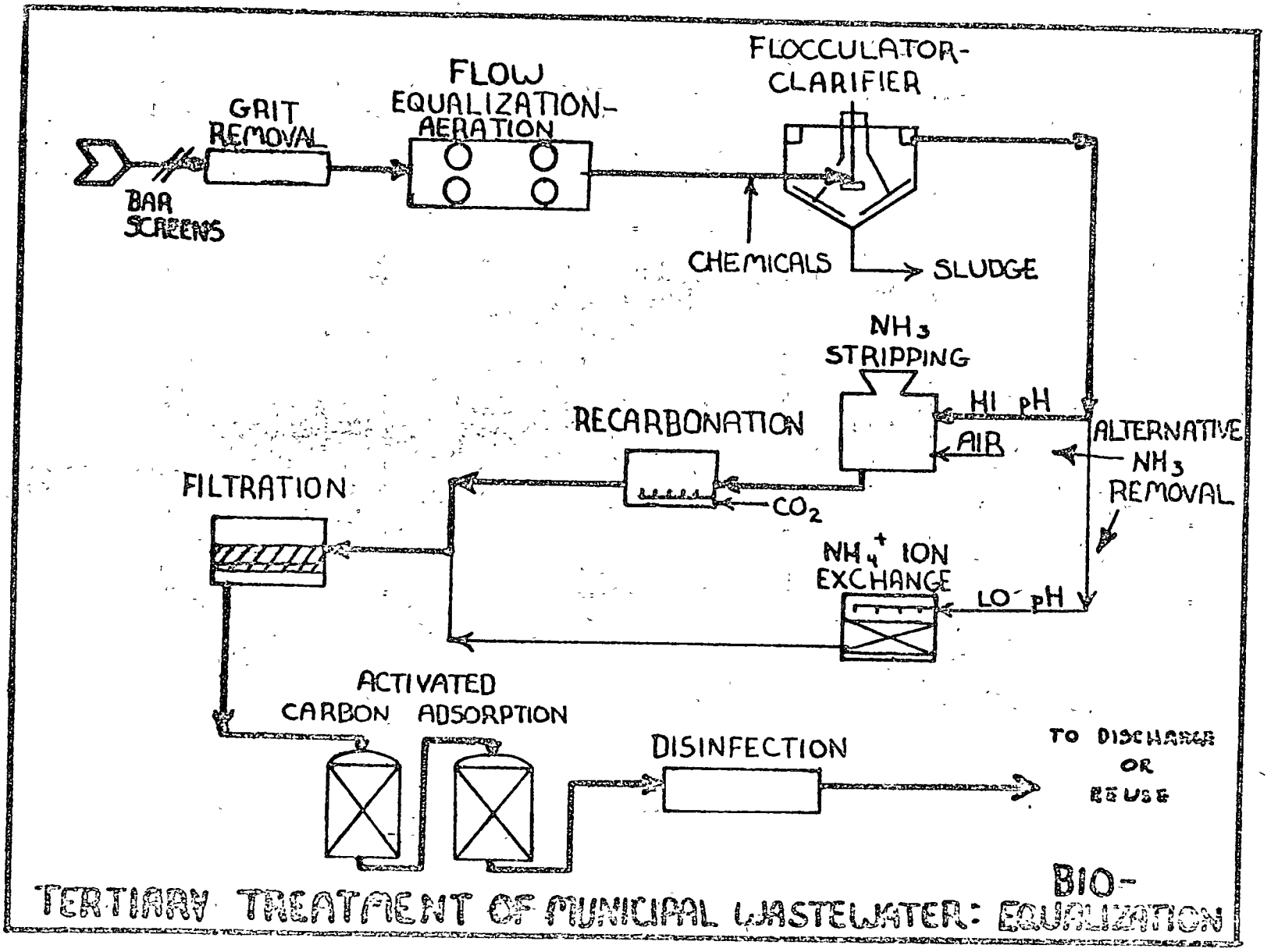


CALCULATION OF FLOW EQUALIZATION VOLUME

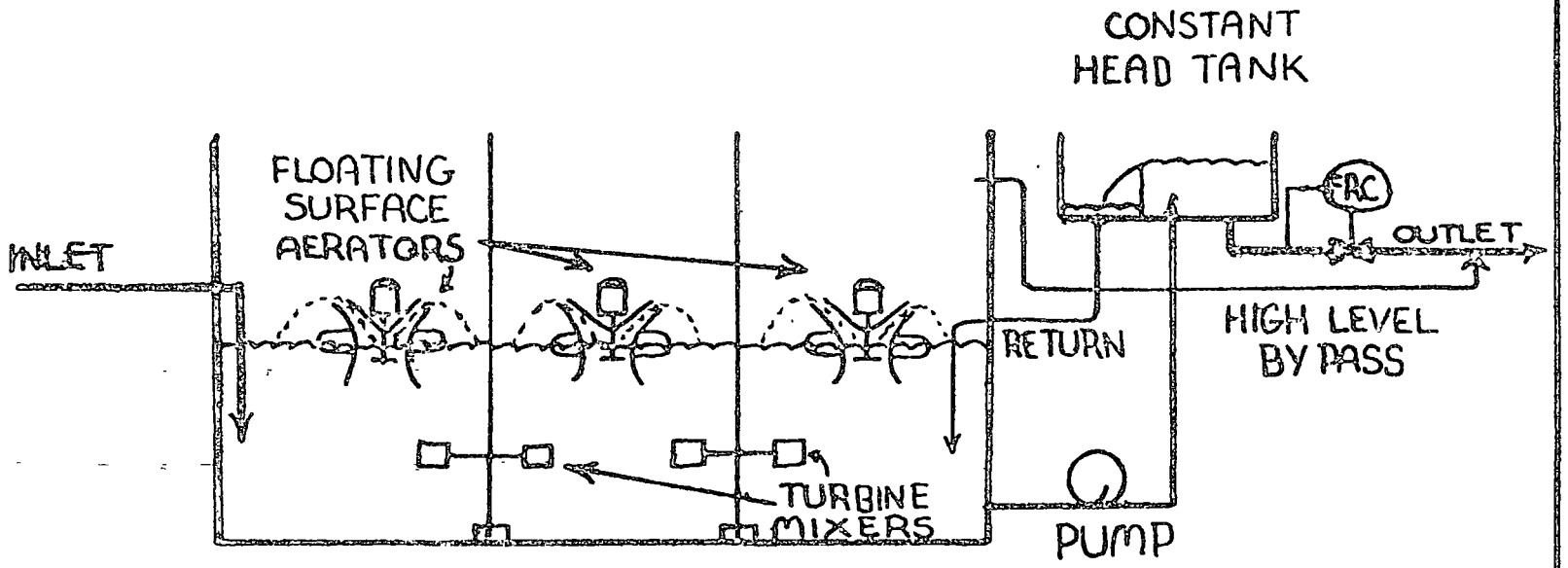
FLOW EQUALIZATION -

SMALL INDUSTRIAL WASTE OPERATION

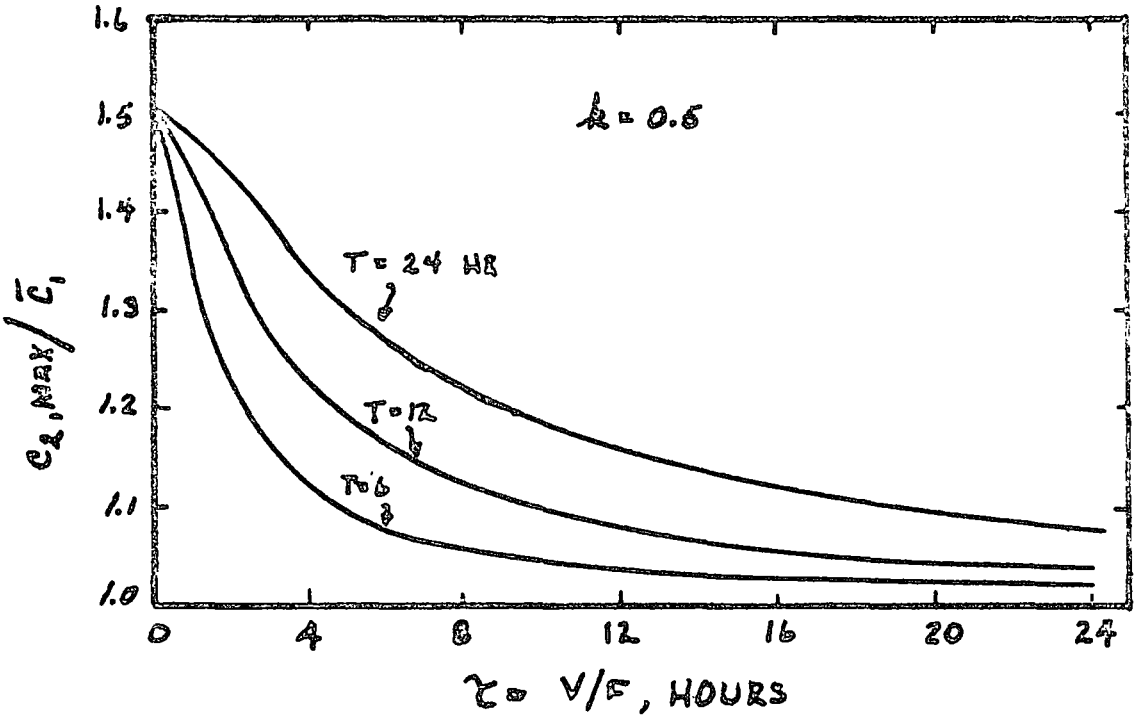


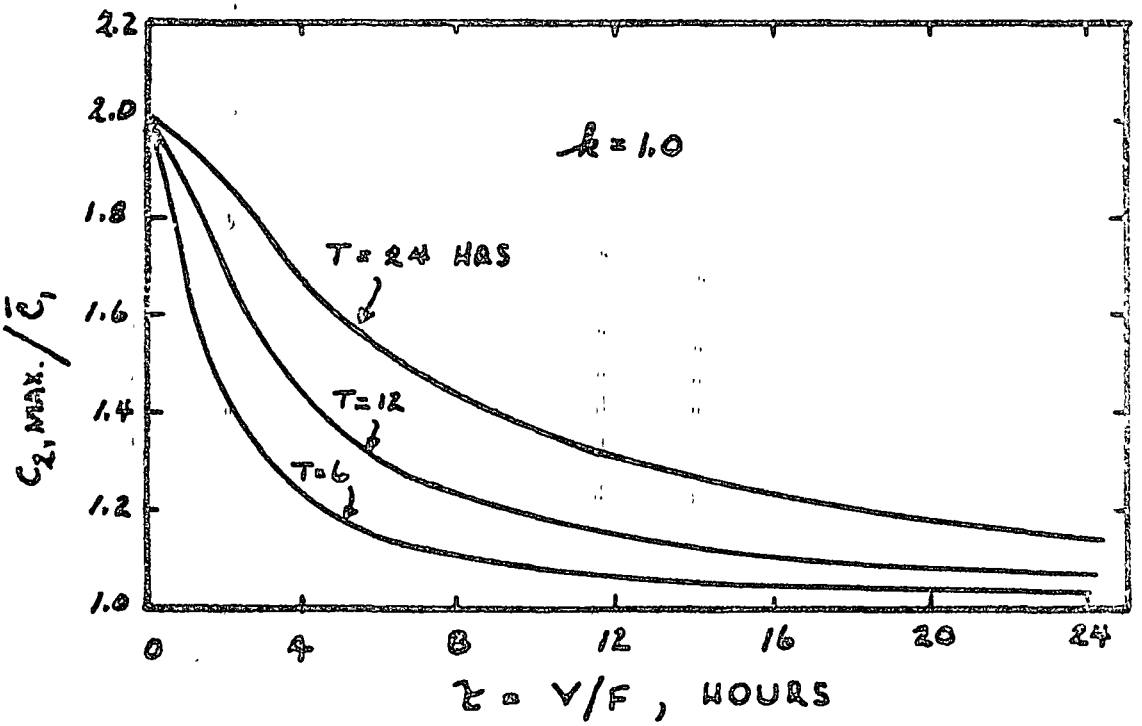


TERTIARY TREATMENT OF MUNICIPAL WASTEWATER:



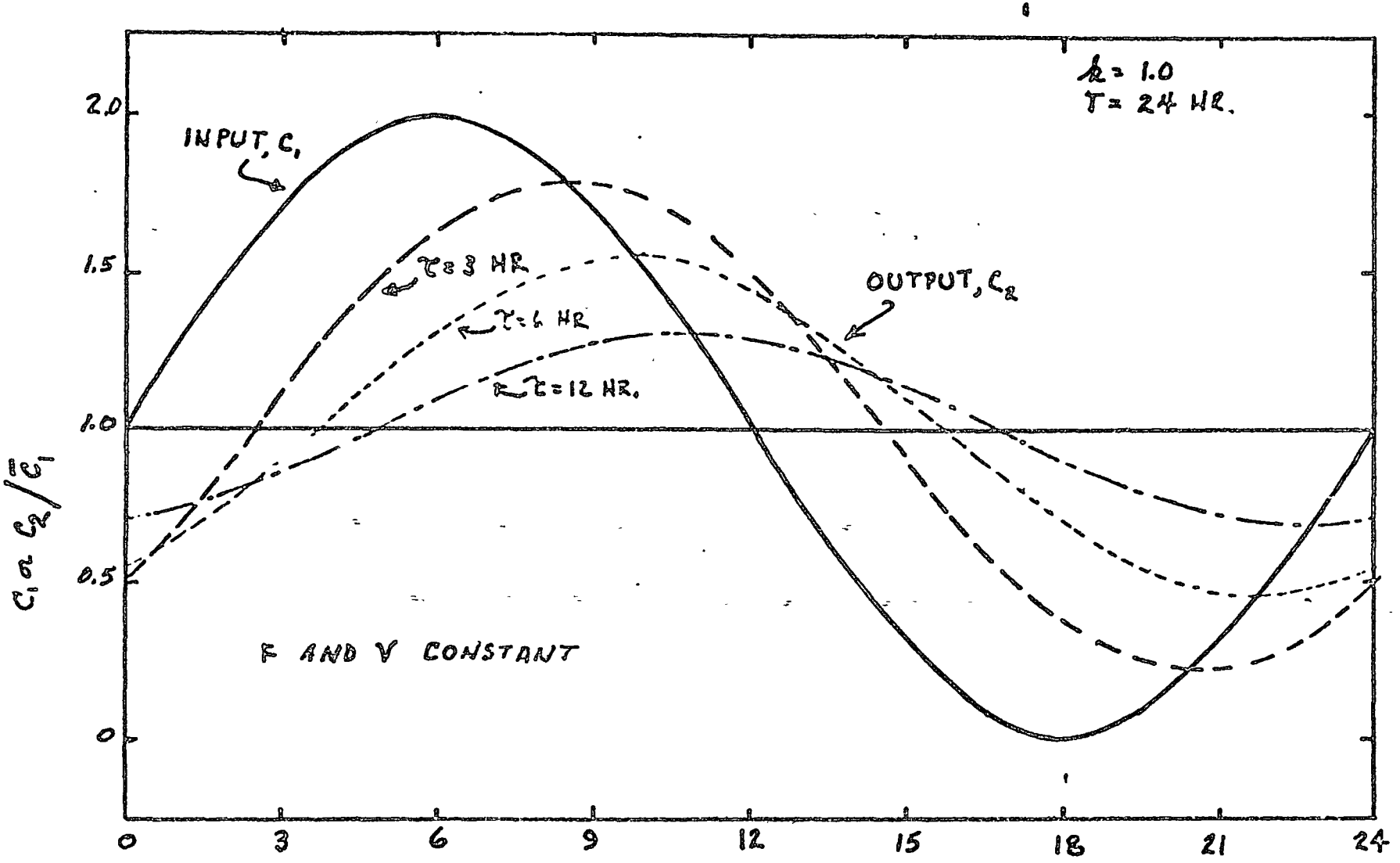
FLOW EQUALIZATION - AERATION BASIN





EQUALIZATION BASIN RESPONSE TO SINUSOIDAL INPUTS -

MAXIMUM DEVIATIONS FROM AVERAGE CONCENTRATIONS



BASIN RESPONSE TO SINUSOIDAL INPUT CONCENTRATION, 24 HR PERIOD

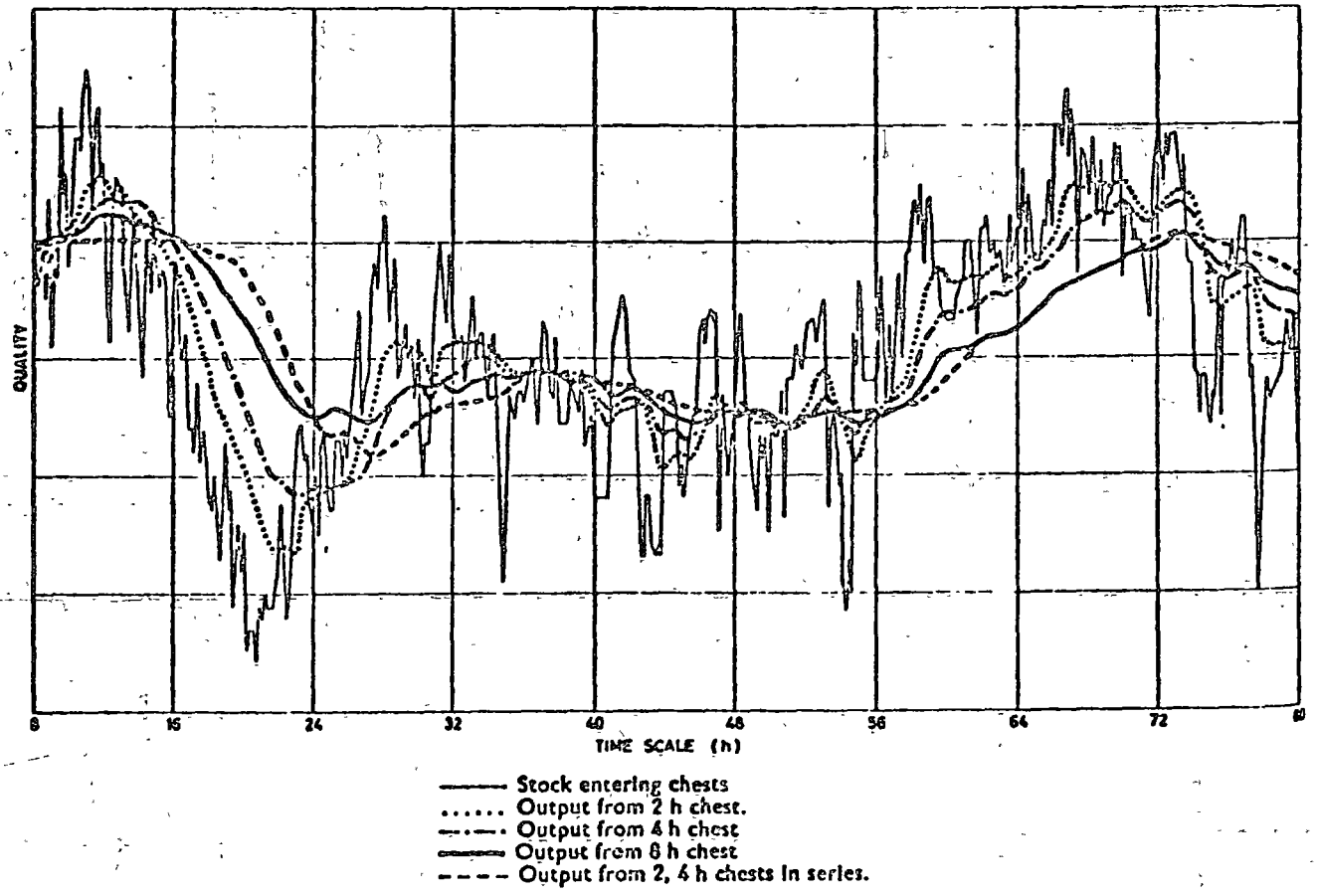


Fig. 2.—*Results of computations of two, four, and eight-hour chests*

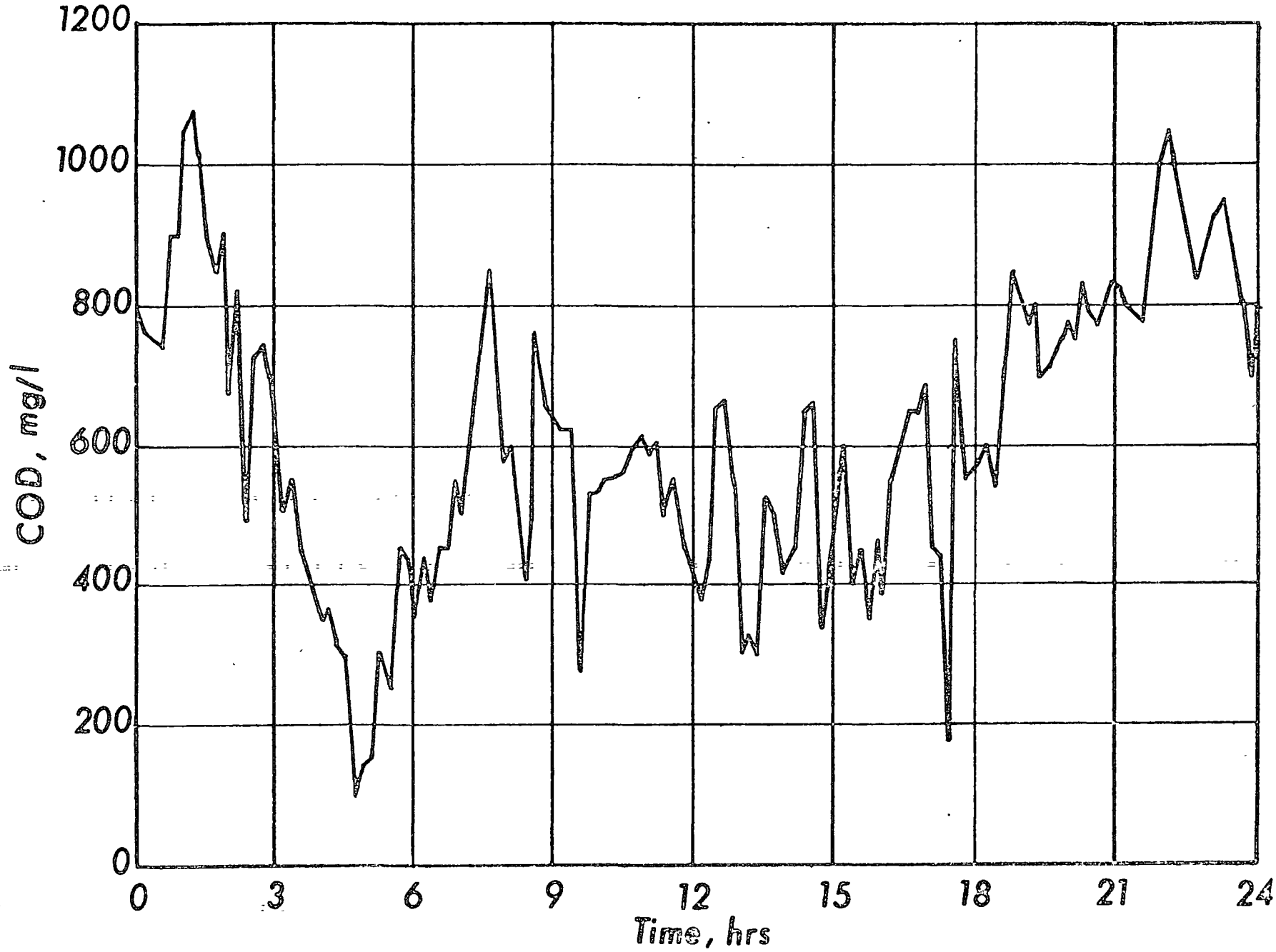


Figure 2 - Typical ne-Concentration Curve

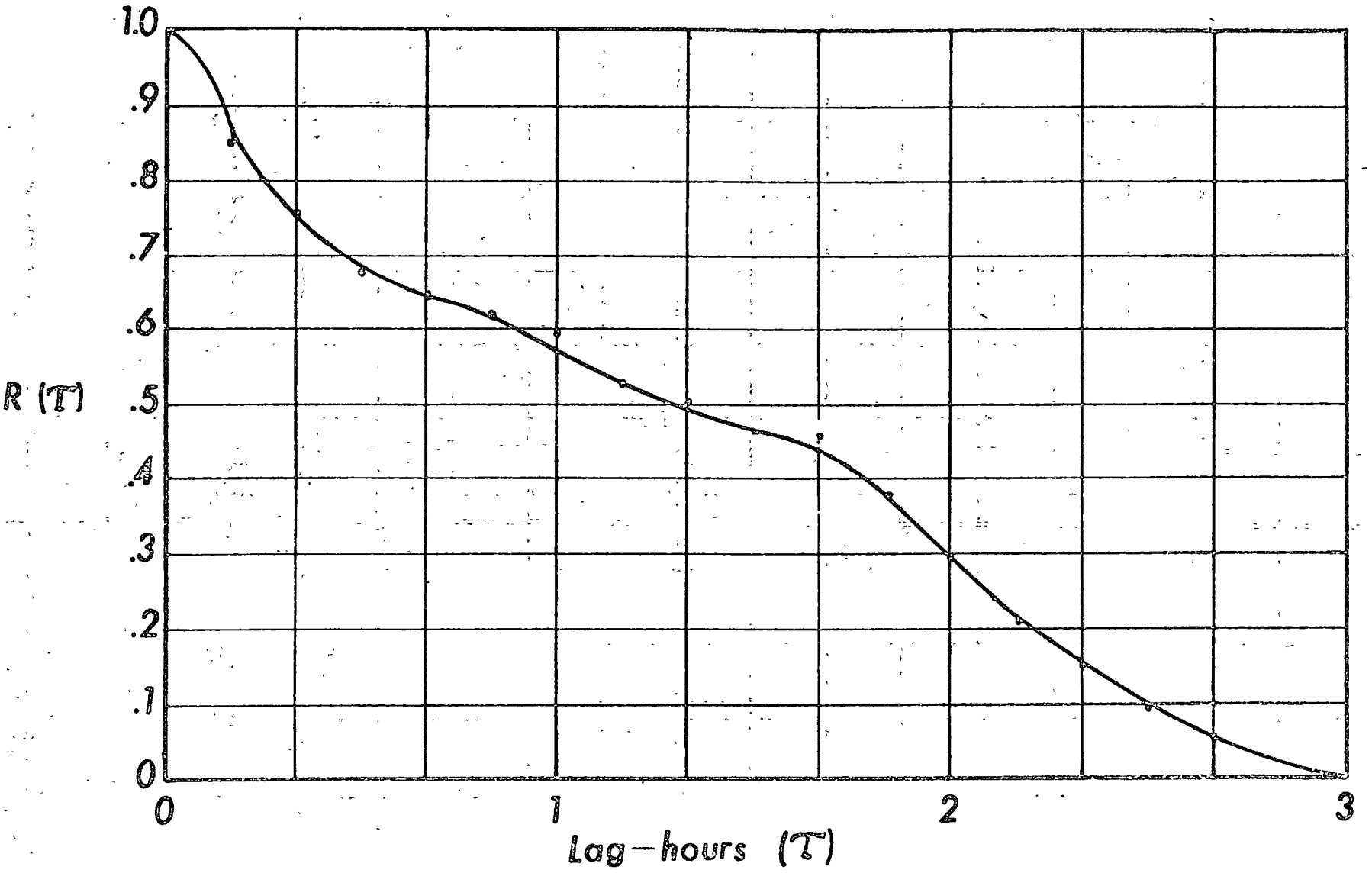


Figure 3 —Auto-covariance function for input COD data

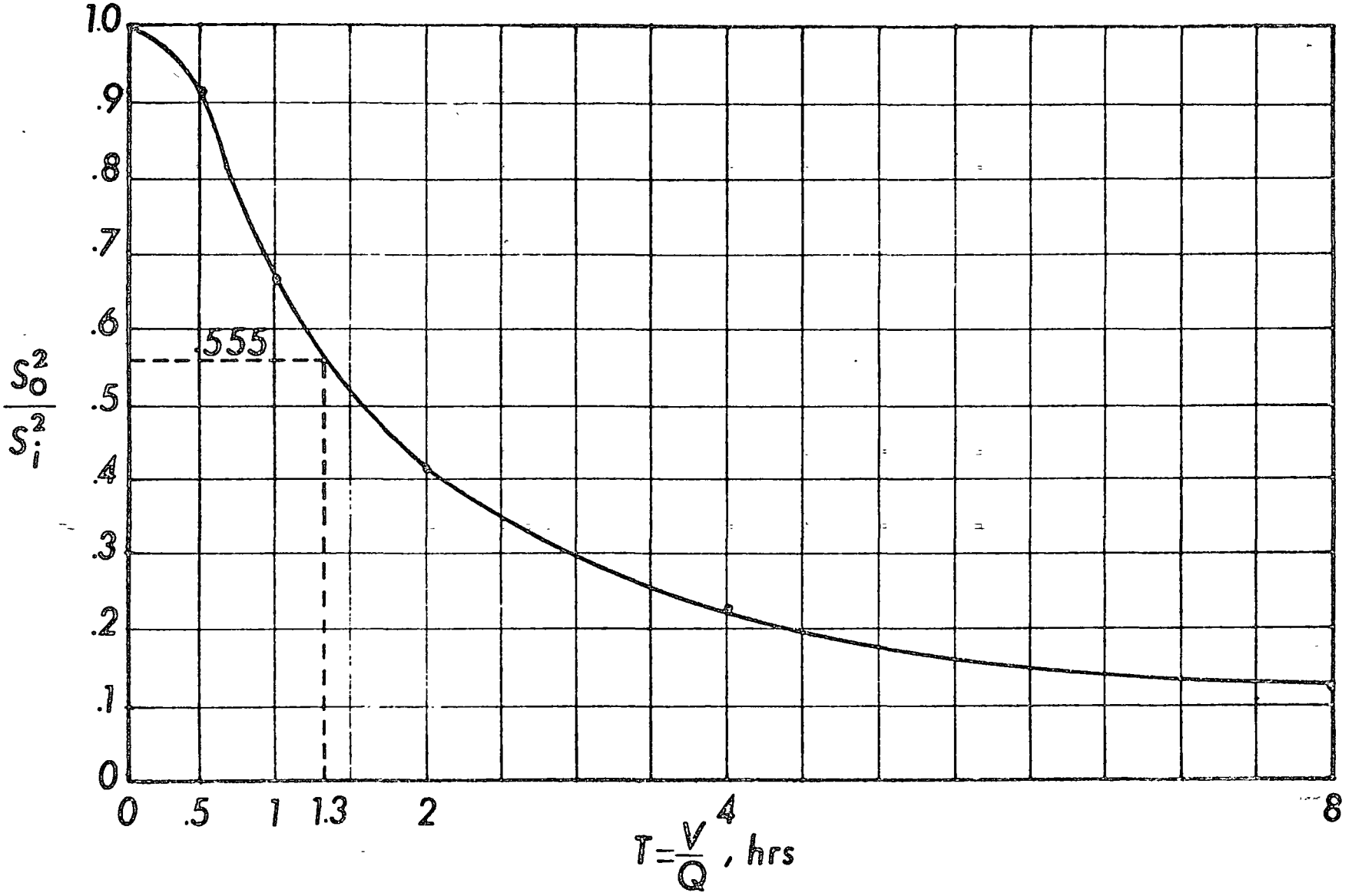


Figure 4 - Ratio of variances as a function of residence time

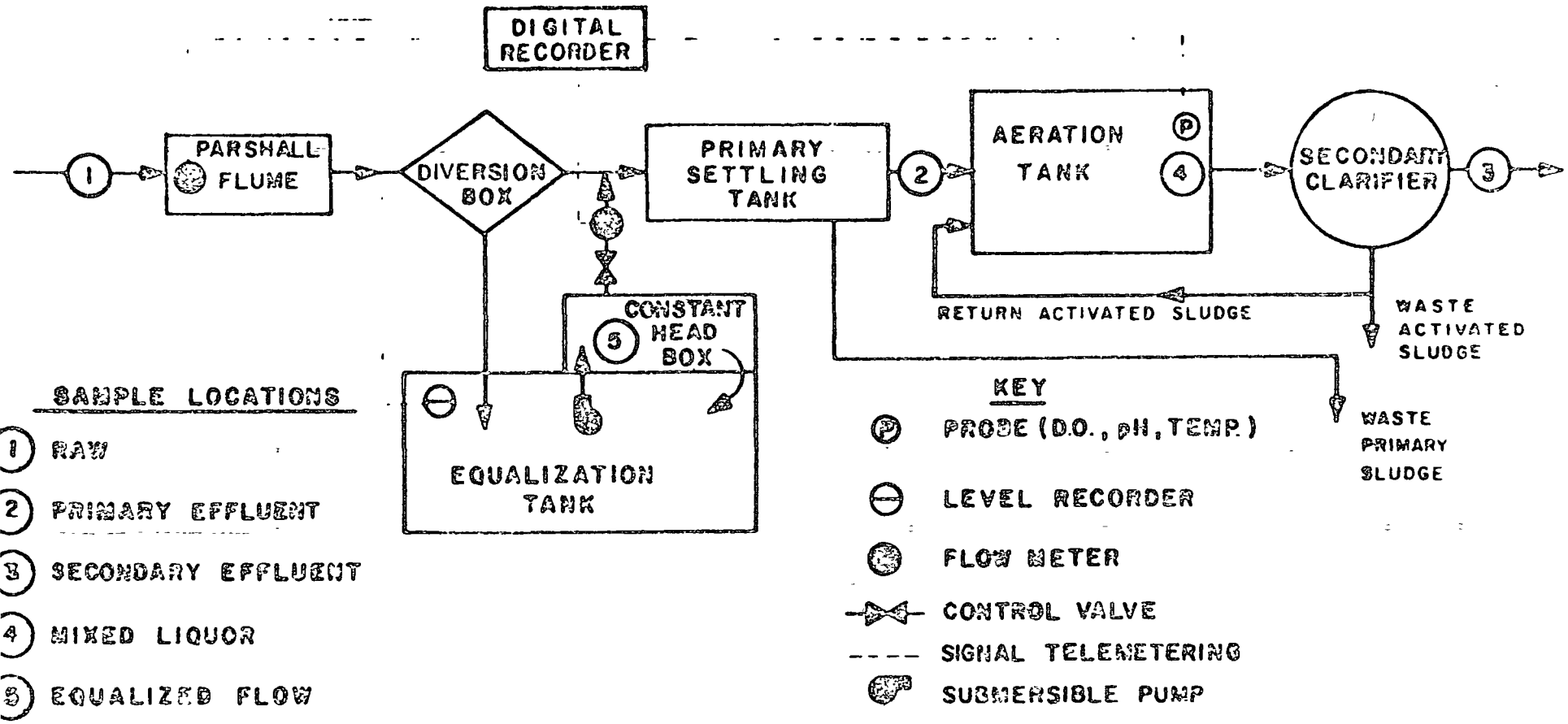


FIGURE 1 SCHEMATIC DIAGRAM OF FACILITIES

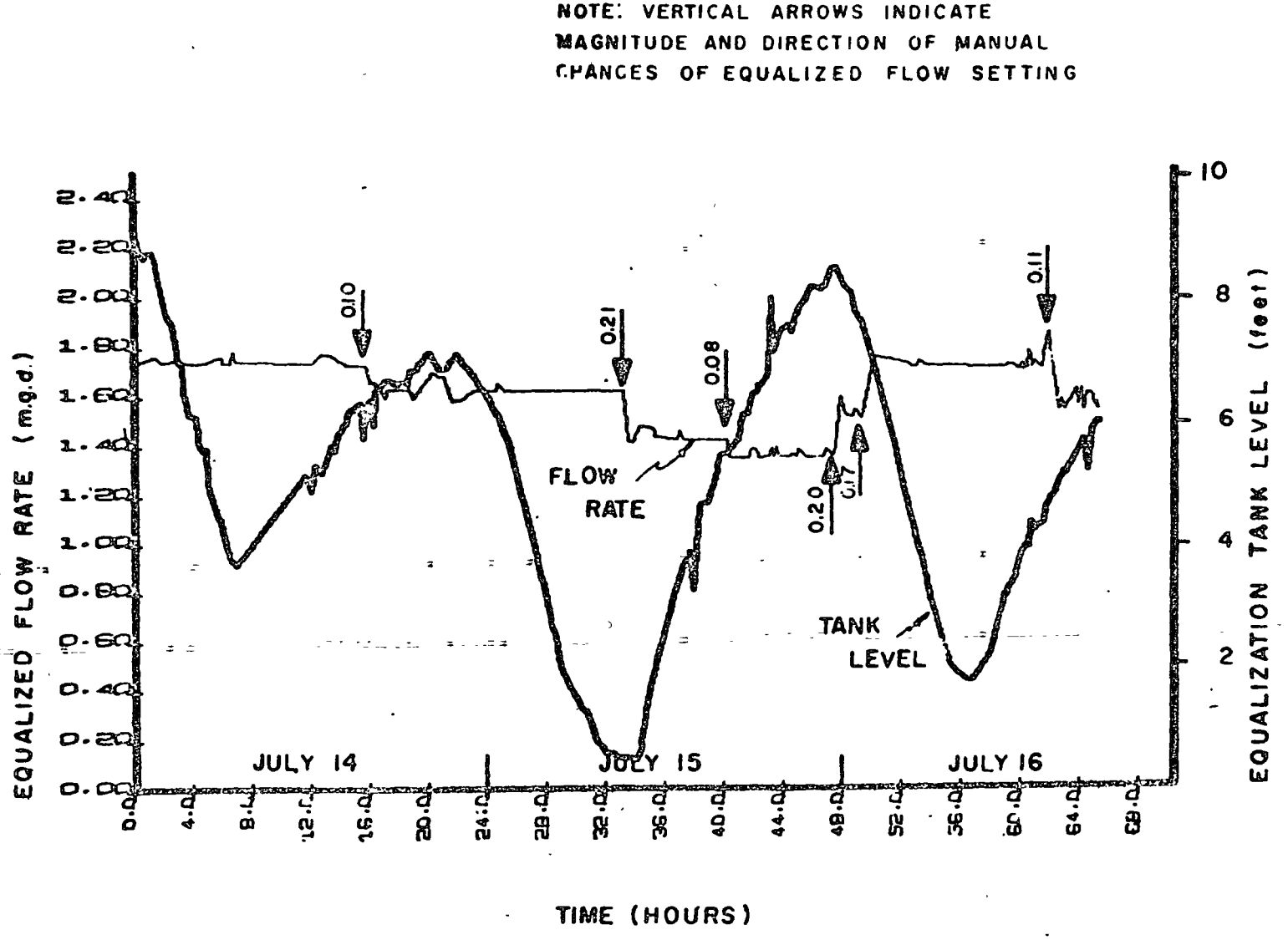
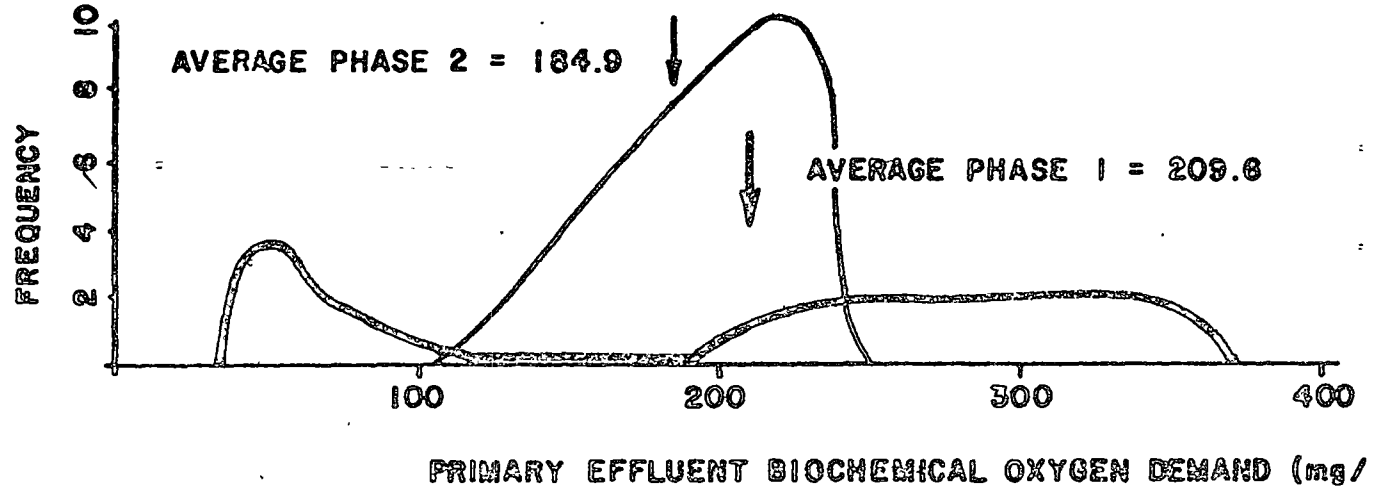


FIGURE 2 EQUALIZED FLOW AND TANK LEVEL



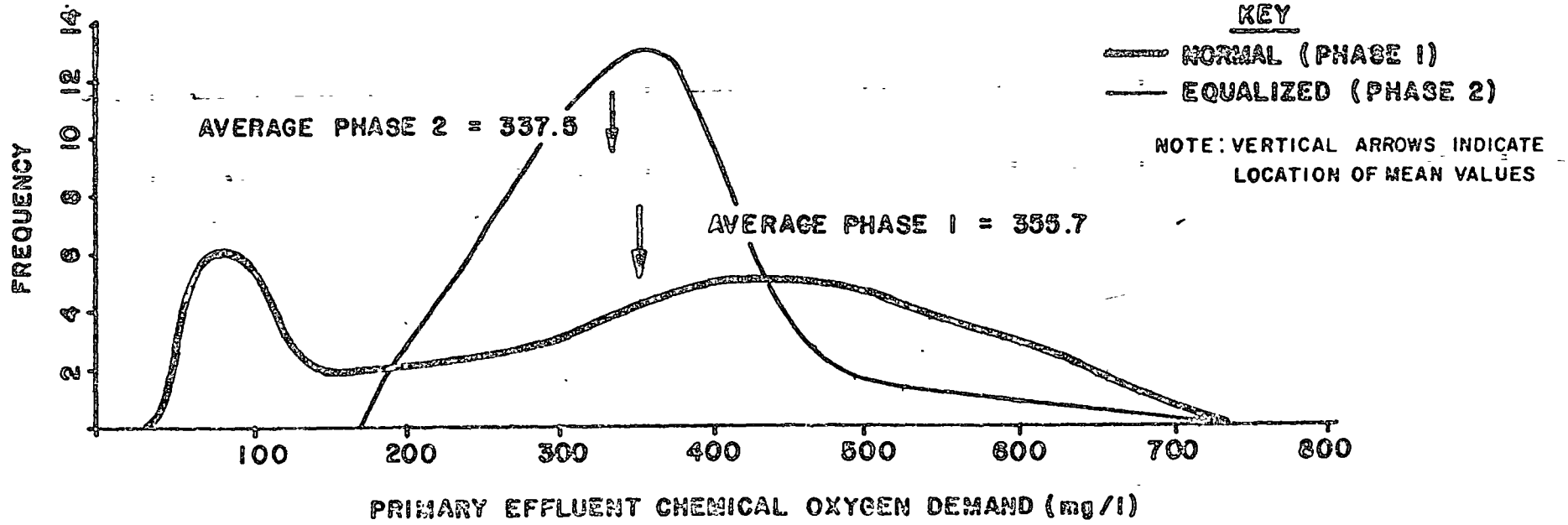


FIGURE 5 EFFECT OF EQUALIZATION ON PRIMARY EFFLUENT
DATA FROM DIURNAL SAMPLING SERIES

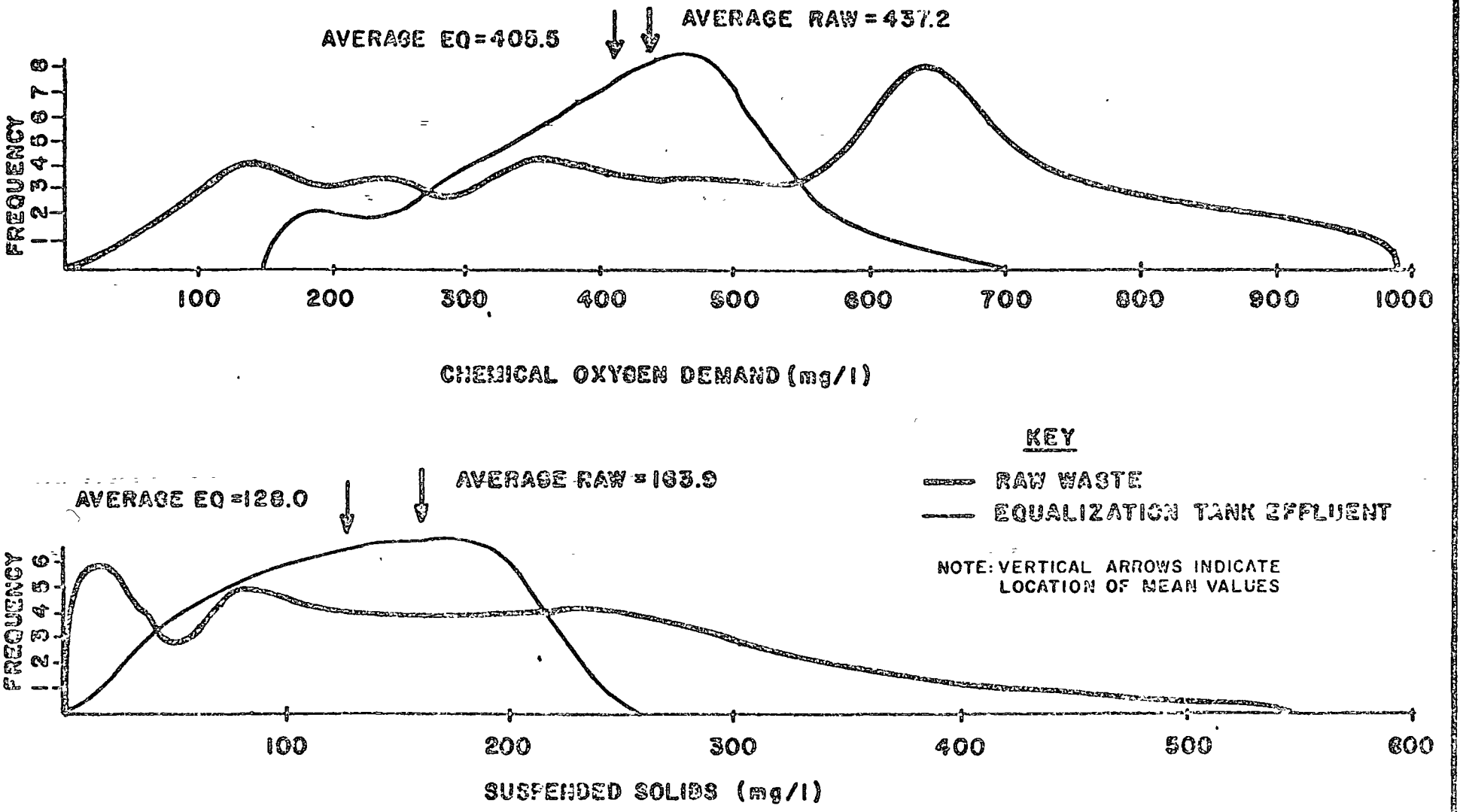
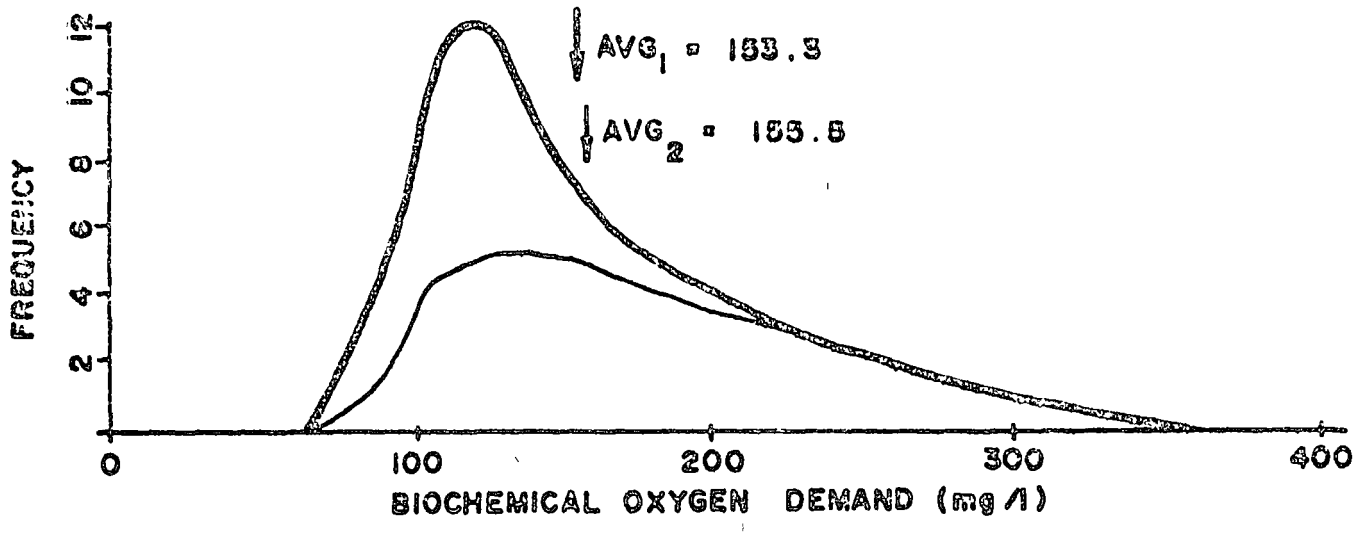
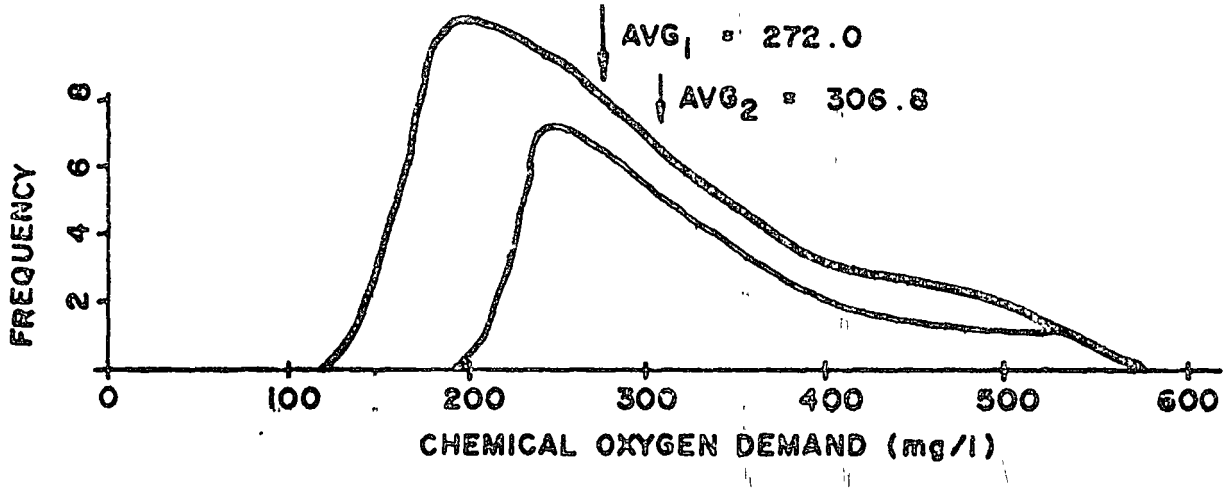


FIGURE-4-FREQUENCY HISTOGRAMS - DIURNAL SAMPLES





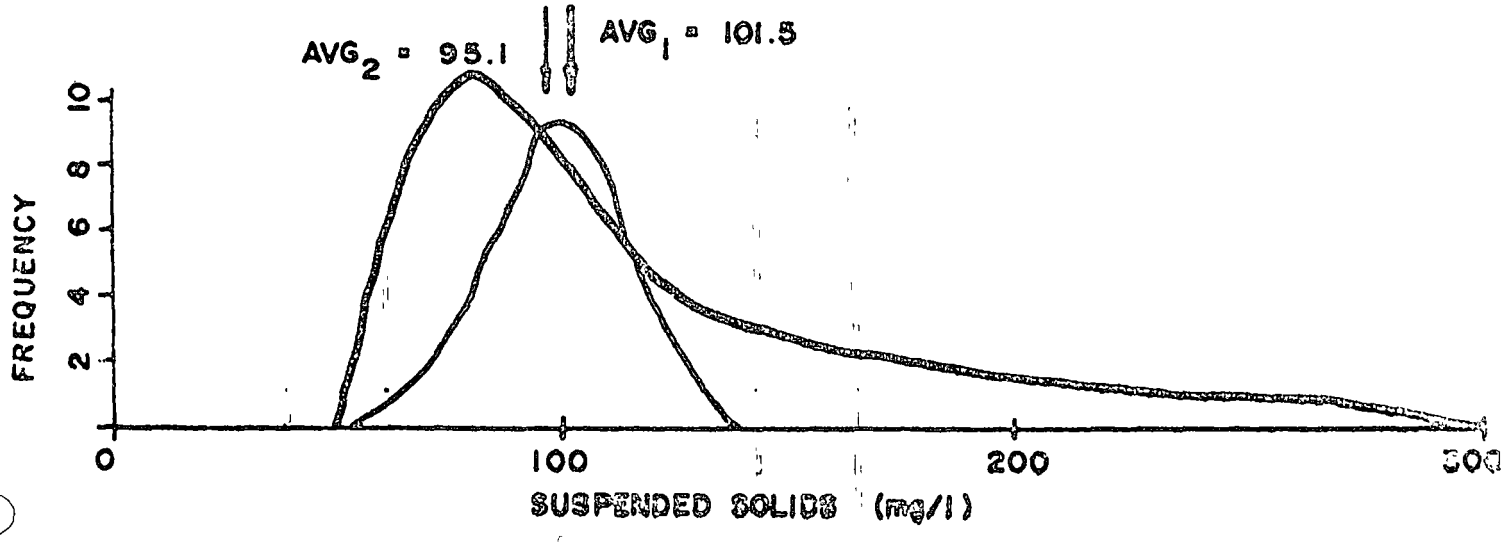


FIGURE 6-EFFECT OF EQUALIZATION ON PRIMARY EFFLUENT DATA FROM DAILY SAMPLING SERIES

TABLE 5

COMPARISON OF MEAN VALUES OF PRIMARY EFFLUENT

PHASE 1 VERSUS PHASE 2

VARIABLE	PHASE 1		PHASE 2				95% CONFIDENCE INTERVAL		
	Mean	Std.Dev.	Mean	Std.Dev.	t	ν	Lower	$(\mu_1-\mu_2)$	Upper
Biochemical Oxygen Demand*	209.6	113.2	184.9	32.5	1.00	34	-23.6		73.1
Biochemical Oxygen Demand (f)*	105.0	64.6	93.1	15.4	0.71	26	-20.7		44.5
Chemical Oxygen Demand	355.7	179.7	337.5	90.3	0.54	71	-47.3		83.7
Chemical Oxygen Demand (f)	226.9	111.2	214.7	41.2	0.52	71	-28.5		48.9
Total Organic Carbon	120.5	59.5	97.3	16.7	2.25	71	3.0		43.4
Total Organic Carbon (f)	82.8	38.2	66.4	12.4	2.45	71	3.3		29.5
Suspended Solids	105.4	58.8	68.0	12.3	3.63	69	17.2		57.6
Volatile Suspended Solids	92.6	49.2	60.5	12.8	3.69	69	15.0		49.2

Data from diurnal sampling program. values weighted with flow.

* Regressed values omitted.

t - Student's t - statistic
ν - Degrees of freedom
f - Analyses performed on filtered aliquots

TABLE 6

EFFECT ON PRIMARY TREATMENT

COEFFICIENT OF VARIATION FOR PRIMARY EFFLUENT

VARIABLE	DIURNAL		DAILY	
	Phase 1	Phase 2	Phase 1	Phase 2
Biochemical Oxygen Demand*	54.0	17.5	35.6	32.7
Biochemical Oxygen Demand (f)*	61.5	16.5	45.4	40.6
Chemical Oxygen Demand	50.5	26.7	29.3	25.1
Chemical Oxygen Demand (f)	49.4	19.1	28.2	39.0
Total Organic Carbon	49.3	17.2	24.1	21.1
Total Organic Carbon (f)	46.0	18.6	25.9	48.2
Suspended Solids	59.2	18.1	44.1	19.0
Volatile Suspended Solids	60.6	21.1	39.6	19.6

Coefficient of variation = (mean $\div$ standard deviation^{-1}) x 100

* Regressed values omitted.

Example Problem

Given the following information, design an activated sludge system that will yield:

1. An average effluent soluble BOD_5 = 15 mg/l
2. A maximum effluent soluble BOD_5 = 25 mg/l
3. An average effluent suspended solids = 30 mg/l at 85 percent volatile content

Kinetic Parameters

1. Activated sludge reaction rate based on BOD_5

   k = 13.11/day at 20°C

2. Sludge synthesis coefficient

   a = 0.55 kg VSS/kg BOD removed

3. Sludge auto-oxidation coefficient

   b = 0.20 kg VSS/day/kg MLVSS

4. Oxygen Utilization Coefficient

   a' = 0.40 kg O_2/kg BOD removed

5. Endogenous oxygen utilization rate

   b' = 0.28 kg O_2/day/kg MLVSS

6. Temperature Coefficient

   θ = 1.03 for BOD reaction rate correction

   = 1.028 for oxygen transfer efficiency correction for mechanical surface aeration

7. Manufacturer's Rated Oxygen transfer efficiency

   N_o = 1.45 kg O_2/hp-hr

   = (3.2 lb O_2/hp-hr)

8. Oxygen transfer coefficient

   α = 0.75

9. Saturation Coefficient

   β = 0.98

Design Conditions

1. Total wastewater flow

   Q = 18,925 m^3/day (5 mgd)

2. Influent waste temperature

   Summer T_i = 40°C (104°F)

   Winter T_i = 38.9°C (102°F)

3. Average extreme ambient temperatures

   Summer T_a = 29.4°C (85°F)

   Winter T_a = 10.6°C (51°F)

4. Wastewater total BOD_5

   Influent S_o = 690 mg/l

5. Wastewater suspended solids

   Influent X_o = < 10 mg/l

6. Influent Nitrogen

   Total Kjeldahl N = 50 mg/l

7. Influent Phosphorus

   Total P = 20 mg/l

Design of Aeration Basin Based on Winter Conditions

1. Calculate Kilograms BOD to be Removed per day (average)

   S_r = (690 - 15) (18.925)

   = 12,774 kg BOD/day

   (690-15) (5 MGD) 8.34 lb/gal

   28,147.5 lb/day

2. Estimate Horsepower Requirements

   hp = (12,774 kg BOD/day)/(20.4 kg BOD removed/hp-day)

   = 626 hp

   $\frac{28,147.5 \text{ lb/day}}{45 \text{ lb BOD removed/hp-day}}$

3. Compute Winter Temperature of Aeration Basin

   $(T_i - T_w)(1 \text{ K-cal/kg-°C})(Q) = (T_w - T_a)(1134 \text{ K-cal/hp-hr-°C})(hp)$

   $(38.9 - T_w)\ (1)\ (787,980) = (T_w - 10.6)\ (1134)\ (626)$

   $(38.9 - T_w)(1)\left(\frac{5 \text{ MGD}}{24 \text{ hr/day}}\right) 3.785 \frac{L}{gal} \frac{kg}{L} = T_w - 10.6$

$T_w = 25.4°C$

Therefore, use $T_w = 26°C$

4. Correct Reaction Rate Coefficient to Winter Conditions

$$K_T = k_{20}\theta^{T-20}$$

$$= (13.11)(1.03)^{26-20}$$

$$= 15.65 \text{ day}^{-1}$$

5. Compute Detention Time in Basin Based Upon BOD Removal and Sludge Settleability for BOD Removal

$$t = S_o(S_o - S_e)/kX_vS_e$$

$$= 690\ (690-15)/(15.65)\ (3000)\ (15)$$

$$= 0.66 \text{ days}$$

$$= 15.8 \text{ hr}$$

Assume optimum F/M for sludge settleability is 0.6 (See Figure 6)

$$t = S_o\ (24)/X_v\ (F/M)$$

$$= (690)(24)/(3000)(0.6)$$

$$= 9.2 \text{ hr} \therefore \text{Use } 15.8 \text{ hr}$$

6. Compute F/M for Design Detention Time

Since BOD removal controls, use $t = 15.8$ hr

$$F/M = (690)(24)/(3000)(15.8)$$

$$= 0.35$$

Assume this F/M will generate a desirable effluent suspended solids of 28 mg/l. This value is less than the design average effluent suspended solids value of 30 mg/l. Figure 6 presents the type of correlation needed to make this design assumption.

7. Compute Basin Volume

$$V = Qt$$

$$= (18,925)(0.66)$$

5 MGD (0.66)

$$= 12,491 \text{ m}^3 \text{ (3.3 mil gal)}$$

8. Compute Biodegradable Portion of MLVSS

$$x = \frac{aS_r + bX_v - \sqrt{(aS_r + bX_v)^2 - 4bX_v(0.77\ aS_r)}}{2\ b\ X_v}$$

$$= 0.5$$

where:

aS_r = (0.55)(18,925)(690-15)/1000 (0.55)(5MGD)(690-15) mg/L 8.3 lb/gal

= 7026 kg/day 15,481

bX_v = (0.2)(12,491)(3000)/1000 0.2(3.3 MG) 3000 mg/L (8.34 lb/gal

= 7495 kg/day 16,513

9. Compute Maximum Allowable Effluent Total BOD

Knowing maximum allowable effluent soluble BOD is 25 mg/l

$$kS_e = S_o(S_o - S_e)/X_v t$$

$$S_o^2 - 25\ S_o = (15.65)(25)(3000)(0.66)$$

$$S_o = 890 \text{ mg/l}$$

$\therefore$ = Equalization requirements should be designed accordingly

10. Compute Summer Average Operating Temperature

$$(T_i - T_w)(1 \text{ K-cal/kg-°C})(Q) = (T_w - T_a)(1134 \text{ K-cal/hp-hr-°C})(hp)$$

$$(40 - T_w)(1)(787,980) = (T_w - 29.4)(1134)(626)$$

$$T_w = 34°C$$

11. Compute Summer BOD_5 Reaction Rate Coefficient, K

Summer Temperature = 34°C

$$K^T = k_{20}\theta^{T-20}$$

$$= (13.11)(1.03)^{34-20}$$

$$= 19.81/\text{mg-day}$$

12. Compute Summer Effluent BOD_5 based on Maximum Influent BOD_5

$$S_e = S_o^2/(S_o + kX_v t)$$

$= (890)^2/[890 + (19.8)(3000)(0.66)]$

$= 20$ mg/l

Compute Oxygen and Horsepower Based on Summer Conditions and Maximum Influent BOD_5 from Equalization

1. Compute Oxygen Requirements

$$\text{kg } O_2/\text{day} = a' S_r + b' x X_v$$

$$= (0.4)(890-20)(18,925)/1000 + (0.28)(0.5)(3000)(12,491)/1000$$

$$= 6586 + 5246$$

$$= 493 \text{ kg/hr}$$

2. Compute Actual Oxygen Transfer Efficiency, N

Using conventional transfer rates of low speed aerators,

Assume $N_o = 1.45$ kg O_2/hp-hr

$$N = N_o[(\beta C_s - C_L)/C_{20}]\ \theta^{T-20}\ \alpha$$

$$= 1.45[(0.98)(7.2) - (2.0)/9.1](1.028)^{34-20}(0.75)$$

$= 0.88$ kg O_2/hp-hr

3. Compute Horsepower Requirements

$$hp = \text{kg } O_2/\text{day required}/N\ (24)$$

$$= 11,832/(0.88)(24)$$

$= 560$ hp ∴ checks with assumed hp level

4. Power Level Check

$$PL = hp/V$$

$$= 560/12.491$$

$= 44.8$ hp/1000 m^3

Compute Excess Sludge Production Based on Summer Conditions and Average Influent BOD_5

1. Compute Summer Effluent Soluble BOD_5 Based on Average Influent Total BOD

$$S_e = S_o^2/S_o + k X_v t$$

$= (690)^2/(690) + (19.8)(3000)(0.66)$

$= 12$ mg/l

2. Compute Excess Sludge Production

$\Delta X_v = X_o + aS_r - bx\ X_v - X_e$

$= 0 + (0.55)(690-12)(18,925)/1000 - (0.2)(0.5)(3000)(12,491)/1000$
$- (30)(18,925)/1000(0.85)$

$= 0 + 7057 - 3747 - 483$

$= 2827$ kg/day

At 85 percent volatile

$\Delta X = 2827/0.85$

$= 3325$ kg/day

Compute Nutrient Requirements Based on Average BOD_5 Removal

1. Compute Winter Nutrient Requirements

$\Delta X_v = X_o + aS_r - bxX_v - X_e$

$= 0 + (0.55)(690-15)(18,925)/1000 - (0.2)(0.5)(3000)(12,491)/1000$
$- (30)(18,925)/1000\ (0.85)$

$= 7026 - 3747 - 483$

$= 2796$ kg/day

Nitrogen:

$N_{required} = 0.123\ x\Delta X_v/0.77 + [0.07(0.77-x)/0.77]\ \Delta X_v$

$= (0123)(0.5)(2796)/0.77 + [0.07(0.77-0.5)/0.77]\ 2796$

$= 223 + 69$

$= 292$ kg/day required

$N_{inf} = (50)(18,925)/1000$

$= 946$ kg/day

Therefore, nitrogen addition is not required. Will have 654 kg/day (35 mg/l) nitrogen leaving activated sludge system.

Phosphorus:

$$P = 0.026\ x\Delta X_v/0.77 + [0.01(0.77-x)/0.77]\ \Delta X_v$$

$$= (0.026)(0.5)(2796)/0.77 + [0.01(0.77-0.5)/0.77]\ 2796$$

$$= 47 + 10$$

$$= 57 \text{ kg/day required}$$

$$P_{inf} = (20)(18,925)/1000$$

$$= 379 \text{ kg/day}$$

Therefore, phosphorus addition is not required.

2. Compute Summer Nutrient Requirements

$$\Delta X_v = 2827 \text{ kg/day}$$

Nitrogen:

$$N = 0.123(0.5)(2827)/0.77 + [0.07(0.77-0.5)/0.77]\ 2827$$

$$= 295 \text{ kg/day}$$

$$N_{inf} = 946 \text{ kg/day}$$

Therefore, nitrogen addition is not required.

Phosphorus:

$$P = 0.026(0.5)(2827)/0.77 + [0.01(0.77-0.5)/0.77]\ 2827$$

$$= 58 \text{ kg/day}$$

Therefore, phosphorus addition is not required.

Compute Summer and Winter Sludge Age

1. Summer Sludge Age

$$G = \frac{X_v}{\Delta X_v} = 0.5 \text{ days}$$ 10 days

2. Winter Sludge Age

$$G = \frac{X_v}{\Delta X_v} = 0.5 \text{ days}$$ 10 days

Design Final Clarifier for Maximum Operating MLVSS

1. Compute Overflow Rate for MLSS of 3500 mg/l

For a MLSS level of 3500 mg/l, assume the zone settling velocity, ZSV, is 1.04 m/hr (3.4 ft/hr) from a correlation such as that presented in Figure 4.

$$O.R. = (1.04 \text{ m/hr})(0.7)(24)$$

$$= 17.5 \text{ m}^3/\text{day}/\text{m}^2$$

2. Compute Area for Clarification

$$A = Q/OR$$

$$= 18{,}925 \text{ m}^3/\text{day}/17.5 \text{ m}^3/\text{day}/\text{m}^2$$

$$= 1081 \text{ m}^2$$

3. Compute Sludge Recycle Rate, r

Assume a desired sludge concentration of 12,800 mg/l from the final clarifier.

$$R(12{,}800)/1000 + \text{EXCESS SLUDGE} + \text{EFFLUENT SOLIDS} = (Q+R)(3500)/1000$$

$$R(12.8 - 3.5) = 66{,}238 - 3325 - 507$$

$$9.3\,R = 62{,}346$$

$$R = 6703 \text{ m}^3/\text{day}$$

$$100\,(R/Q) = 35.4 \text{ percent}$$

4. Compute Area for Thickening

Choose design solids flux rate for a desired underflow concentration of 12,800 mg/l. Assume solids flux rate equals 73.2 kg/m^2/day from a correlation such as that presented in Figure 5.

$$A = (Q + R)(\text{MLSS max})/(\text{solids flux})(1000)$$

$$= (18{,}925 + 6703)(3500)/(73.2)(1000)$$

$$= 1225 \text{ m}^2$$

Since area for thickening is greater than area for clarification, thickening controls. Therefore, use area of 1225 m^2.

5. Compute Clarifier Diameter

$$A = \frac{\pi d^2}{4}$$

$$d = (1225/0.785)^{1/2}$$

$$= 40 \text{ m}$$

Final Effluent Quality

From a correlation such as that presented in Figure 7, assume 0.4 mg BOD/mg VSS for a sludge age of 0.5 days.

Average effluent suspended solids	=	30 mg/l
Average effluent VSS	=	25.5 mg/l
Total effluent suspended solids	=	50 mg/l
Total effluent VSS	=	42.5 mg/l
BOD content of VSS	=	0.4 mg BOD/mg VSS
Total effluent BOD average	=	15 + 0.4 (25.5)
	=	25 mg/l
Total effluent BOD maximum	=	25 + 0.4 (42.5)
	=	42 mg/l

It should be noted that the maximum BOD considers that the maximum soluble BOD and the maximum effluent suspended solids will occur at the same time which is unlikely.

Summary Process Design Table

Activated Sludge

F/M (kg BOD/day/kg MLVSS)	=	0.35
Detention Time (days)	=	0.66
Basin Volume (m^3)	=	12,491
Depth (m)	=	3.66
MLVSS (mg/l)	=	3000
MLSS (mg/l) @ 85 percent volatile	=	3500
Oxygen Requirements (kg/day)	=	11,832
Power Requirements (hp)	=	560
Power Level (hp/1000 m^3)	=	44.8
Basin Temperature		
Summer, T_w	=	35.5°C
Winter, T_w	=	25.5°C

Oxygen Transfer, N (kg O_2/hp-hr)	= 0.88
Nutrient Requirements	
Nitrogen (kg/day)	= 292
Phosphorus (kg/day)	= 57
Secondary Clarifier	
Overflow Rate (m^3/day/m^2)	= 17.5
Surface Area (m^2)	= 1081
Diameter (m)	= 40
Water Depth Above Cone (m)	= 4.27
Excess Secondary Sludge (kg/day)	= 3325
Volatile Content (%)	= 85
Underflow Concentration (%)	= 1.28
Underflow Quantity (m^3/day)	= 261
Recycle Ratio (%)	= 35.4
Recycle Flow (m^3/day)	= 6703

DEMANDA QUIMICA DE OXIGENO (D.Q.O.)

1.1 Generalidades.

Esta prueba se usa extensamente para determinar la capacidad de polución del agua negra y, sobre todo, de los desechos industriales. Se basa en el hecho de que prácticamente todos los compuestos orgánicos se oxidan para producir CO_2 y H_2O por la acción de oxidantes fuertes, bajo condiciones ácidas.

Desde luego esta reacción no depende de que los compuestos sean asimilables biológicamente o nó. Por ejemplo la glucosa y la lignina se oxida completamente. Por lo tanto, los valores de la DQO son en general mayores que los de la D.B.O.

La prueba de la D.Q.O. no diferencia entre la materia oxidable biológicamente y la materia orgánica inerte, ni establece la rapidez con que el material biológicamente activo es estabilizado bajo condiciones que existen en la naturaleza.

La prueba de DQO se efectúa sólo en 3 hs. o menos comparada con 5 días que requiere la D.B.O.

1.2 Agentes Oxidantes.

- Permanganato de potasio - da resultados menores que la D.B.O. (5 días).
- Sulfato Cérico.
- Iodato de potasio.
- Dicromato de Potasio.

Este último es el más efectivo en la oxidación de la materia orgánica. La solución tiene que ser altamente ácida y estar a elevada temperatura para que la oxidación sea completa. Deben usarse condensadores de reflujo para evitar pérdida de materia orgánica vólatil.

Algunos compuestos orgánicos, entre ellos, el ácido acético y los ácidos grasos, se oxidan por el dicromato sólo en presencia de un catalizador (iones de plata).

Los compuestos aromáticos y la piridina no se oxidan en ninguna circunstancia.

1.3 Química de la oxidación por el dicromato de potasio.

La reacción de oxidación se efectúa como sigue:

$$(CHO) + (Cr_2O_7) = + H^+ \_\_\_\_ 2(Cr)^{3+} + CO_2 + H_2O$$

Se usa dicromato de grado analítico, secado a 103°C.

Se recomienda una normalidad 0.25 N para la solución de dicromato. Como una solución 0.25 N de oxígeno es equivalente a $0.25 \times 8 \frac{gr}{lt} = 2 \frac{gr}{lt} = 2 \frac{mgr}{ml}$ de oxígeno, 1 ml. de la solución 0.25 N de dicromato representará 2 mgr. de oxígeno.

1.4 Proceso estándar para encontrar la DQO por el método del dicromato de potasio.

1.4.1 Proceso en general.

La determinación de la D.Q.O. se hace agregando a la muestra dicromato en exceso. Una cierta cantidad es consumida por la materia oxidable presente en la muestra, permaneciendo un exceso en solución. El exceso se determina usando un agente reductor, normalmente ión ferroso (Fe++). La diferencia entre el dicromato agregado y el remanente es el dicromato consumido. La reacción que tiene lugar es como sigue:

$$6Fe^{++} + (Cr_2O_7) = + 14H^+ \text{ —— } 6Fe^{3+} + 2Cr^{3+} + 7H_2O$$

Como fuente de iones Fe^{++} se usa sulfato ferroso de amonio (SFA). Como las soluciones de Fe^{++} se oxidan fácilmente, estas soluciones se deben estandarizar cada vez que se usen, lo que se puede hacer con solución de dicromato 0.25 N.

Indicador.- Para determinar el momento en que la oxidación de la materia orgánica termina, se usa Ferroín (1,10 fenantrolina monohidratada). El cambio de color es del verde azul al café sucio.

1.4.2 Limitaciones.

Se puede cuantificar la porción carbonosa de los compuestos de nitrógeno, pero no hay reducción en el dicromato por amoníaco del desecho o por el liberado de materias protéicas (excepto en presencia de cloruros).

Los compuestos de cadena abierta se oxidan más fácilmente si se agrega sulfato de plata, pero los cloruros, fluoruros o ioduros reaccionan con él para producir precipitados que se oxidan sólo parcialmente.

Los catalizadores (sulfato de Ag) no ayudan a la oxidación de los hidrocarburos aromáticos, pero sí a la de los alcoholes y ácidos de cadena abierta.

En presencia de amoníaco, aminas ó de materia nitrogenada, se pueden presentar cíclicamente durante el proceso Cl o Cl^- a través de la formación de cloraminas. El proceso dura por varias horas de digestión, si no hay catalizador.

Como a bajas D.Q.O. la presencia de cloruros afecta más los resultados, el método se puede aplicar a D.Q.O. mayores que 50 p.p.m. Para aguas con D.Q.O. menores a 25 p.p.m. los resultados pueden indicar solo un orden de magnitud.

1.4.3. Interferencia por cloruros.

Cuando no se usa sulfato de Ag como catalizador, los cloruros presentes se oxidan por el dicromato, de manera que se debe aplicar una corrección. Se determina el contenido de cloruros en una muestra separada y se deduce el consumo de oxígeno del resultado obtenido:

$$1 \frac{g}{lt} \frac{Cl}{(35.5)} \quad \text{equivalen a} \quad 0.23 \frac{g}{lt} \frac{\text{oxígeno}}{(8.0)}$$

En efecto:

$$\frac{35.5}{lt} Cl = \frac{8}{lt} Ox.; \therefore 1\ Cl = \frac{8}{35.5} = 0.23\ Ox.-$$

Cuando se use catalizador no se puede aplicar la corrección, desde luego.

1.4.4 Muestreo y almacenamiento.

Si existe materia inestable, las muestras se deben examinar inmediatamente. Si tienen sólidos sedimentables deben ser homogenizadas cuidadosamente. Debe procurarse evitar pequeños volúmenes de muestra (lo que sucedería si la D.O.O. es alta); en este caso se harán diluciones en matraces aforados y se realizará la prueba en la dilución que dé mejores resultados con el método como se verá más adelante.

1.4.5 Proceso en detalle.

1.4.5.1 Aparatos.

Matraz esférico con cuello esmerilado, (20/40), cap. 300 ml), y refrigerante de Friedrichs.

1.4.5.2 Reactivos.

1- Sol. valorada de $K_2Cr_2O_7$, 0.250 N.

Cantidad necesaria de la sal:

Como $(Cr_2\ 0_7)$ = ——— $2Cr^{3+}$, hay un cambio de valencia de 6.

K - 39.102 x 2 = 78.204

Cr - 51.996 x 2 = 103.992

0 - 16.000 x 7 = 112.0000

∴ P.M. = 294.196

∴ Sol. 1N = $\frac{294.196}{6}$ = 49.1 $\frac{gr}{lt}$; 0.25 N = 12.259 $\frac{gr}{lt}$

El dicromato se seca a 103°C durante 2 hrs. y luego se diluye a 1000 ml.

2- Acido sulfúrico concentrado.

3- Sol. valorada de Fe $(NH_4)_2 (SO_4)_2\ 6H_2O$, 0.25 N. (SFA).

Preparación.

a) 98 gr. sulfato ferroso amoniacal se disuelven en agua destilada.
b) Se agregan 20 ml de H_2SO_4 concentrado.
c) Se enfría y se diluye a 1000 c.c.-

Esta solución se debe titular el día que se vaya a utilizar.

Titulación.- A 25 ml de solución valorada de bicromato diluída a 250 ml. se le agregan 20 ml de H_2SO_4 y se deja enfriar.
Se titula con sulfato ferroso amoniacal usando 2 o 3 gotas de Ferroín como indicador.

Normalidad = $\frac{ml\ K_2Cr_2O_7 \times 0.25}{ml\ Fe(NH_4)_2(SO_4)_2}$.- Vire: Verde a café.-

1.4.5.3 Pasos.

1o.-50 ml muestra o parte alícuota diluída a 50 ml.-

2o.- 25 ml. sol. val. dicromato.

3o.- 75 ml. H_2SO_4 conc.- Verter cuidadosamente y mezclando.

4o.- Se fija el condensador y se somete a reflujo por 2 hs.

5o.- Se deja enfriar y se lava con 25 ml. de agua destilada.

6o.- Se pasa el contenido a un matraz Erlenmeyer de 500 ml.

7o.- Se lava el matraz esférico 4 o 5 veces con agua destilada, vertiendo cada vez en el Erlenmeyer, y se diluye en éste a 350 ml.

8o.- Se deja enfriar a la temperatura ambiente.

9o.- Se titula con SFA, agregando 3 gotas de Ferroín.-

1.4.5.4. Testigo.

Se hacen las mismas operaciones con 50 ml. de agua destilada.

1.4.5.5 Catalizador.

Cuando se use catalizador, se agrega directamente a la mezcla, antes del reflujo, 1 gr. de Ag_2SO_4.

1.4.5.6 Cálculo y deducción de la fórmula utilizada.

La fórmula es:

$$\frac{mg}{lt} \quad D.Q.O. = \frac{(a-b)\ c \times 8000}{ml\ muestra} - d \text{ , en que}$$

a = ml $Fe(NH_4)_2(SO_4)_2$ usados para el testigo.

b = " " " " la muestra.

c = normalidad del $Fe(NH_4)_2(SO_4)$ 2.

d = corrección por cloruros = mg/lt de Cl - x 0,23.

Deducción de la fórmula:

Sabemos que el peso de una substancia A expresada como B está dada por:

$$PA/B = PA/A \quad \frac{P.E.B.}{P.E.A.} \qquad (1), \text{ en que}$$

$P_{A/B}$ = peso de A como B, gr.:

$P_{A/A}$ = peso de A como A, gr.:

P.E. = peso de un equivalente - gramo, gr.-

Además, el número de equivalentes- gramo que reaccionan es:

$$N_A V_A = N_B V_B \qquad (2),$$ en que

N= normalidad (de A ó B), $\frac{\text{No. de P. E.}}{\text{lt}}$;

V= volumen (de A o B), lt.-

Por lo tanto el peso de A como A expresado en gramo es:

$$P_{A/A} = N_A V_A \text{ P.E.}_A$$

el cual sustituído en (1), conduce a:

$$P_{A/B} = N_A V_A \text{ P.E.}_A \frac{\text{P.E.}_B}{\text{P.E.}_A} = N_A V_A \text{ P.E.}_B \text{ .-}$$

Si llamamos $K_{A/B}$ = a la concentración de A expresada como B en $\frac{gr}{lt}$, tendrémos :

$$\frac{P_{A/B}}{V_M} = K_{A/B} = \frac{N_A V_A \text{ P.E.}_B}{V_M} \text{ ,}$$

donde V_M es el volumen de la muestra, en lt.

Por lo tanto, la concentración en $\frac{mgr}{lt}$ será :

$$K_{A/B} = \frac{N_A V_A \text{ P.E.}_B \times 1000}{V_M} \qquad (4)$$

en donde V_A y V_M tienen las mismas unidades, lt. ó ml. por ejemplo.

En nuestro caso tendremos, de acuerdo con el esquema:

a-b = diferencia entre los vólumenes de sulfato ferroso amoniacal consumido en el testigo y la muestra.

a-b = contenido real de materia orgánica en la muestra.
a-b = cantidad real de dicromato consumida por la materia órganica de la muestra.
a-b = cantidad de sulfato ferroso amoniacal consumido en la titulación.
a-b = cantidad de oxígeno que representa el contenido real de materia orgánica en la muestra.

Considerando las dos últimas expresiones y la fórmula (4), se trata de expresar la cantidad de sulfato ferroso amoniacal (A) como oxígeno (B). Por tanto :

$$K_A/B = D.Q.O.; \qquad \therefore$$

$$D.Q.O. = \frac{N_A\ (a-b)\ 8000}{V_M}$$

Como la corrección por cloruros, D, es sustractiva, y haciendo $C = N_A$, la expresión queda en la forma presentada en los Métodos Estándar :

$$D.Q.O. = \frac{(a-b) \times 8000}{V_M} \qquad \text{- d. -}$$

LAND DISPOSAL OF SLUDGE*

Disposal of wastewater sludges on land is practiced in many areas. In some cases the land serves as a dumping ground for sludges, while in other instances the sludge is applied to and mixed with the soil as a fertilizer or soil conditioner. The organic matter as well as the inorganic nutrient in sludge is beneficial to the soil. Common dumping grounds for liquid and dewatered sludges include abandoned mines, quarries and lagoons and sanitary landfills.

The application of liquid sludges to the land results in a number of benefits. The sludge need not be dewatered. The savings gained by eliminating the conditioning and dewatering of the sludges should be compared to the additional cost for transporting the water associated with the sludge. However this water is a source of irrigation water for the soil. An additional advantage is an increase in the removal of nutrients (nitrogen and phosphorus) from the wastewater during treatment. These nutrients which are associated with the sludges are released when the sludge is processed and the nutrients are returned to the treatment plant. Some of the reported data indicate that 100 percent of the nitrogen and about 4 percent of the phosphorus in the sludge are released during wet oxidation of the sludge. Some of the reported data for application of digested sludges to land are summarized in Table I.

Liquid sludges have also been used to develop and improve low grade soils such as dredged sand. The sludges are most commonly transported by truck although in some cases pipelines have been used.

TABLE I

LAND APPLICATION OF DIGESTED SLUDGE

Type of Sludge	Solids Content (percent)	Approximate Loading (Kg/Ha-year)	Reference
Digested primary and activated sludges	4.0	5600	(2)
Digested Primary sludge	6.5	22,400 to 224,000	(4)
Digested Primary sludge	4.1	6720	(5)

*Joseph F. Malina, Jr.

TABLE I (cont)

Type of Sludge	Solids Content (percent)	Approximate Loading (Kg/Ha-year)	Reference
Digested primary and activated sludges	--	4500	(5)
Digested primary and activated sludges	6.0	136,600	(4)

The liquid sludge should be applied at such a rate so that there is no possibility of pollution of ground water or streams.

A variety of crops have been grown in soils on which sludge was applied. The growth characteristics and crop yields compared favorably with the crops grown in soils which received the equivalent amount of chemical fertilizer. Sludge is not generally applied to crops which are intended for human consumption in the raw form.

The cost of land disposal was compared with various sludge treatment processes used by the Metropolitan Sanitary District of Greater Chicago. These data are summarized in Table II. The estimated cost for land disposal will be the basis for the comparison.

TABLE II

COST COMPARISON

Method	Relative Cost per kg
Digestion and liquid application to land (distance to site 80 km)	1.0
Drying and Sale as Fertilizer	3.0
Digestion and Lagooning	3.26
Wet Oxidation	3.33
Dewatering and Incineration	3.8

The relative costs of sludge disposal by various methods were evaluated by Riddell and Cormack (1966). These costs were based on distance to disposal site for various populations. The methods of sludge disposal which were considered are listed below.

1. Application of liquid sludge on the land by tank truck includes thickening and digestion. Hauling the sludge by tank truck was used for the city of 10,000 people and transportation by pipelines was used for larger populations.
2. Dewatered sludge to landfill includes thickening, digestion vacuum filtration and trucking to the disposal site.

3. Incineration and ash disposal in a landfill includes thickening, digestion, vacuum filtration, incineration, and trucking the ash to the disposal site.

4. Fertilizer production includes thickening, digestion, vacuum filtration, heat drying, and sale at U.S. $5.00 per ton.

The following sludge characteristics and design values were used:

1. Per capita solids contribution = 0.2 lb/day.
2. Volatile content of raw sludge = 75 percent.
3. Thickener loading = 15 lb/sq ft /day.
4. Solids concentration after thickening = 5 percent.
5. Digestion time = 15 days.
6. Reduction of volatiles in digestion = 50 percent.
7. Digested sludge suspended solids concentration = 3.5 percent.
8. Conditioning chemical requirement = 15 percent.
9. Filter Yield = 3 lb/sq ft/hr.
10. Filter cake moisture = 75 percent.
11. Dried sludge moisture = 6 percent.

Spreading of liquid sludge on land is the most economical method of disposing of sludge equivalent to that produced by a city of 100,000 people or less when disposal sites are available within 25 miles. For disposal of sludge equivalent to that produced by a city of a million people, the limiting distance is extended to 90 miles. For small installations, dewatering of sludge prior to disposal is necessary for economical operation when the disposal site is over about 30 miles from the treatment plant. Incineration and fertilizer production are feasible only in very large installations, and then only when the disposal site is over about 100 miles away.

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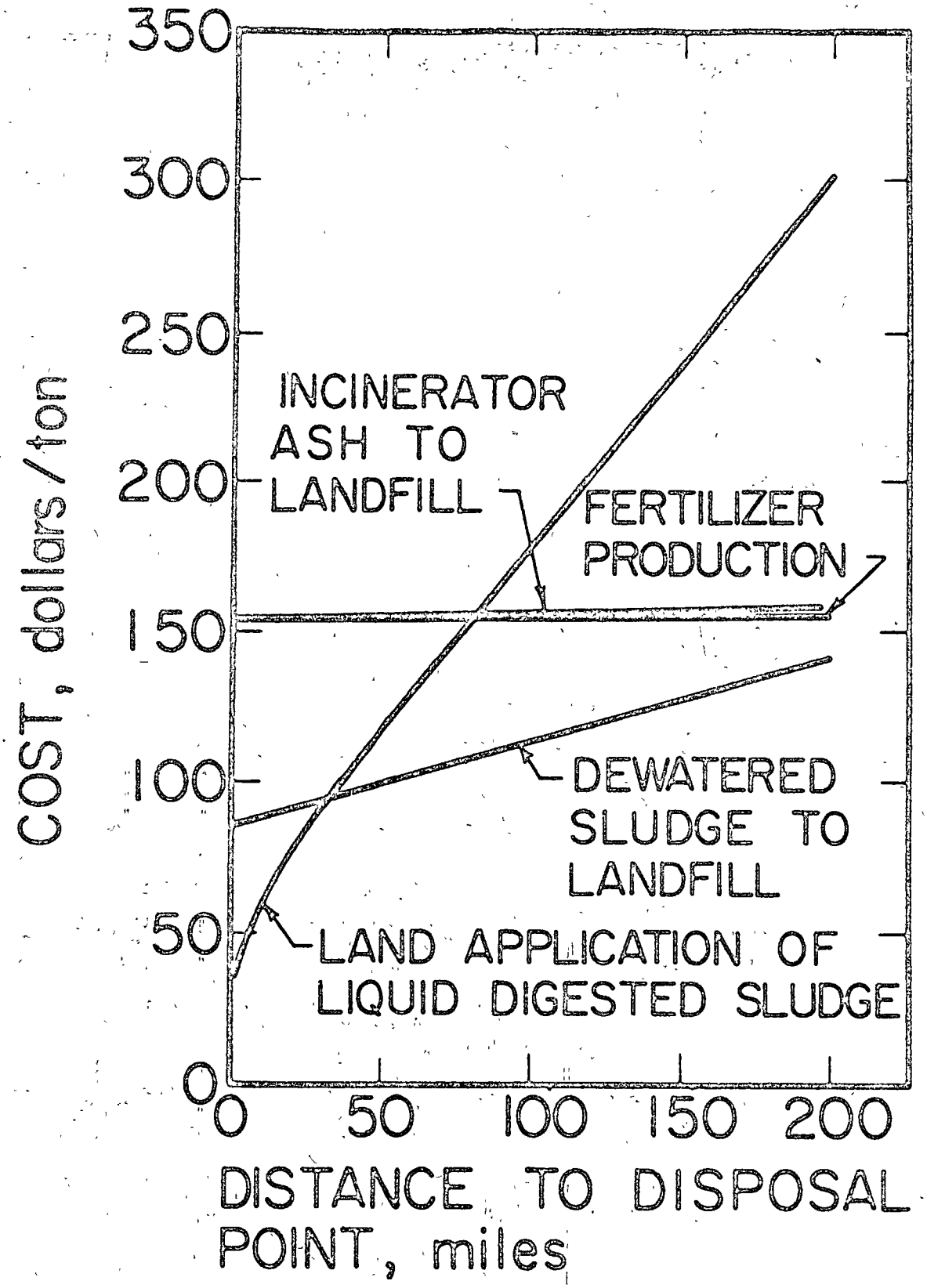

FIGURE 1. COST OF DISPOSAL OF APPROXIMATELY 5000 gpd OF SLUDGE BY VARIOUS METHODS. (CITY OF 10,000 PEOPLE - AFTER RIDDELL AND CORMACK, 1966).

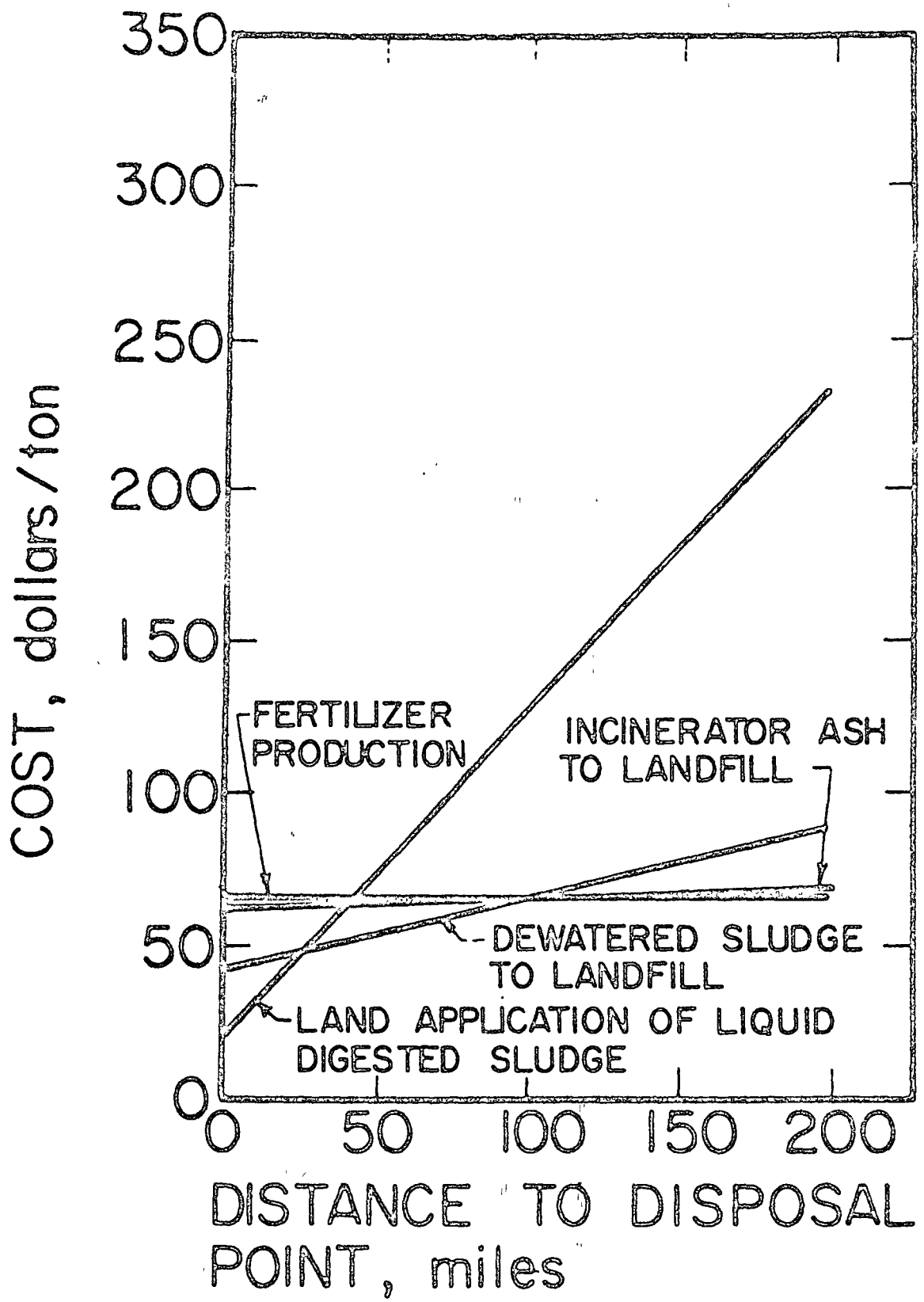

FIGURE 2. COST OF DISPOSAL OF APPROXIMATELY 50,000 gpd OF SLUDGE BY VARIOUS METHODS (CITY OF 100,000 PEOPLE - AFTER RIDDELL AND CORMACK, 1966).

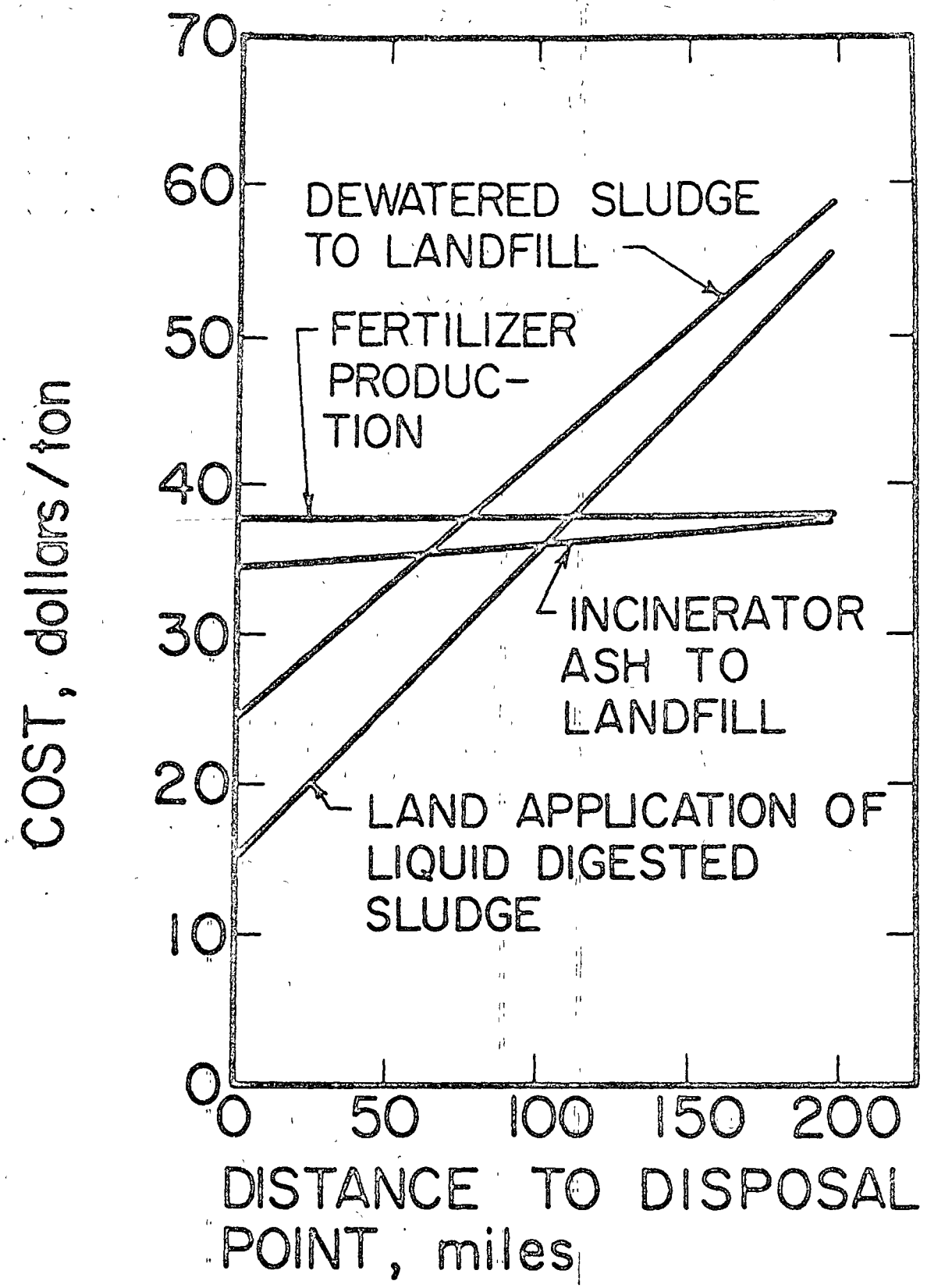

FIGURE 3. COST OF DISPOSAL OF APPROXIMATELY 500,000 gpd OF SLUDGE BY VARIOUS METHODS (CITY OF 1,000,000 PEOPLE - AFTER RIDDELL AND CORMACK, 1966).

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ULTRAHIGH RATE FILTRATION OF MUNICIPAL WASTEWATER

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Introduction

Filtration with sand or other granular media has been used for the removal of suspended solids from wastewater in tertiary treatment systems following biological processes or chemical coagulation and sedimentation. However, the use of ultrahigh rate in-depth multilayered filtration also has great potential for application to the treatment of raw wastewater. Investigations by Tchobanoglous (1) on multilayer filtration indicated that with the proper selection of material and loading conditions the entire depth of the filter can be employed in the filtration process, thus effecting a more efficient use of the filter. Frank (2) and Donovan (3) have demonstrated the feasibility of using high rate in-depth dual media filtration for the efficient removal of suspended solids at concentrations normally encountered in municipal wastewater.

The removal of suspended or colloidal material from water by filtration is accomplished by one of a number of mechanisms which may be generally classified as straining or transport-attachment. The multiplicity of filtration studies and the variety of conditions specific to each study have addressed the large number of potential filtration mechanisms (4,5,6,7,8,9). However, the physical and chemical complexities of the filtration process have defied for years the effective theoretical characterization. Numerous mathematical models have been developed to describe filter performance under controlled laboratory conditions, but none of these models are applicable to the design of filters.

The highly unpredictable nature of municipal wastewater complicates the development of a valid design model further. The direct adaptation of water filtration models was impossible. However, the models do present the relative significance of the numerous variables and provide a starting point for the design of a filter.

The objective of this paper is the evaluation of a multilayered filtration system for the in-depth removal of suspended solids from untreated municipal wastewater at ultrahigh flow rates. Pilot-scale multimedia filters were operated using municipal wastewater.

Filtration System

A schematic diagram of the filtration system is presented in Figure 1. The head loss in the filters was monitored by means of manometers connected to the filters. The filter design embodied two important considerations: a) the determination of reasonable flow conditions which would permit simple sampling techniques; and b) the versatility necessary to cope with unpredictable operations conditions. The columns were constructed of 1/8-inch steel plate bent into a channel resulting in a cross-sectional area of 0.1 square feet. The sides of the channel were flared at the open face to permit fastening of a 1/2-inch transparent plexiglas face plate which was held in place by C clamps and sealed by a 1/8-inch rubber gasket material coated with silicone lubricant. The top and bottom of the channel were also flared to permit attachment of the removable cover plate and the flow dispersing chamber. The medium in the dispersing chamber consisted of: a) a 3/4-inch pipe inlet deflected by a 1.5-inch diameter cone; b) a 3-inch layer of marbles; c) a 1-inch layer of 1/4-inch gravel; d) a 1-inch layer of 1/8-inch gravel; e) a 2-inch layer of 2 mm garnet. Sample taps consisting of 1/8-inch nipples were secured in the rear wall with epoxy at a spacing of 1.0-inch on center. Serum caps covered the ports, and permitted the use of No. 18 sampling needles to monitor the chamber pressure. The filters were operated at flow rates of 10, 20, and 30 gallons per minute per square feet (gpm/sq ft). A detailed discussion of the experimental equipment and the characterization of the filter media are presented elsewhere (10).

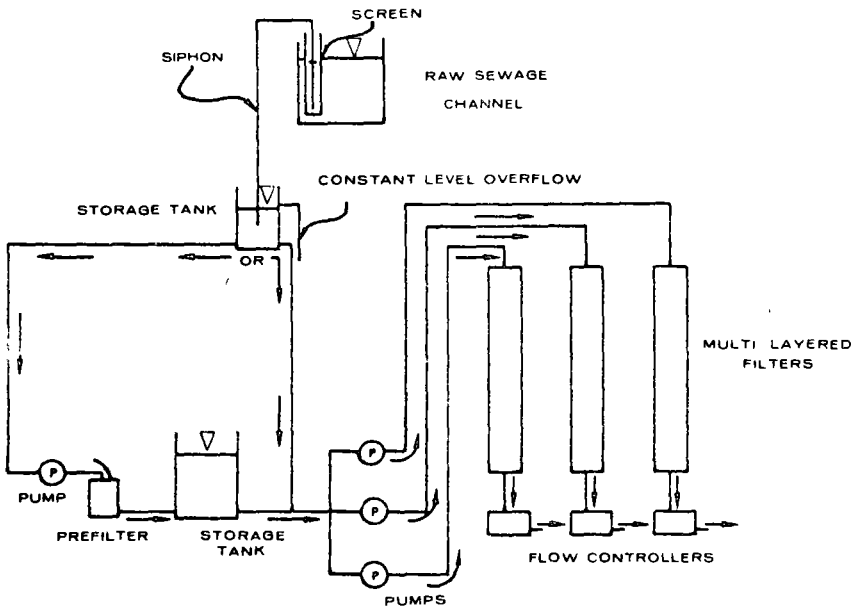

FIG. 1
Flow Diagram for Wastewater Filtration

The characteristics of the filter media used are presented in Table 1, and the three filter designs are summarized in Table 2. The nonuniformity coefficient was defined as the ratio of the 60 percentile size seive to the ten percentile size.

TABLE 1

Characteristics of Filter Media

Material	Sphericity	Mean Diameter (MM)	Specific Gravity
PVC Pellets	0.90	4.4	1.20
Anthracite Coal	0.73	1.85	1.68
Silica Sand	0.96	0.77	2.65
Garnet Sand	0.78	0.49	4.08

TABLE 2

Filter Design

Media	Depth (inches)	Non-Uniformity Coefficient		
PVC	8	1.07	1.07	1.07
Coal	5	1.07	1.15	1.45
Sand	3	1.07	1.22	1.39
Garnet	2	1.13	1.13	1.13
Media Inter-mixing		None	Intermediate	Intense

The experimental work was performed at the Govalle Wastewater Treatment Plant in Austin, Texas. The wastewater used in these studies was passed through bar screens, degritted and skimmed for grease removal. The underflow sludge collected in the skimming tank was returned into the primary effluent channel from which the supply to be filtered was drawn. A screen box constructed of wood and standard 14 x 18 mesh window screen was placed within the channel.

A prefilter was used in order to prolong the length of the runs of the multilayered filters. The prefilter was designed based on the requirement of supply to three filters at a maximum loading of 30 gpm/sq ft. The prefilter was constructed from 3/8-inch plexiglas with dimensions of 30 inches high by 5-5/8 inches

square. The calculated inside cross-sectional area was 0.22 square feet. Four spray nozzles located approximately eight inches above the medium were used for surface wash. Provision for air wash also was included. The underdrain system consisted of a 3/4-inch pipe with perforations in the horizontal plane placed in four inches of one to one and one-half inch stones covered by two inches of 1/8 inch gravel. The medium used in the prefilter consisted of one foot of four by five mesh PVC pellets. The inlet at the top of the filter was provided with a three-inch diameter disc located approximately one inch below the entrance port to distribute the influent. A pressure gage and a pressure relief system were built into the prefilter.

Experimental Results

The equipment was designed specifically for this study and was constructed and hydraulically tested in the laboratory before location at the treatment plant. The mean BOD and suspended solids concentration in the wastewater during these studies were 150 mg/l and 155 mg/l, respectively. The volatile content of the suspended solids was 86.5 percent. Experimental determinations included the essential variables with emphasis placed on trubidity and suspended solids.

The relationship between total head loss and time for the multilayered filters is presented in Figure 2(a) for flow rates of 10, 20, and 30 gpm/sq ft. These linear results indicate in-depth removal of suspended solids and no surface mat was observed.

The in-depth removal potential of PVC pellets was evaluated in more detail to determine the headloss in the filter and the penetration of suspended solids into the medium. A typical incremental headloss with depth curve for increasing time is illustrated in Figure 2(b). These curves are similar to those observed in water filtration, however the time scale is only 60 minutes for filtration of wastewater compared to 60 hours commonly encountered for water treatment.

The total removal of suspended solids throughout the depth of the filter nor the internal removal function could be determined from the headloss curves. Therefore, the prefilter efficiency, the dependence on varying influent concentrations and removal efficiency with depth were evaluated. The results of loading the filter at 40 gpm/sq ft under a wide variety of influent suspended solids concentrations are presented in Figure 3. The data indicate that as the influent concentration increases, the efficiency of removal increases. The depth-efficiency relationship for the filtration of wastewater is illustrated in Figure 4. These curves simulate the mathematical functions developed for water filtration.

Three multimedia filters described above were operated in parallel at an average influent suspended solids concentration of 150 mg/l. The effects of hydraulic loading and degree of media intermixing are illustrated in Figure 5. These data indicate that the non-intermixing filter was more efficient in suspended solids removal. The filter efficiencies at a 30 gpm/sq ft loading were 63.5 percent for non-intermixing, 56 percent for intermediate intermixing, and 58.5 for intense intermixing. The data indicate a decrease of efficiency with increase in loading; however, the rate of decrease is relatively small. A three-fold

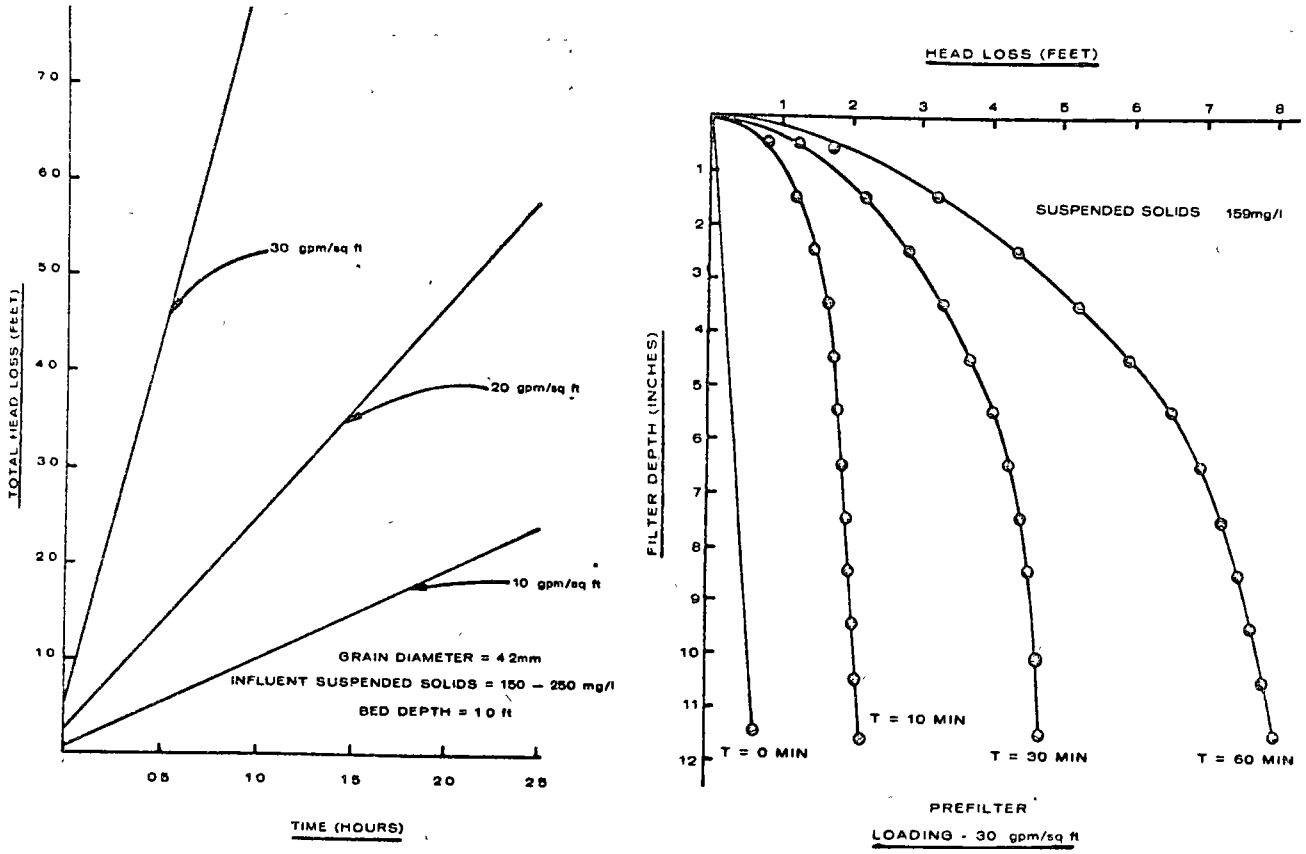

FIG. 2
Headloss-Depth-Time Relationship for PVC Pellets

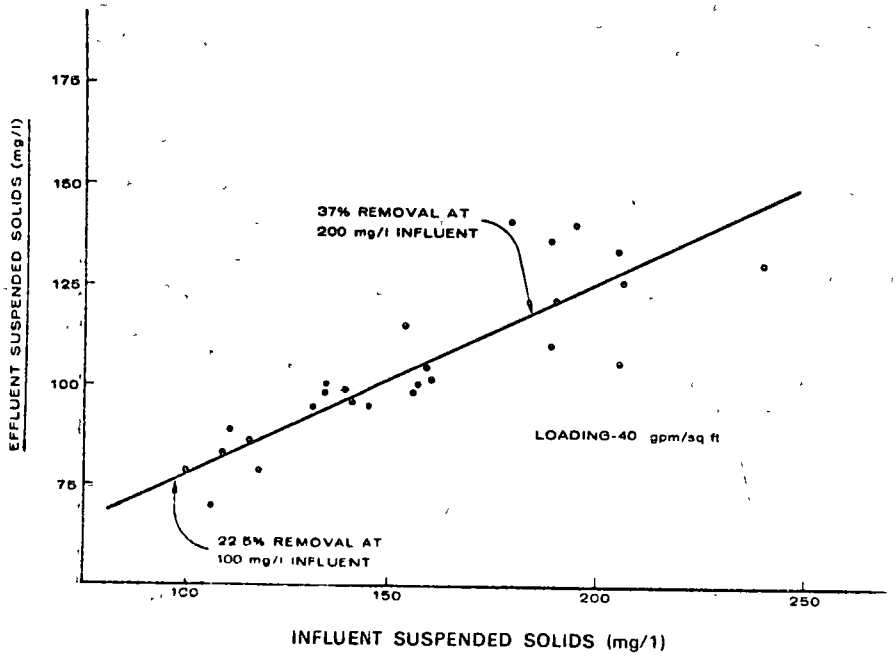

FIG. 3
Suspended Solids Removal by PVC Pellets

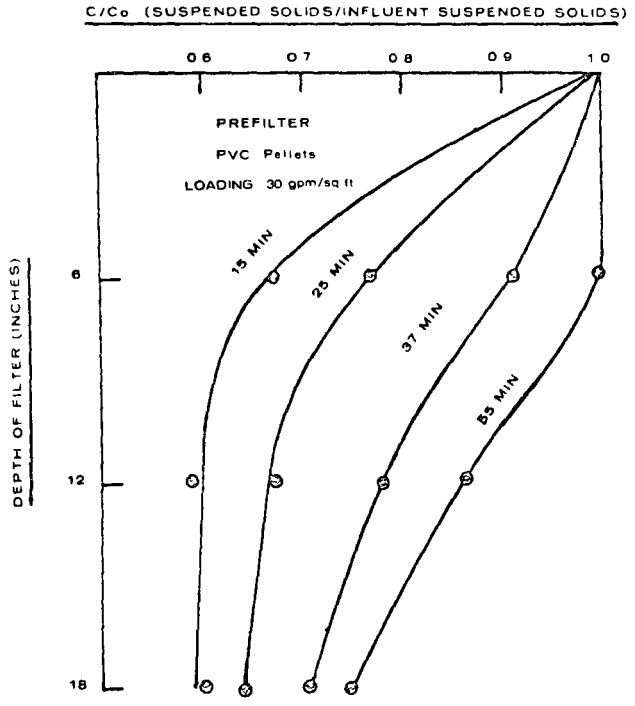

FIG. 4
Efficiency-Depth-Time Relationship for Raw Sewage Filtration

increase in loading resulted in decreases of only seven percent from 70.5 percent to 63.5 percent. The depth headloss relationship is presented in Figure 6. These data indicate that the headloss in the non-intermixed filter was less than in the other filters. The headloss curves for the non-intermixed filter are presented in Figure 7 and illustrate the rapid headloss buildup under average suspended solids loading conditions. A nine foot headloss developed after 20 minutes at 30 gpm/sq ft. This observation obviates the need for a pressure filter system, if this type of treatment were to be used in a full-scale system.

Once the filter had reached the terminal headloss, a backwash was necessary. The filter was cleaned rapidly and a two-minute backwash was sufficient. However, after backwashing, large flocculent material accumulated on the surface of the filter. This material was too large to be removed hydraulically and would present a significant problem in full-scale operation. A four-foot depth of water overlaid the filter at the beginning of the backwash cycle resulting in a substantial dilution of the sludge. The average maximum solids concentration in the sludge ranged between 1,000 and 4,000 mg/l.

In backwashing the PVC prefilter the surface spray resulted in destruction of the large floc that previously had been a problem after backwashing, and the air wash resulted in an unexpected benefit. If the water level in prefilter were dropped to a point that provided an air gap between the filter surface and the outlet, and the air wash was operated for 30 seconds, most of the entrapped suspended solids moved above the surface of the filter medium and within five minutes settled into a sludge blanket containing three to five percent solids.

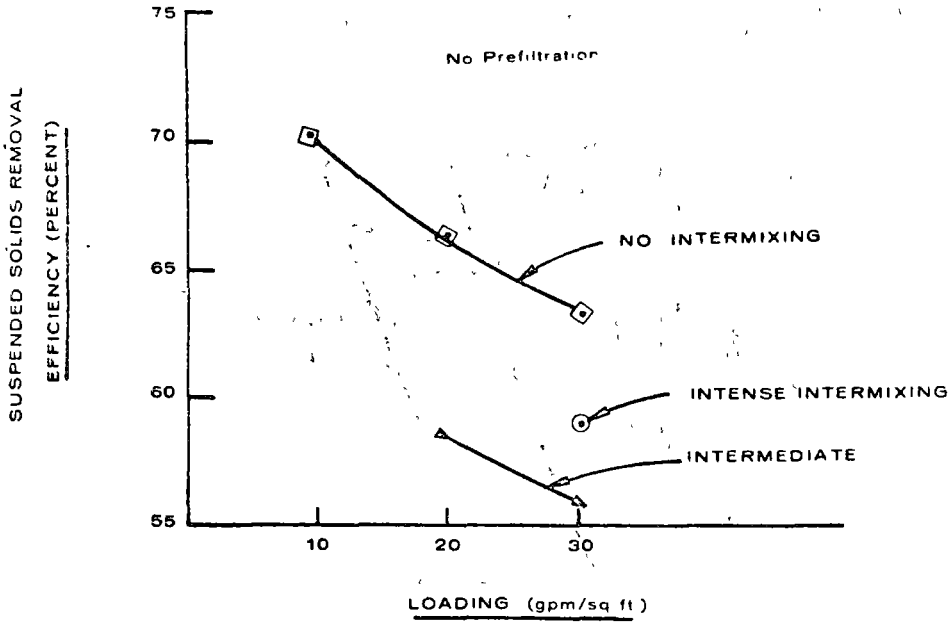

FIG. 5
Efficiency of Multilayered Filtration of Raw Sewage

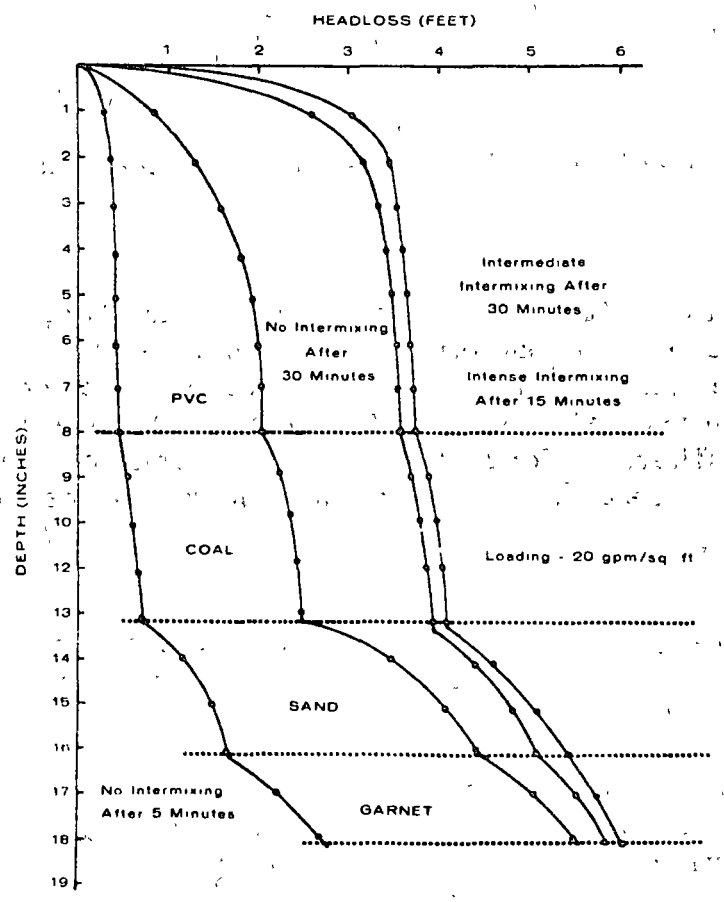

FIG. 6
Headloss for Multimedia Filters at Terminal Headloss

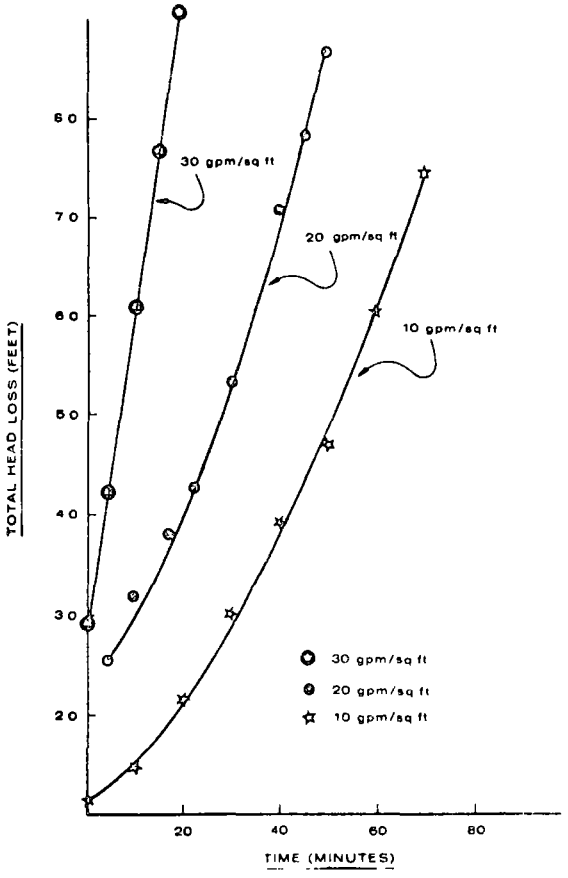

FIG. 7
Total Headloss for Multilayered Filtration of Wastewater

A device similar to the Patterson siphon used in many European water filtration plants could remove the sludge directly to the sludge handling facilities, and eliminate the need for thickening. After removal of the sludge, the filter was backwashed to an expansion of about 50 percent to remove the residual solids entrapped in the filter. Chlorination of the backwash water was included primarily to eliminate the growth of microorganisms within the filter.

Design Model

The various theoretically valid mathematical models did not provide a suitable design relationship. Therefore, the filter design models must be based on an empirical relationship.

Sakthivadivel (11) showed the validity of the hydraulic radius theory relating the hydraulic conductivity as a function of porosity. The relationship of headloss and the volume of solids removed was independent of the concentration of suspended solids as well as the hydraulic rate. This phenomenon appeared to be applicable to wastewater filtration.

The experimental data observed for the prefilter corroborate this relationship and are presented in Figure 8. The slope of the headloss buildup with solids removed is constant regardless of loading; however, there is a difference in the extrapolated intercept. The equation which describes this function is:

$$HL = ae^{b\int ECQdt} \quad (1)$$

in which

HL = headloss (ft)
E = efficiency
C = influent suspended solids concentration (pounds/gal)
Q = hydraulic loading (gpm/sq ft)
dt = increment of time

The calculated constraints for these equations are presented in Table 3 and illustrate the mathematical uniformity of slope under the various influent conditions. These constants increased significantly at extremely low influent suspended solids concentration, for example 50 mg/l. However, at higher than average influent concentrations, for example 180 mg/l, the exponent constant decreased.

The efficiency of the filter varied exponentially with time in the same manner as the headloss function:

$$E = a'e^{b't} \quad (2)$$

The constants of this function also varied with the depth of medium. The variation of constants for various depth of a PVC filter is presented in Table 4.

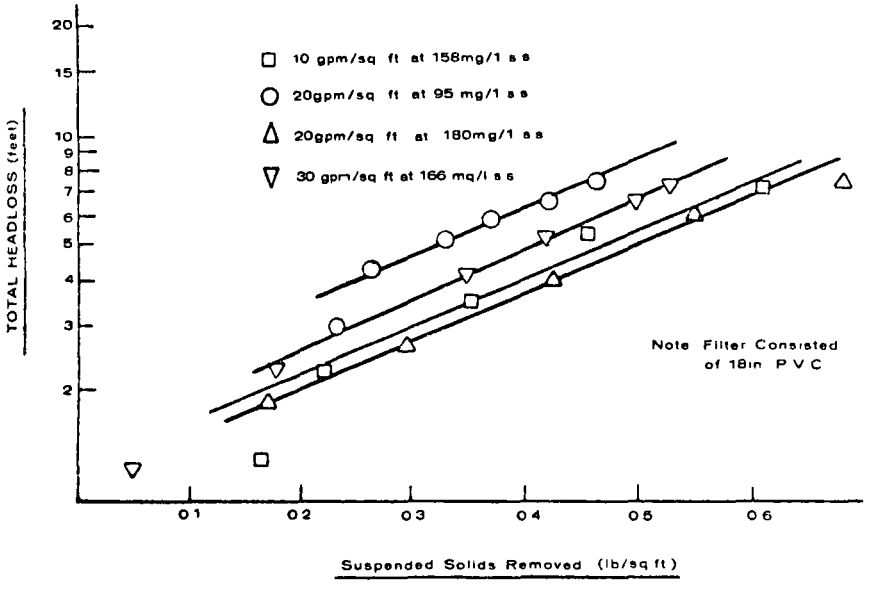

FIG. 8
Suspended Solids Removal

TABLE 3

Constants of Empirical Equation: $HL = ae^{b\int EQCdt}$

Q(gpm/sq ft)	C (mg/l)	a	b
10	158	1.16	3.20
20	95	1.87	3.23
20	180	1.11	3.02
30	166	1.36	3.20

TABLE 4

Constants for Empirical Equation $E = a' e^{b't}$

Filter Depth (inches)	a'	b'
6	0.85	-2.72
12	0.61	-1.27
18	0.46	-0.46

Note: Constants for filtration time in hours.

The effects of depth and time on the suspended solids removal efficiency for PVC under constant conditions are presented in Figure 9 . These data indicate that in a filter of sufficient depth operating under relatively constant influent conditions, the efficiency is independent of time and the equation can be approximated as:

$$HL = ae^{b\bar{E}cqt} \tag{3}$$

The above equation can also be written for the multilayer filter, but with the constants a and b chosen for the entire filter as a unit. This approach was shown to be empirically valid and is illustrated in Figure 10. The constants determined graphically for this function resulted in:

$$HL = 3.25\, e^{1.90 \int EQCdt} \tag{4}$$

The design of a filter of this type must include several conditions and constraints: a) each layer of the multilayered filter should be sufficiently deep to keep from

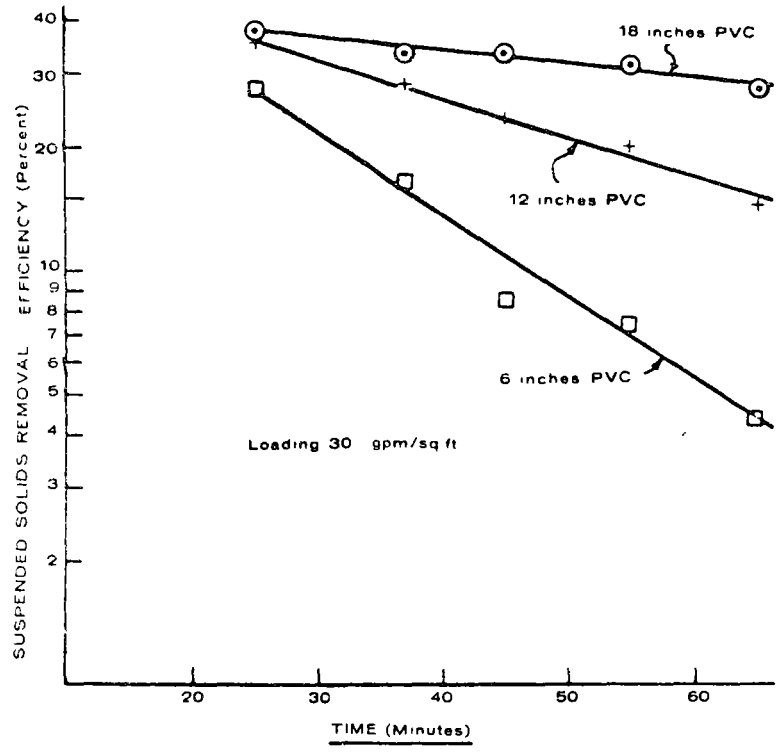

FIG. 9
Suspended Solids Removal Efficiency for Various Depths of PVC Pellets

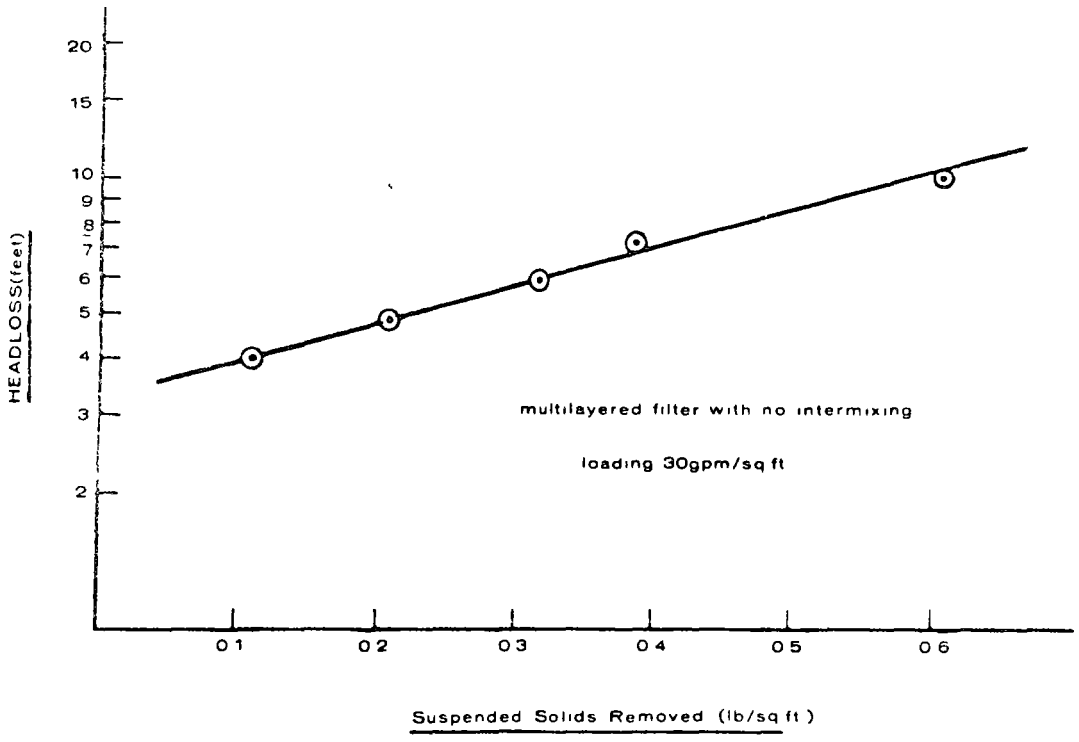

FIG. 10
Headloss and Suspended Solids Removal for Multi-Layered Filter

early breakthrough to the immediately lower layer; b) the filtration system should have the capacity to withstand the maximum suspended solids and hydraulic loadings; the design flows in the operation of this filtration process must be the maximum hourly or maximum three to four hour flow; c) the rate of headloss buildup combined with the maximum pumping capacity must not be exceeded by the time requirements of the backwash. For example, if the rate of headloss buildup is 100 ft/hr with maximum pump capacity of 100 feet and a typical backwash down time of 15 minutes, five filters would be required with one constantly being backwashed. Therefore, the time of run is confined to one hour, which also would mean that the design conditions would have to be for the maximum hourly flow and/or suspended solids loading.

Using the constants developed for the case investigated, the required design parameters are calculated by estimating the most serious conditions expected. As an example assume:

HL	=	$4.0\,e^{1.2\ EQCt}$
Maximum SS	=	450 mg/l
Hydraulic Loading	=	30 gpm/sq ft
Efficiency	=	70 percent
Pump Capacity	=	100 psi (231 feet)

Therefore:

$$231 = 4.0\,e^{1.2(0.70)\ (6.75\ lb/hr\ sq\ ft)t}$$
$$4.05 = 1.2\ (0.70)\ (6.75)\ t$$
$$t = 0.71\ hr\ or\ 42\ min.$$

The area needed for the filtration facility must include the loading and backwash requirements. The area required is based on the flowrate divided by the loading, and the backwash requirement is included as a percentage of this calculated loading area. Therefore, the requirement for a 14-minute backwash cycle is:

$$14/42 = 0.33$$

Therefore, 33 percent additional area is required to maintain constant backwash of the system. In a four filter treatment plant, one filter would be being backwashed continuously.

Process Potential

The multilayered filter can remove from 60 to 65 percent of the influent suspended solids and provides the same degree of treatment as primary clarification. It should also be noted that the results of this study are for a moderately weak wastewater. However, the data indicate that the efficiency of filtration increased with increased suspended solids concentration. The multimedia filter would require considerably less land than a primary clarifier. For example, a clarifier designed to operate at 1.0 gpm/sq ft (1440 gal/day-sq ft) would require from 10 to 30 times as much land as multimedia filters, depending on the hydraulic loading.

The land value purposely was not included in evaluating the economics to illustrate the competitiveness of the process. A comparison of the cost of a 20 MGD facility is presented in Table 5. The capital cost is $192,000 for filtration and greater than $207,000 for primary sedimentation.

The results of the studies on backwashing indicate that an air wash coupled with a very low rate hydraulic wash for a short period would remove most of the entrapped material in the form of a sludge blanket containing two to five percent solids.

Conclusions

(1) A new concept in municipal wastewater treatment is introduced which provided a design model for the ultrahigh rate in-depth multilayered filtration of untreated municipal wastewater.

(2) The use of PVC pellets as a fourth medium overlaying coal, sand and garnet in the multimedia filter was the major contribution to the success of the process. The large grain size was responsible for prevention of surface mat formation which made the process unfeasible.

TABLE 5

Cost Comparison of Primary Sedimentation with Multilayered Filtration

Primary Sedimentation	
Capitol Cost	$207,000 (12) 315,000 (13)
Filtration	
Disc Screen	15,000
Tanks and Controls	65,000
Media	17,000
Piping	80,000
Pumps, Motor and Base 5 @ $3,000	15,000
	$192,000

Note: Design for 20 MGD facility 1970 ENR Construction Cost Index

(3) The suspended solids removal efficiency at the ultrahigh loading rate of 30 gpm/sq ft ranged between 60 and 65 percent, and the efficiency increased as the influent concentration increased.

(4) A non-intermixed media filter was more efficient in the removal of suspended solids and rate of headloss increase than a moderately and intensely intermixed media.

(5) A backwash technique that produces a two to four percent sludge was possible using an air backwash followed by a short settling period. After sludge removal, the normal backwash with surface wash was employed.

(6) An empirical relationship for filter design was developed, which can be applied after observing the total headloss and filter efficiency with time.

(7) The cost of the filtration process is economically competitive with primary clarification, excluding the cost of land. A conservative estimate of the difference of land requirements for a 20 MGD facility would be 12,000 square feet for clarification and 400 square feet for filtration, representing a savings of approximately 97 percent.

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10. W. R. Hancuff, Jr. and J. F. Malina, Jr., Technical Report CRWR, EHE, Center for Research in Water Resources, The University of Texas, Austin, 115 (1972).

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12. U.S. Environmental Protection Agency, Technology Transfer, Washington, D.C. (1971).

13. U.S. Federal Water Pollution Control Administration, Rept. No. TWRC-6, Robert A. Taft Water Research Center, Cinn. Ohio (1968).

MCKINNEY-ECKENFELDER MATH MODEL COMPARISON

SUBSTRATE REMOVAL

1. $S_e = \frac{S_a}{K_1 t + 1}$ (McKinney)

where: S_a = influent BOD concentration, mg/l

S_e = effluent BOD concentration, mg/l

t = aeration time, units consistent with K_1

K_1 = overall BOD removal coefficient, mg/l BOD removed per mg/l BOD remaining per day

2. $S_e = \frac{S_o}{kX_v t + 1}$ or $\frac{S_o - S_e}{X_v t} = kS_e$ (Eckenfelder)

where: S_o = influent BOD concentration, mg/l

k = BOD removal rate, mg/l BOD removed per mg/l VSS per day

X_v = volatile suspended solids concentration (VSS), mg/l

$kX_v = K_1$

DEGRADABLE SOLIDS (Active Mass)

1. $X_d = \frac{K_2 S_e}{1/G + K_3}$ (Mc Kinney)

where: X_d = degradable solids concentration, mg/l

K_2 = sludge synthesis factor, mg/l active mass formed per mg/l oxygen demand remaining per day

G = sludge age, days

K_3 = endogenous metabolism factor, mg/l degradable mass oxidized per mg/l degradable mass remaining per day

2. $M_a = \frac{xX_v}{0.7} = \frac{aS_r/t}{1/G + k_b}$ (Eckenfelder)

where: $M_a = X_d$

x = degradable fraction of VSS

a = mass yield rate, lb VSS produced per lb substrate metabolized

S_r = substrate removed, mg/l

$aS_r/t = K_2 S_e$

$k_b = K_3$

RESIDUAL SOLIDS (About 20% of the oxidized cellular material remains as inert volatile solids)

1. $X_r = 0.2 K_3 X_d G$ (McKinney)

where: X_r = endogenous mass concentration (VSS basis), mg/l

2. X_v (non-biodegradable) = $0.2 k_b M_a G$ (Eckenfelder)

Note: $X_v = X_d + X_r$

INERT SOLIDS (Composed of inert influent solids-both volatile and inorganic-accumulated in the system and the portion of cellular material inorganically inert-about 10%)

1. $X_i = f_i SS\ G/t + 0.1\ (X_d + X_r)$ (McKinney)

where: X_i = inert solids accumulated, mg/l

f_i = fraction of influent suspended solids which are biologically inert (about 55%)

SS = influent suspended solids concentration, mg/l

2. $X_i = X_v/f_v - X_v$

where: f_v = % volatile of MLSS

TOTAL SOLIDS ACCUMULATION

1. $X_T = X_d + X_r + X_i$ (McKinney)

$\triangle X_T = X_T/G$

2. $X_T = X_v + X_i$ (Eckenfelder)

$\triangle X_v = X_T/G$

EFFLUENT SOLIDS

1. $X_e = f_e X_T$ (McKinney)

where: X_e = effluent suspended solids, mg/l

f_e = fraction of system solids lost at peak influent flow rate and at maximum system solids concentration

EFFLUENT BOD

1. Eff. $BOD_5 = S_e + 0.84 (X_e) X_d/X_T$ (McKinney)

2. Eff. $BOD_5 = S_e + f (X_{v_e})$ (Eckenfelder)

where: f = BOD_5 equivalence of effluent VSS

X_{v_e} = effluent VSS

OXYGEN REQUIREMENTS (Oxygen Uptake Rate)

The oxygen uptake rate at the selected sludge age can be calculated as the oxygen equivalent of the removed substrate per day less the oxygen equivalent of the solids degraded per day.

1. $R_r = \frac{1.5 (S_a - S_e)}{t} - \frac{1.42 (X_d + X_r)}{G}$ (McKinney)

where: R_r = oxygen uptake rate (mg/l-day)

2. Alterratively, the daily oxygen requirements can be computed as follows:

$$R_r = \frac{0.5\ (S_a - S_e)}{t} + 1.42\ (0.7)\ (K_3)\ (X_d) \qquad \text{(McKinney)}$$

3. $$R_r = \frac{a'\ (S_r)}{t} + 1.42\ (x)\ k_b\ X_v \qquad \text{(Eckenfelder)}$$

where: a' = synthesis oxygen demand rate, lb O_2/lb substrate synthesized

REFERENCE

Goodman, B. L. and Englande, A. J., "A Unified Model of the Activated Sludge Process," Journal Water Pollution Control Federation, 46, 312 (1974).

PRE AND POST TREATMENT OF BIOLOGICAL EFFLUENTS*

TERTIARY TREATMENT - processes employed following secondary treatment for the removal of non-biodegradables (refractory organics), dissolved salts, nutrients (nitrogen and phosphorus) and microorganisms (bacteria and viruses)

POLLUTANTS

Refractory Organics - ABS, aromatics, chlorinated hydrocarbons, etc.

Dissolved salts - Sulfates, chlorides, hardness, etc.

Nitrogen and Phosphorus - NH_3, NO_3, organic nitrogen, ortho, and poly-phosphates

Microorganisms - pathogenic bacteria, cysts and viruses

The characteristics of some secondary sewage effluents are shown in Table 1. Typical requirements for a reclaimable water are shown in Table 2. The average increase in constituents by one reuse of water is shown in Table 3.

TREATMENT PROCESSES

A. NITROGEN REMOVAL

1. Ammonia Stripping

$$NH_4^+ \rightleftharpoons NH_3\uparrow + H^+$$

At high pH the equilibrium shifts to right and the NH_3 is liberated as a gas; at pH 8.0, 8% of N as NH_3; at pH 11.0, 98% as NH_3 (77^oF).

TABLE 1

CHARACTERISTICS OF SECONDARY SEWAGE EFFLUENTS

Constituent	Location			
	Stevenage, G.B.[1]	Amarillo[2]	Tahoe[3]	Haddenfield[4]
Total solids, mg/l	728	557		520
Suspended Solids, mg/l	15	11		
BOD	9	10		
COD, mg/l	63		120	90
Surface Active Matter,, mg/l	2.5		1.8	2.0
Organic Carbon, mg/l	20			
Phosphate (as P), mg/l	9.6	9.0	9.2	10.5
Nitrogen (as N), mg/l	43.9	22.3	31.0	21
Sulfate, mg/l	85	78		
Chloride, mg/l	69	83		45
Color	50			
pH	7.6	.7.7		7.8
Hardness, mg/l $CaCO_3$	249	250		98
Alkalinity, mg/l $CaCO_3$		334		160

[1]Eden, G. E. et al, Chem. and Ind. p. 1517, 1966 (Br.)

[2]Treatment of Sewage Plant Effluent for Industrial Reuse, Eimco Corporation, 1966.

[3]Culp, G. and Slechta, A., Final Report, USPHS Dem. Grant 86-01

[4]Downing, D. G. et al, Desal Process, AIChE, May 1967.

TABLE 2

DESIRED QUALITY OF RECLAIMABLE WATER AT WINDHOEK, S.W. AFRICA*

Constituent	Conc. mg/l
NH_3-N	5
NO_3-N	10
Total N	20
PO_4	1
P.V. filtered	5
P.V. total	10
BOD_5 filtered	5
BOD_5 total	10
SS	50
TDS	600

* Cillie et al

TABLE 3[1]

AVERAGE USE INCREMENTS FOR 22 U.S. CITIES

Constituent	Avg. increase, mg/l
Na	66
Ca	18
Mg	6
NH_4	15
Cl	74
SO_4	28
HCO_3	100
NO_3	10
SiO_3	15
PO_4	24
TDS	320
BOD	16
COD	87

[1]Neal, J. H., Advanced Waste Treatment by Distillation, AWTR-7 U.S.P.H.S. Report 999-Wp-9, 1964.

Kuhn (1) showed 92% NH_3 removal from sewage effluent with a pH of 11.0 and an air rate of 3740m^3/m^3 (500 ft^3/gal) in a 2.13 ft tower packed with Rashig rings at 12.21 liters/m^2 (0.3GPM/ft^2) loading. Prather (2) showed 95% removal of NH_3 from refinery waste (initial N = 100 mg/l) at 3600m^3/m^3 (480 ft^3/gal) and pH > 9.0. Culp and Slechta (3) obtained 98% removal of ammonia (initial cone = 26 mg/l) at a pH of 10.8. The detention time was 0.5 minutes and the air rate 562m^3/m^3 (750 ft^3/gal). The estimated cost of nitrogen removal by air stripping is \$5.54/1000m^3 (\$21/MG) for 93% removal and \$8.45/1000m^3 (\$32/MG) using lime. If phosphate removal is combined with ammonia stripping, the cost is reduced by \$0.95/1000m^3 (\$3.60/MG).

2. Nitrogen Removal by Ion Exchange

$$2NH_4^+ + Na_2R \rightleftharpoons (NH_4)_2R + 2Na^+$$

Preferential adsorption shows

$$Ca^{++} < Mg^{++} \lesssim NH_4^+ < K^+ < Na^+$$

so that all Ca^{++} and Mg^{++} will also be removed. Poor economics for high hardness waters. Estimated costs are \$11.80/1000m^3 (\$44.50/MG) (mostly regenerant). Economics would require regenerant reuse.

B. PHOSPHATE REMOVAL

Removal with lime; 400 mg/l (as CaO) and a pH of 11.6 reduced phosphorus (as PO_4) from 21.5 mg/l to 1.0 mg/l. 1.0-1.3 mg/l of polyelectrolyte was also used in a separation bed. (Culp and Slechta);

350 mg/l lime at pH 11 effected complete removal of phosphates and partial demineralization due to the removal of temporary hardness. NH_4 was reduced (see (a)), and removal or organic nitrogen and suspended solids also occurred. Complete bacterial removal was observed (Cillie, et al).

Removal with alum (300 mg/l); residual less than 0.2 mg/l (Parkhurst). Wuhrmann removed phosphorus by precipitation with ferric chloride ($FeCl_3$) and lime. Fe^{+++} dosages ranged from 20 - 30 mg/l with lime dosages governed by the alkalinity of the water to raise the pH to 8.0 - 8.3. The lime dosage averaged 1.5:1 of the alkalinity (i.e. 200mg/l alkalinity requires 300-350 mg/l lime). In one series of experiments phosphorus (as P) was reduced from 3 mg/l to 0.3 mg/l with 10 mg/l Fe and 110 mg/l lime.

NUTRIENT REMOVAL IN STABILIZATION PONDS

Stabilization ponds have been used for nutrient removal by algae. The problems associated with this process are the seasonal instability of algal removal of nutrients and the difficulty of separating algae from the treated wastewater. Cillie obtained 63% removal of total nitrogen from a Bio filter effluent after 14 days in a pond to which 10 percent settled sewage was added (to aid denitrification). The algae was separated by flotation with alum. Parkhurst showed 50 percent reduction in total nitrogen in a stabilization pond treating settled sewage with a

retention period of 60 days. Ninety percent algal removal and substantially complete removal of phosphate was effected by flotation or sedimentation with alum.

CHEMICAL COAGULATION OF SECONDARY EFFLUENTS

Chemical coagulation is employed for the initial treatment of secondary effluents. Coagulation is accomplished using alum and a polyelectrolyte or lime. If the effluent is from a post oxidation pond, alum (100-250 mg/l) will effectively flocculate the algae and other solids in the effluent. Separation is accomplished by flotation or sedimentation. Stander reports considerably superior results with flotation. Lime treatment of a biological treatment effluent will yield phosphate removal at high pH values which can be followed by air stripping of ammonia. Results reported from three sources are summarized in Table 4.

A new process developed by the Microfloc Corporation adds alum and a polyelectrolyte and applies the coagulated mixture directly to a separation bed. The separation bed is made up of several materials of differing specific gravity and particle size resulting in a graded filter media from coarse to fine. The effluent is applied at a rate of 203.5 liters/min/m^2 (5 gpm/ft^2) and backwashed at a rate of 610.5 liters/min/m^2 (15 gpm/ft^2).

TABLE 4

CHEMICAL COAGULATION OF SEWAGE EFFLUENT

Characteristic	Stevenage[1]		Windhoek[2]		Lancaster[3]		Tahoe[4]	
	inf	eff	inf	eff	inf	eff	inf	eff
BOD	3	1	30	1	25	4	20-40	< 1
COD	41	25	12*	1	170	55	80-160	30-60
SAA	0.8	0.7	8	4	2.5	1.5	1.1-2.9	1.1-2.9
TOC	11	10	-	-	-	-	-	10-18
P	8	1.5	10	Nil	13	0.1	8-10	< 0.3
N	1.2	0.8	35	15	13	5.3	-	-
SO_4	66	99	108	220	55	220	-	-
Cl	74	77	-	-	-	-	-	-
pH	7.8	7.4	8.5	8.0	8.5	6.6	-	-
SS	10	3	-	-	70	14	5-20	0.2-3.0
TDS	-	-	-	-	585	610	-	-

*permanganate value

[1]Coagulation with alum, 40 mg/l; Eden, G. E., et al.

[2]Oxidation pond effluent; 220 mg/l alum, followed by lime and chlorine; Cillie, G. G., et al., Adv. in Wat. Poll. Res., p. 1 (1966).

[3]Coagulation of oxidation pond effluent with 300 mg/l alum followed by dissolved air flotation; Parkhurst, J. D., Adv. in Wat. Poll. Res., Vol. 2, p. 27 (1966).

[4]Culp, G.

ACTIVATED CARBON ADSORPTION

Residual refractory organics after coagulation are removed by adsorption with activated carbon. Carbon treatment may in some cases use powdered carbon added prior to coagulation although the economics of this treatment are not favorable. Continuous carbon columns or counter flow fluidized beds are the most common systems used. Flow rates average 203.5-325.6 liters/min/m^2 (5-8 gpm/ft^2) with column depths up to 4.27 m (14 ft). Data from the Tahoe studies showed maximum adsorption of 0.5 kg (0.5 lbs)/COD/kg (lb) carbon and 0.03 kg (lbs) ABS/kg (lb) carbon. Thermal regeneration of the carbon is accomplished at 1600-1800^{o}F in a steam atmosphere where the adsorbed organics are volatilized. A carbon loss of 5-9% with each regeneration is estimated. The process effluent should have a BOD < 1.0 mg/l and a COD < 15 mg/l for domestic sewage. The present estimated costs of this treatment is based on regeneration of 71.7 kg carbon/1000 m^3 (600 lbs carbon/MG) at $0.044/kg ($0.02/lb) or $3.17/1000 m^3 ($12.00/MG). Power and labor will result in a cost of about $3.96/1000$m^3$ ($15/MG). Total construction costs are estimated at $625,000 for a 9450 m^3/day (2.5 mgd) plant to $1,860,000 for a 37,900$m^3$/day (10MGD) plant. (This includes the total tertiary treatment system.)

Stander in South Africa has reported that ammonia can be removed by chlorination to monochloramine prior to applying the effluent to a coke column.

ION EXCHANGE

Ion exchange can be employed for the partial demineralization of pretreated sewage effluent. Sanks and Kaufman employed a strong acid resin and a weak base resin with CO_2 removal between the cycles. An exchange efficiency on the cation unit of 93% at a regeneration level of 4 kg H_2SO_4/100 liters (1.25 lbs H_2SO_4/ cu. ft.) [5% acid] was obtained with regenerant recovery. The overall efficiency (including regenerant makeup and reuse water) was 84% with 20-25% leakage. The anion unit was regenerated with 1.61 kg NH_3/100 liters (1 lb NH_3/ cu. ft.) [2%], and resulted in 86% exchange efficiency with 35% leakage. Reuse water requirements ranged from 1.475-2.14 m^3/m^3 (11-16 gal/ft^3). Spent regenerant was 3.3% of the water treated.

Studies have also been conducted using weakly basic phenolic resins for reversible sorption of ABS and other organics.

To minimize resin fouling and degeneration pretreatment by coagulation, sand filtration and carbon adsorption are necessary.

The recently developed Desal process uses weakly basic anion exchange structures that form a bicarbonate salt with solutions of carbon dioxide and also have a favorable chloride-bicarbonate selectivity coefficient. Two flow sheets have been proposed as shown in Figure 1. In the first, the effluent is passed through the anion exchange unit, exchanging the anions for bicarbonate:

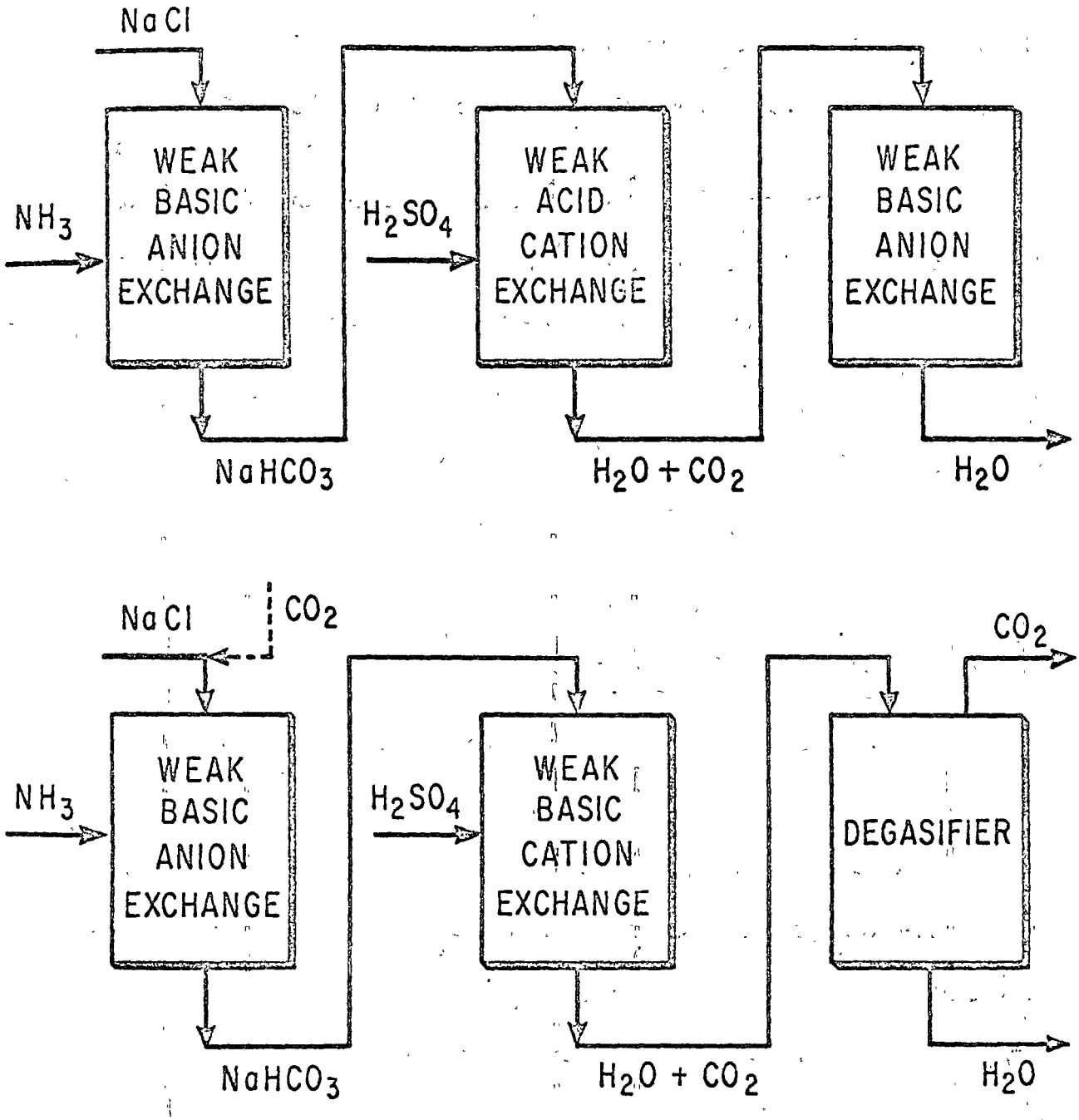


FIG. I. DESAL ION EXCHANGE PROCESS

$$(R\text{-}NH)HCO_3 + NaCl \longrightarrow (R\text{-}NH)Cl + NaHCO_3$$

The second unit contains a weak acid cation exchange resin. In this unit, the bicarbonate salts are converted to carbonic acid.

$$R\text{-}COOH + NaHCO_3 \longrightarrow RCOO\text{-}Na + CO_2 + H_2O$$

The third unit also contains the weak basic anion unit in the free base form in which the CO_2 is absorbed:

$$R\text{-}N + CO_2 + H_2O \longrightarrow (R\text{-}NH)HCO_3$$

After exhaustion, the first unit is regenerated back to the free base form with ammonia, caustic, or lime.

$$(R\text{-}NH)Cl + NH_3 \longrightarrow (R\text{-}N) + NH_4Cl$$

The cation unit is regenerated with sulfuric acid:

$$2RCOONa + H_2SO_4 \longrightarrow 2RCOOH + Na_2SO_4$$

Since the third unit is already in the bicarbonate form, the flow pattern is reversed for the next cycle.

An alternate operation replaces the third unit with a degasifier for Cl_2 removal and provides for injection of CO_2 to the feed stream of the first unit.

The flow sheets for two water renovation processes are shown in Figures 2 and 3. The South West African Process (Stander) treats Bio filter effluent followed by maturation ponds to municipal water supply. The El Paso Products plant treats municipal sewage effluent

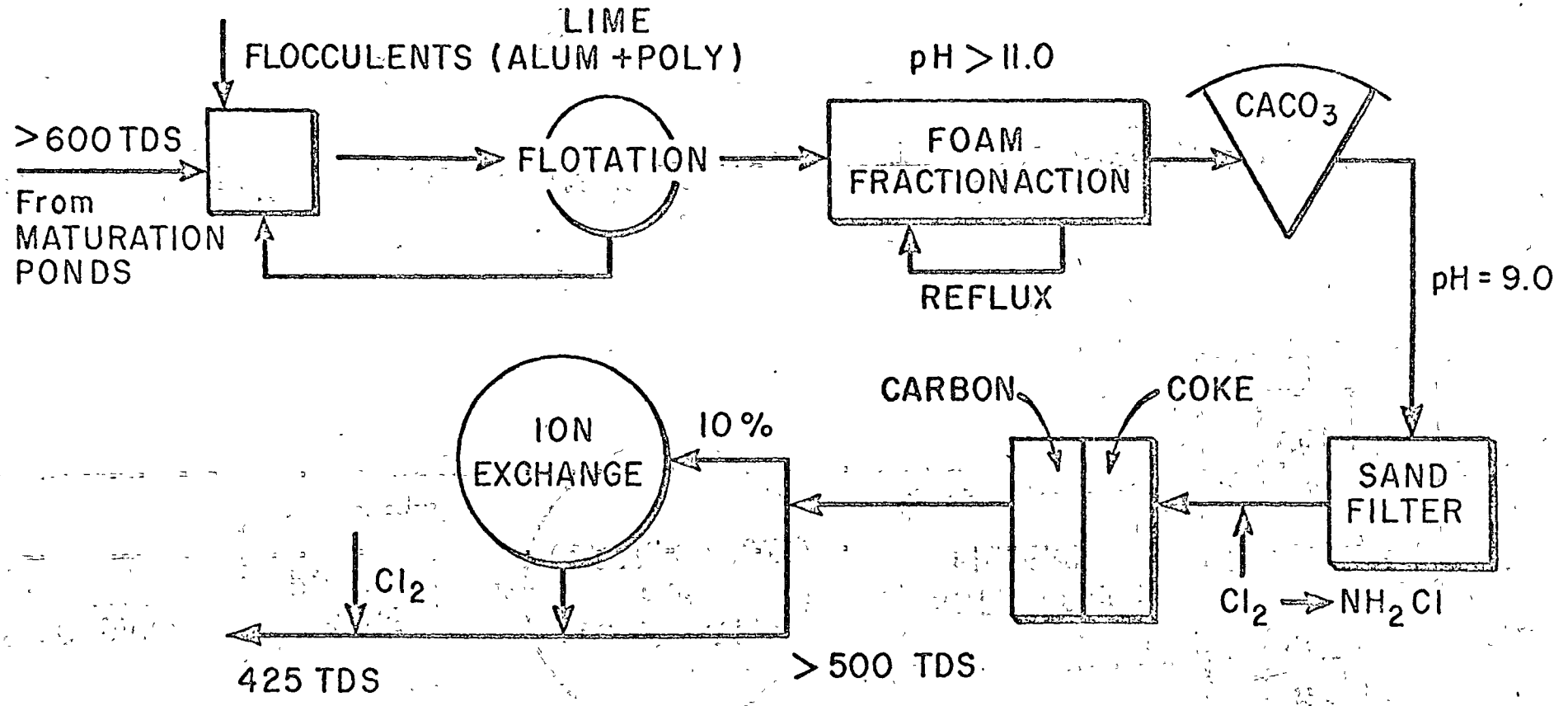


FIG. 2. WATER RENOVATION PROCESS - SOUTH WEST AFRICA

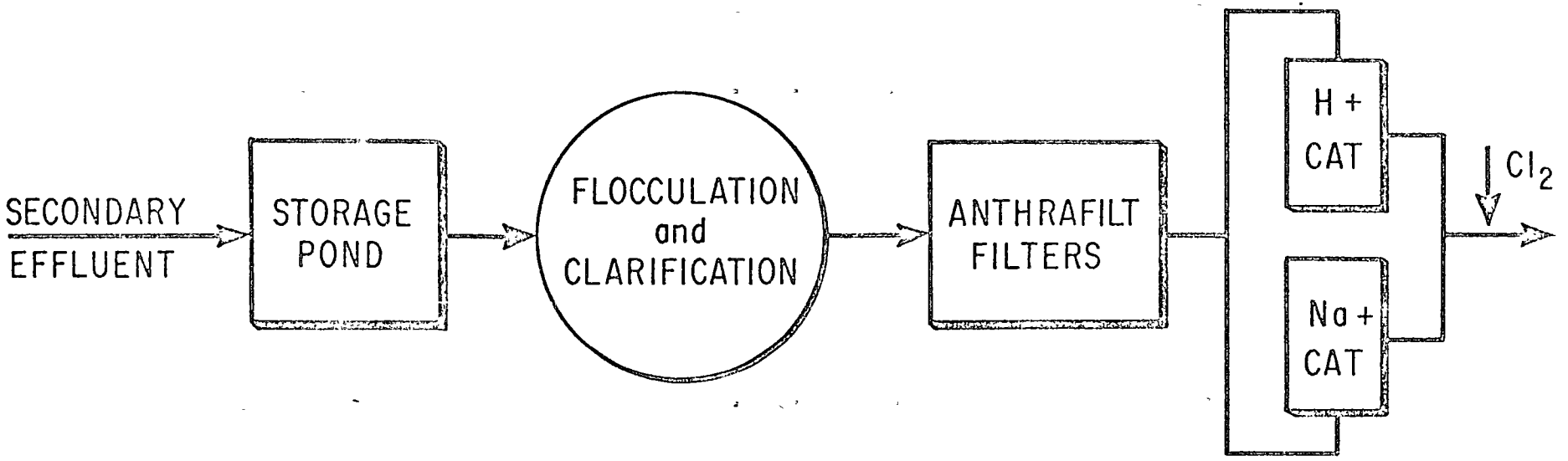


FIG. 3. WATER RENOVATION PROCESS – EL PASO PRODUCTS, TEXAS

after activated sludge for industrial process water and cooling water.

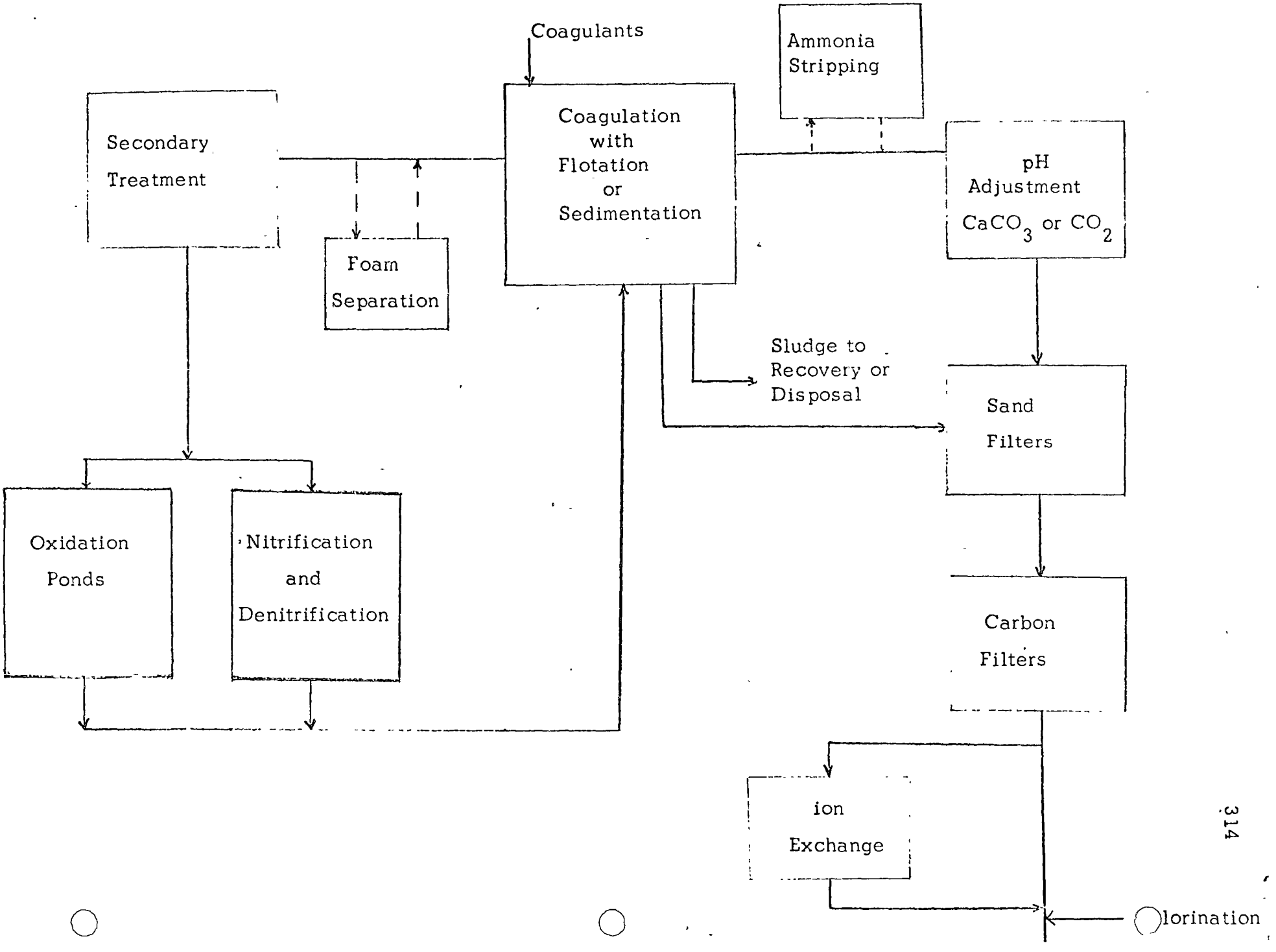
A general flow sheet for water renovation is shown in Figure 4.

ECONOMICS

Sewage effluent treatment by coagulation, sand and carbon filtration for 9450 m^3/day (2.5 mgd) has been reported to cost $625,000 to construct and $38/1000 m^3 ($0.144/1000 gal) to operate, including labor, amortization over 20 years at 3% interest. (Roderick and Culp). Treatment of sewage effluent (activated sludge) at El Paso Products including lime and alum coagulation, filtration through anthracite and cation exchange and chlorination is estimated $95/1000 m^3 ($0.36/1000 gal) for 18,950 m^3/day (5 mgd) [not including amortization]. Sanks and Kaufman have estimated ion exchange to remove 350 mg/l of dissolved solids at $50 and $39.60/1000$m^3$ ($0.19 and $0.15/1000 gal) for a 3790 m^3/day (1 mgd) and a 37,900 m^3/day (10 mgd) plant, respectively. The costs include amortization but not operating labor. Chlorination can be expected to range from $2.64/1000 m^3 ($0.01/1000 gal) to $1.58/1000 m^3 ($0.006/1000 gal) for a 3790 m^3/day (1 mgd) and 37,900 m^3/day (10 mgd), respectively.

Figure 4.

General Process for Water Renovation



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Tertiary Treatment of Secondary Industrial Effluents By Activated Carbon[a]

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TERTIARY TREATMENT OF SECONDARY INDUSTRIAL EFFLUENTS BY ACTIVATED CARBON

The increasing water needs for industrial and municipal use combined with the growing demand for more aesthetic waters for recreational purposes have made the reduction of organic pollutants imposed upon our natural waters a matter of national concern. The rapidly increasing number of pollution sources along our waterways has moved regulatory bodies to place more stringent restrictions on the qualities of wastewater discharges returned to the natural system. These restrictions and the rising cost of industrial water have caused an emphasis to be placed on the development of wastewater treatment systems producing a high quality effluent.

Many studies have been directed to a solution to this problem. Tertiary treatment of biologically treated wastewater is being considered as a practical solution. Adsorption of biologically resistant materials from secondary effluents is being investigated and of the adsorbent materials thus far evaluated, activated carbon has shown the most promise in this application.

Activated carbon is a general term applied to carbonaceous material with certain adsorptive and catalytic properties. Activated carbon is generally manufactured from raw materials such as wood, coal, lignite, sugar, vegetation, petroleum hydrocarbons, and other organic materials. These raw materials are charred in the presence of catalytic agents such as magnesium chloride or zinc chloride, then activated by treatment with oxidizing gases, which dissipate the more readily oxidizible portions of the char. The resulting carbon is highly porous containing internal surface areas as great as 2500 square meters per gram. Variations in the raw material, temperatures, additives and procedures used, result in activated carbons with widely diverse adsorptive properties (1).

The treatment of water and wastewaters followed two basic schemes. Some applications include the addition of powdered activated carbon to raw water with

subsequent separation of the carbon by coagulation and settling. The passage of raw water through a bed of activated carbon in a downward direction or in a countercurrent fashion has also been applied.

The batch mixing scheme which has been primarily used in municipal water treatment for removal of tastes and ordors, has the advantage of allowing a very small activated carbon particle to be used, which results in high adsorption rates and allows a closer control of the effluent quality. The practice is not favored among process engineers due to the required separation and the difficulty of regeneration, which are necessary at the present time for economical operations.

The use of granular activated carbon columns is generally considered to be the most practical scheme for treatment of industrial wastewaters for the following reasons; the relative ease of separation of the spent carbon for regeneration and the ability to treat water in spite of large changes in concentration without seriously affecting the effluent quality. However, many problems such as excessive residual organics, excessive head losses, corrosion of plant facilities and accumulation of dissolved solids in equipment must be effectively countered.

While continuous column operation is considered more practical than batch mixing operations, improvement of separation techniques may make powdered activated carbon treatment more desirable. The adsorptive characteristics of a steady state adsorbent-adsorbate system are affected by many factors. They may be classified into three general categories:

(1) Environmental factors,

(2) Characteristics of the adsorbent, and

(3) Characteristics of the adsorbate.

While the combined effects of these factors is difficult to predict, the following tendencies have been observed:

An increase in the rate of adsorption generally occurs with:

(1) An increase in adsorbate concentration,

(2) A decrease in particle size,

(3) A smaller size adsorbate molecule, and

(4) An increase in the surface area of the adsorbent.

An increase in the adsorptive capacity of the adsorbent in a system occurs with:

(1) A decrease in pH of the adsorbate,

(2) An increase in adsorbate concentration, and

(3) An increase in surface area of the adsorbent.

Experimental Procedures

The removal of many biologically resistant materials such as the pesticides and surface active agents may be estimated quite readily by established procedures When one compound is of primary concern these procedures may be directly applicable to estimate the concentration of the compound. However, the presence of several compounds of comparable concentrations seriously limits the use of direct measurement techniques. Any estimate of the concentration of biologically resistant materials using the biochemical oxygen demand (BOD) would obviously have little meaning. The chemical oxygen demand (COD) is also seriously limited in this application. Total organic carbon (TOC) offers a reasonable estimate of the organic concentrations in biologically treated wastewaters and is used as the organic parameter in this study. The TOC is estimated utilizing a Beckman Total Carbon Analyzer. The sensitivity of this instrument is $\pm$ 0.5 mg/l with a precision of $\pm$5%.

Laboratory evaluation of activated carbon treatment of biologically treated industrial wastewaters is seriously limited when secondary treatment units are not yet in operation. The volume of treated wastewater supplied from bench-scale treatment units is not sufficient to permit a complete evaluation of the effectiveness of continuous treatment using an activated carbon column. When evaluation is required under these conditions and no similar treated wastewater is available, the investigator must rely on batch mixing tests for preliminary

TABLE 1

WASTE CHARACTERISTICS

WASTE	COD mg/l	TOC mg/l
REFINERY WASTE NO. 1	86	23
REFINERY WASTE NO. 2	40	16
PETROCHEMICAL WASTE	107	33

TABLE 2

ACTIVATED CARBON CHARACTERISTICS

CARBON	RAW MATERIAL	MESH
A	PETROLEUM HYDROCARBONS	18x40
B	ANTHRACITE COAL	12x30
C	LIGNITE	12x20
C	LIGNITE	4x12
D	WOOD	8x12

feasability information.

Effluents from laboratory and plant scale activated sludge reactors were filtered through Whatman Number 42 filter paper to remove the suspended materials prior to testing The COD and the TOC concentration of each waste is listed in Table 1

The commercially available activated carbons tested were soaked in distilled water for 24 hours, rinsed three times in distilled water and dried to a constant weight at 103°C. A portion of each carbon was pulverized with a mortar and pestle and passed through a 270 mesh sieve which corresponds to a size opening of 0.053 mm. The original mesh size and the raw material are listed in Table 2.

Other investigators have reported that the particle size has little effect on the equilibrium adsorption. (2) (3) The agitation time required for a system to reach equilibrium has been reported to be from 5 minutes to several weeks for powdered carbon and from a week to 5 months for granular carbon. (2) (4) (5) These times were reported for various pure compound solutions and for secondary effluents. It appears that determination of the time required for complete equilibrium to be achieved is limited by the accuracy of the tests for solute concentrations. The data observed for a system involving 2-4 dichlorophenol and pulverized activated carbon indicates that adsorption is essentially complete in less than 30 minutes. Tests on the biologically treated industrial wastewater yielded similar results as shown in Figure 1 Pulverized activated carbon was used in the majority of the tests, but several tests were conducted using granular activated carbons.

Various pulverized activated carbon dosages were added to 500 ml flasks containing 250 ml of a wastewater sample. Each flask was agitated for a period of two hours by means of a Burrel shaker. The activated carbon was removed by

filtration and the filtrate analyzed for residual organic carbon. The systems containing granular carbon were agitated for periods up to 320 hours.

Carbon column tests were conducted using 2, 4 dichlorophenol solutions in the column system shown in Figure 2. Concentration time profiles from each column were recorded.

Results and Discussion

The analysis of steady state adsorption data may take several forms. The most common form is the adsorption isotherm. Among the equations applied to equilibrium adsorption data are the Langmuir equation:

$$x = \frac{x_m bC}{1 + bC}$$

x = number of moles of solute adsorbed per gram of carbon at concentration C

x_m = number of moles required to form a monolayer on the carbon surface

C = concentration at equilibrium

b = constant

and the Brunauer, Emmet, Teller (B.E.T.) Model:

$$s\ \frac{x}{x_m} = \frac{AC}{(C_s - C) + 1 + A(-1)\ C/C_s}$$

where

C_s = saturation concentration of the solute

A = constant

These equations may be deduced from either kinetic considerations or the thermodynamics of adsorption. The Langmuir equation is valid for single layer

molecule adsorption, while the B.E.T. Model reflects apparent multi-layer adsorption. (6).

The familiar Freundlich isotherm is of empirical origin, but has since been derived by assuming a logrithmic distribution of adsorption sites, a treatment valid only when there is no appreciable interaction between adsorbed molecules. (7).

$\frac{x}{m} = AC^n$

C = equilibrium concentration

$\frac{x}{m} = \frac{\text{lb adsorbate adsorbed}}{\text{lb carbon}}$

A, n = constants

The adsorption of organic solutes by activated carbon may be considered to occur in three consecutive steps:

(1) transport of the solute to the exterior surface of the adsorbent,

(2) diffusion of the solute into the pores of the adsorbent, and

(3) adsorption of the solute on the interior surfaces of the adsorbent. (6).

The rate of adsorption from wastewaters will be controlled by one of these steps. It has been reported by several investigators that the second step appears to be the controlling factor. (4) (8).

It has also been reported that the rate is related to the fractional saturation of the adsorbent. (2) (5). Since the adsorption capacity is dependent on the concentration of the solute, it is apparent that the concentration of the solute generally has a dominant influence on the adsorptive characteristics of a steady state adsorption system.

Since a mathematical representation of the adsorption characteristics for unknown mixed solutes present in biologically treated industrial wastewaters is difficult, if not impossible, the analysis of the data was approached from a practical point of view.

The data observed during the long-term batch tests indicates that commercially available activated carbon can adsorb up to 85% of the biologically resistant organic material present in treated industrial effluents Two carbons, from the same source, but of different particle size, were tested. While the smaller mesh size exhibited a higher rate of adsorption in the early stages of the tests, the removal after 320 hours of contact time was essentially the same for both samples of carbon. The bulk of the adsorption was observed to have taken place in each system tested after 100 hours contact time. The effects of initial concentrations of dichlorophenol solutions on the adsorption rate are illustrated in Figures 3 and 4.

A typical plot of the data from batch equilibrium tests using a system composed of industrial effluent and pulverized activated carbon is shown in Figure 5. The linear logarithmic relationship between adsorptive capacity and concentration indicates that the Freundlich isotherm defines the adsorption phenomenon in this system.

Isotherm data of this type may be used to compare the relative suitability of various types of activated carbon for use in the treatment of individual wastewaters to remove refractory organic material. It may also be used to estimate the carbon requirements. Assuming the adsorptive capacity to be the x/m value, corresponding an initial concentration which will be exceeded by 80 - 90 % of the time, and adjusting for regeneration efficiency; the carbon regeneration rate or the overall carbon dosage may be estimated. (Table 3)

Another application of the isotherm data has been proposed by Allen et al., (8) which incorporates the Freundlich isotherm intoan equation predicting an activated carbon column performance:

$$\frac{\text{lu } c_i/c_f}{c^n} = -\frac{T_r K q W \ln y}{vp}$$

TABLE 3

ISOTHERM DATA

CARBON	WASTE	C_o mg/l TOC	1/n	K mg/100 mg	X/M C_o mg/100 mg	LOW, C mg/l
A	REFINERY Waste #1	23	1.06	2.1	59	5
B	"	23	2.41	0.015	26	7.4
C	"	23	0.94	0.16	45	5
D	"	23	1.16	0.30	14	3.6
A	REFINERY WASTE #2	16	1.80	0.10	16	5.6
B	"	16	1.55	0.70	48	4.6
C	"	16	2.49	0.04	38	4.2
D	"	16	1.39	0.35	15	4.4
A	PETRO-CHEMICAL WASTE	33	0.98	0.08	27	11
B	"	33	3.05	7×10^{-3}	36	8.8

Where A and n are the constants from the Freundlich equation concentration and c is the local liquid concentration.

Concentration - time profiles were calculated for an activated carbon column removing dichlorophenol from solution. A comparison of the calculated and experimental values are shown in Figure 6.

Summary

Activated carbon treatment of secondary industrial effluents will remove up to 85% of the refractory organic material expressed as TOC. TOC proved to be a suitable parameter for determining the organic removal characteristics of activated carbon treatment. The Freundlich isotherm was used successfully to describe the adsorption process in initial screening studies and has a suitable application in the prediction of carbon column effluent profiles in conjunction with the equation proposed by other investigators.

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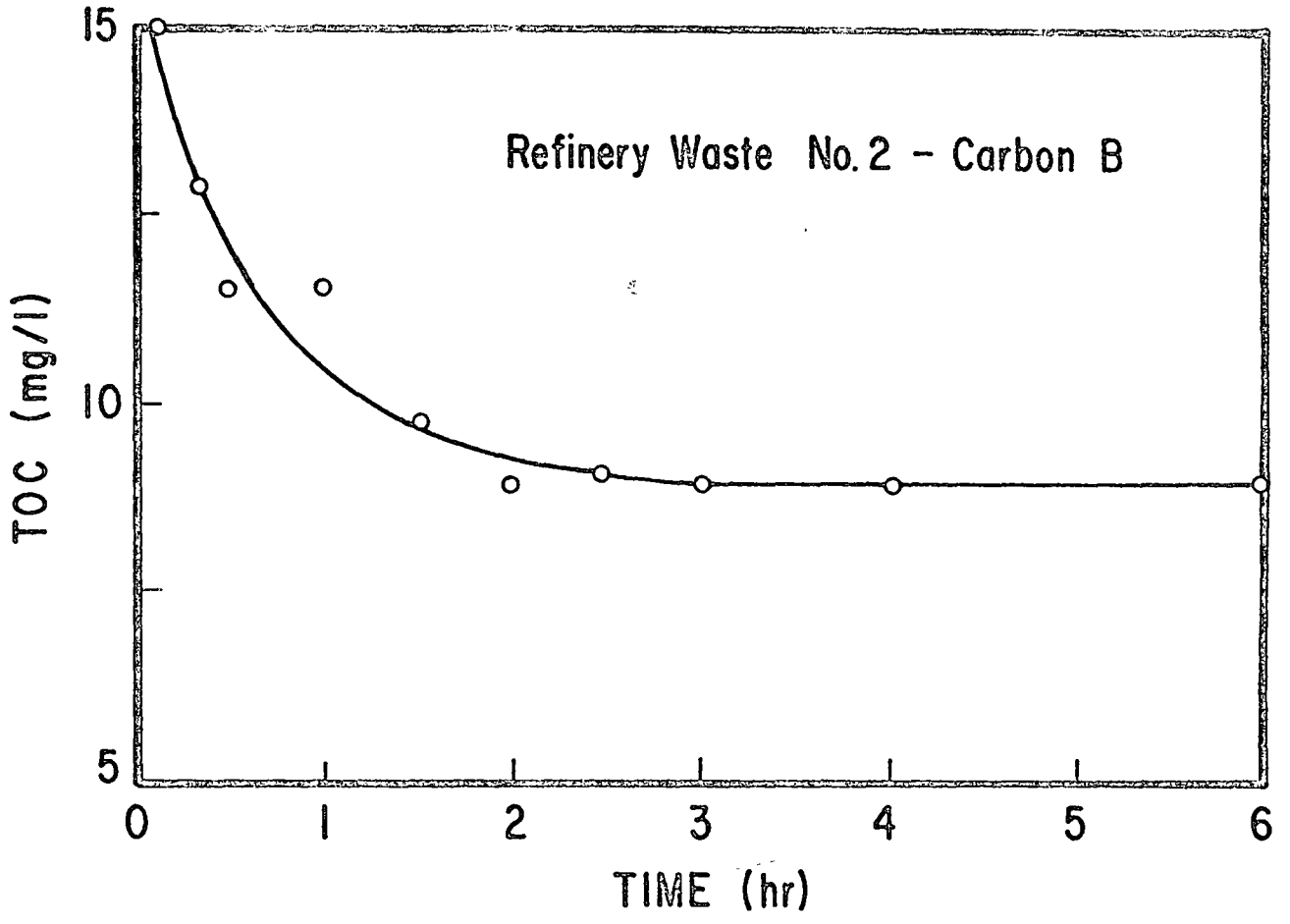

FIG. 1 - ADSORPTION RATE - PULVERIZED ACTIVATED CARBON

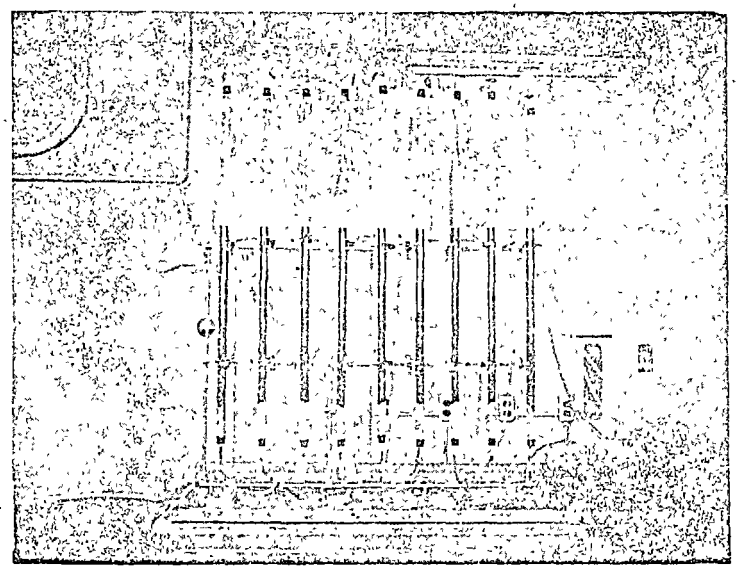

Fig. 2 - Carbon Test Columns

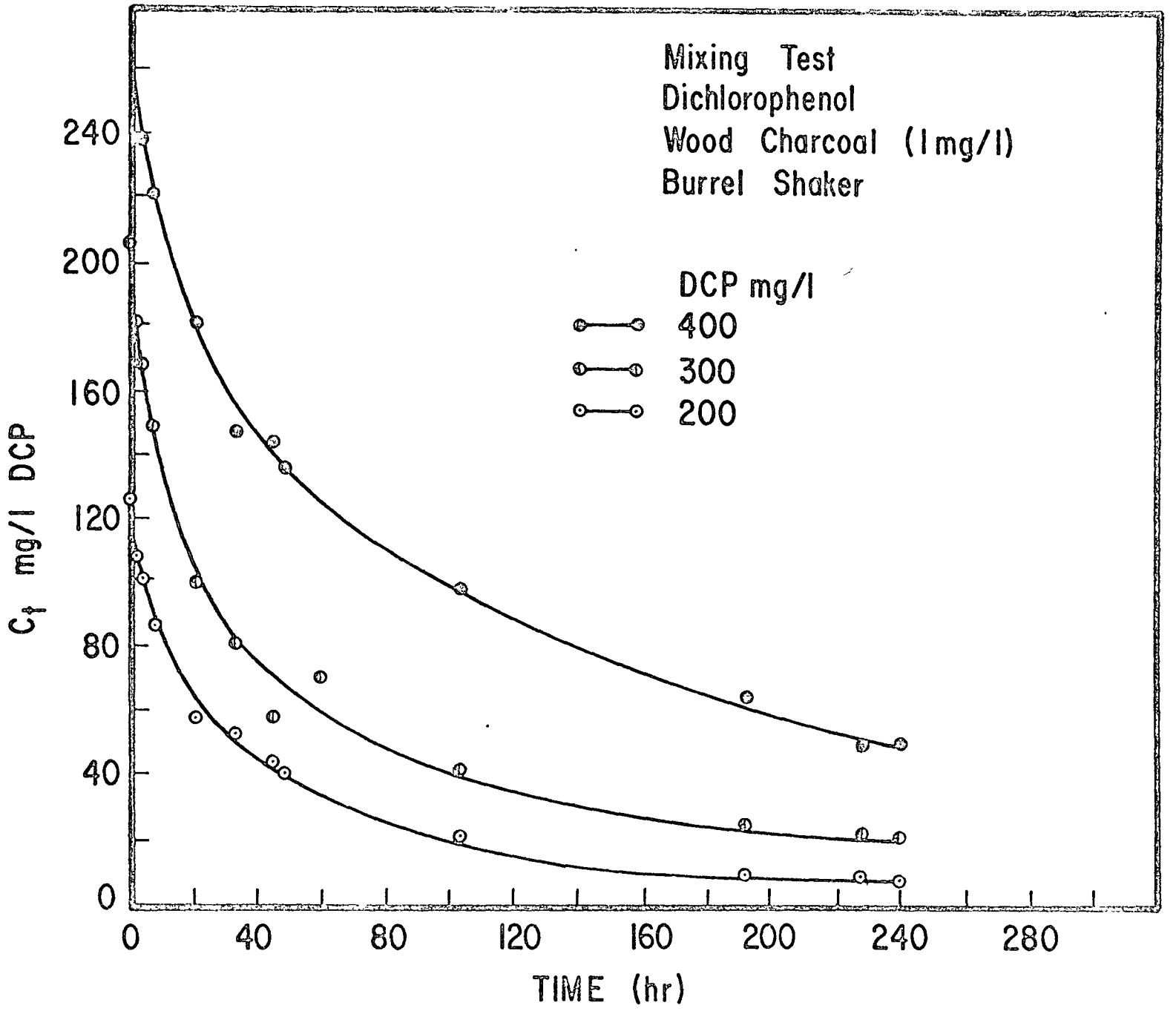

FIG. 3 - ADSORPTION RATES

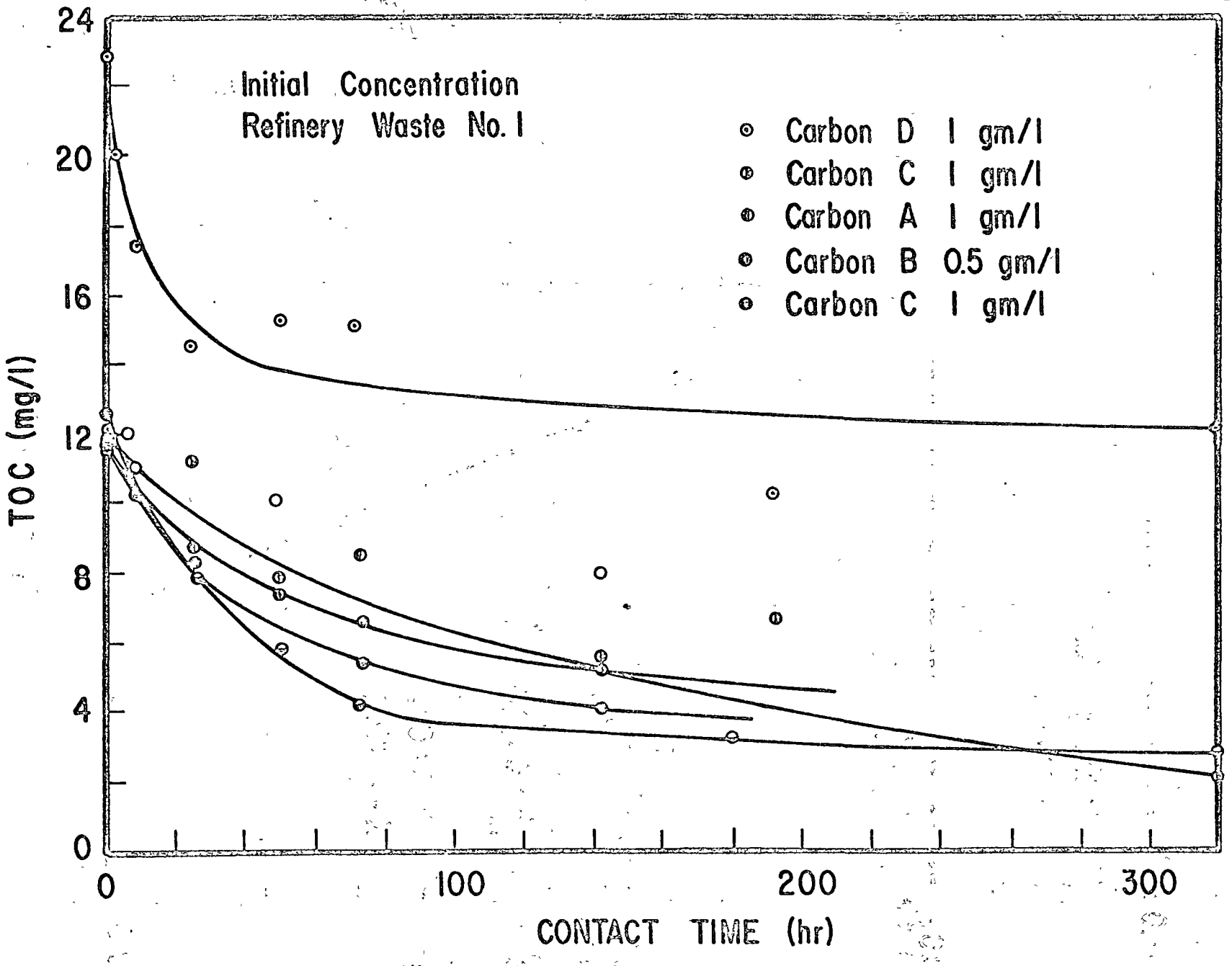

FIG. 4 - REDUCTION OF ORGANIC CARBON IN REFINERY WASTEWATER

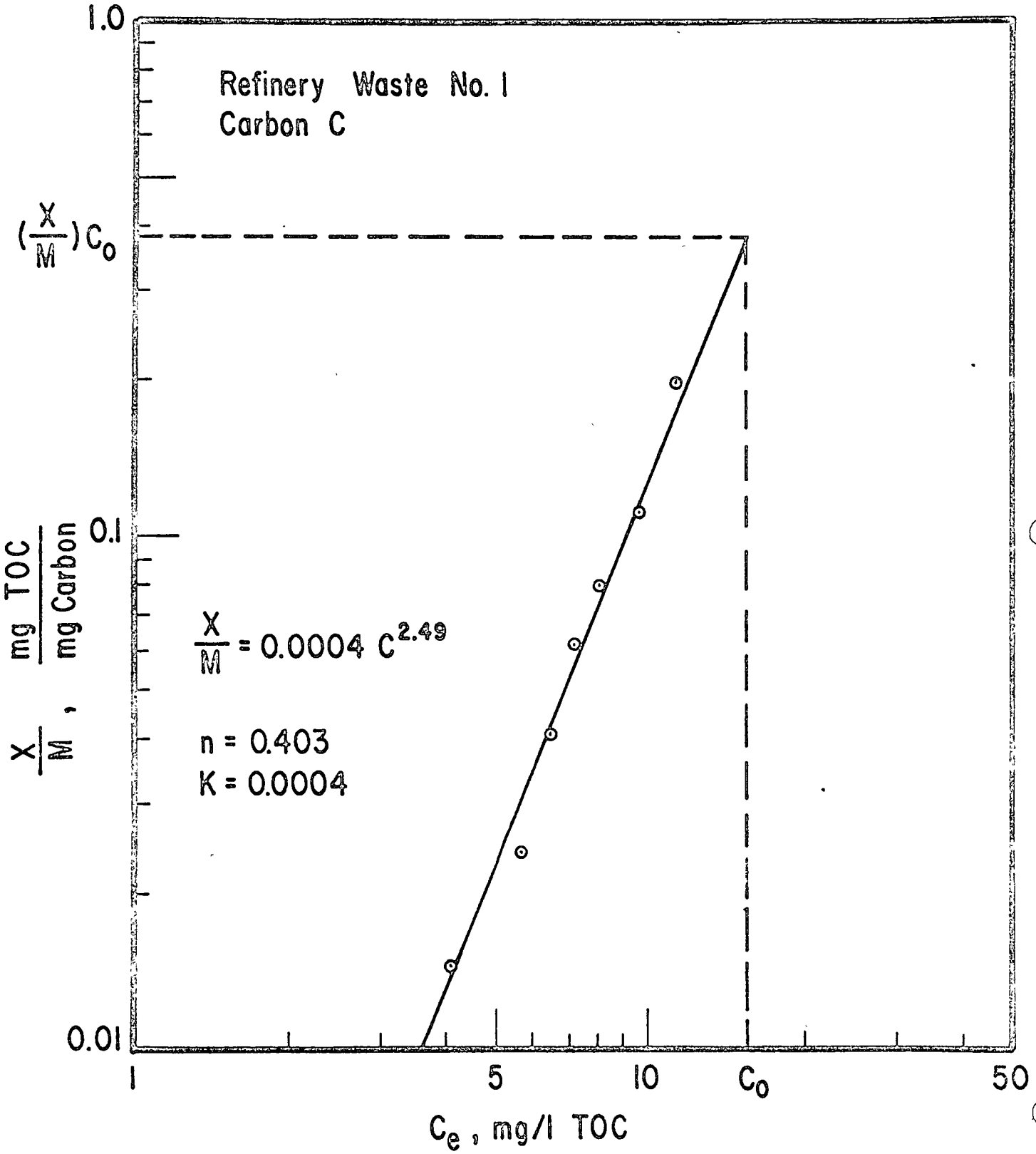

FIG. 5 - ADSORPTION ISOTHERM

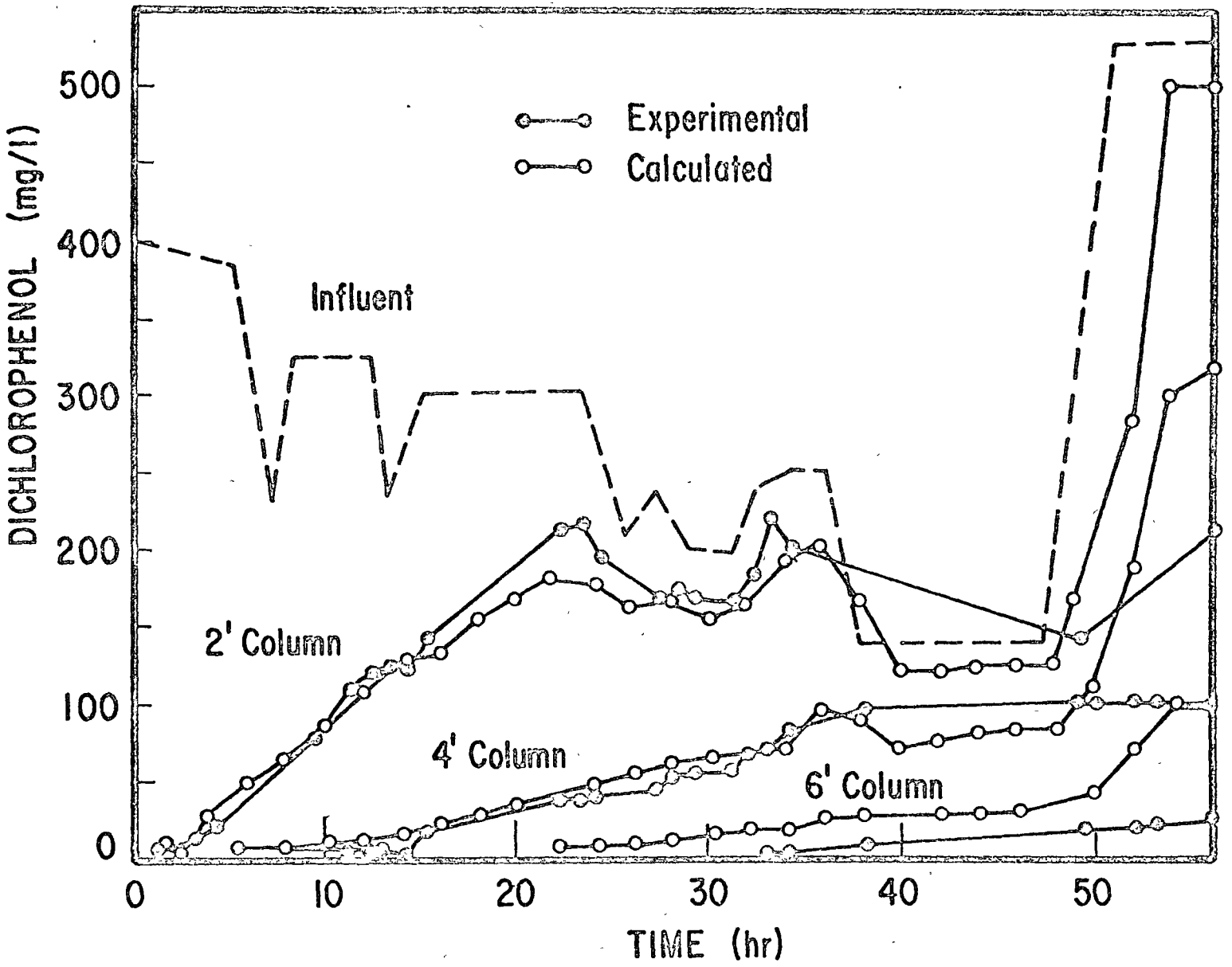

FIG. 6 - BREAKTROUGH CURVE COMPARISON