

# Elimination of Toxic Metals from Wastewater by an Integrated Wastewater Treatment/Water Reclamation System\*

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## Abstract

The overall effectiveness of a pilot-scale, integrated wastewater treatment/water reclamation plant for the removal of the eight toxic metals listed in the U.S. Environmental Protection Agency *National Interim Primary Drinking Water Regulations* (arsenic, barium, cadmium, chromium, lead, mercury, selenium and silver) was investigated. Certain unit processes in the system were shown to be capable of acting as additional safety barriers against toxic metal contamination. The most significant processes for toxic metal removal were denitrification, chemical mixing/clarification and active carbon treatment.

## Introduction

Research in the field of water reclamation technology at the National Institute for Water Research has recently been concerned with the investigation of the capability of *integrated* wastewater treatment/water reclamation systems (with combinations of biological and physical-chemical processes) to produce water of potable quality *directly* from raw sewage. These integrated systems have been shown to have considerable economic and operational advantages over the two individual systems (Van Vuuren and Taljard, 1979).

Part of the study comprised a series of investigations into the capability of an integrated system to remove a wide range of toxic pollutants. One of these investigations, namely, an evaluation of the capability of the system as a whole, as well as its various unit processes, to remove toxic metals, is described in this paper. The metals selected for the investigation were those listed in the *National Interim Primary Drinking Water Regulations* (U.S. Environmental Protection Agency, 1975), which established maximum contaminant levels for *inter alia*, eight toxic metals in drinking-water, namely arsenic, barium, cadmium, chromium, lead, mercury, selenium and silver (Table 1).

The principal forms found in aqueous solution, main industrial sources, and toxic effects of the metals and their salts are listed in Table 2 (Cheremisnoff and Habib, 1972; Shen, 1973; Sorg, 1979; Sorg, Csanady and Logsdon, 1978; Sorg and Logsdon, 1978; Tate and Trussell, 1977).

It is of the utmost importance that any system reclaiming water for potable reuse should be capable of the effective removal of these toxic metals.

For the investigation, solutions of the eight metals were

TABLE 1  
U.S. ENVIRONMENTAL PROTECTION AGENCY  
*NATIONAL INTERIM PRIMARY DRINKING WATER  
REGULATIONS FOR TOXIC METALS*

Metal	Maximum contaminant level ( $\mu\text{g}/\text{l}$ )
Arsenic	50
Barium	1 000
Cadmium	10
Chromium	50
Lead	50
Mercury	2
Selenium	10
Silver	50

injected into the feed water to the various units of a pilot-scale, integrated wastewater treatment/water reclamation plant, samples of effluent from the units collected, and the concentrations of the metals determined.

## Plant Description

The investigation was carried out on a pilot-scale, integrated wastewater treatment/water reclamation plant, situated adjacent to the Daspoort sewage works, Pretoria, and operated on screened raw sewage at a flow rate of 2,4 m<sup>3</sup>/h (Figure). A brief description of the various stages of the process is given below:

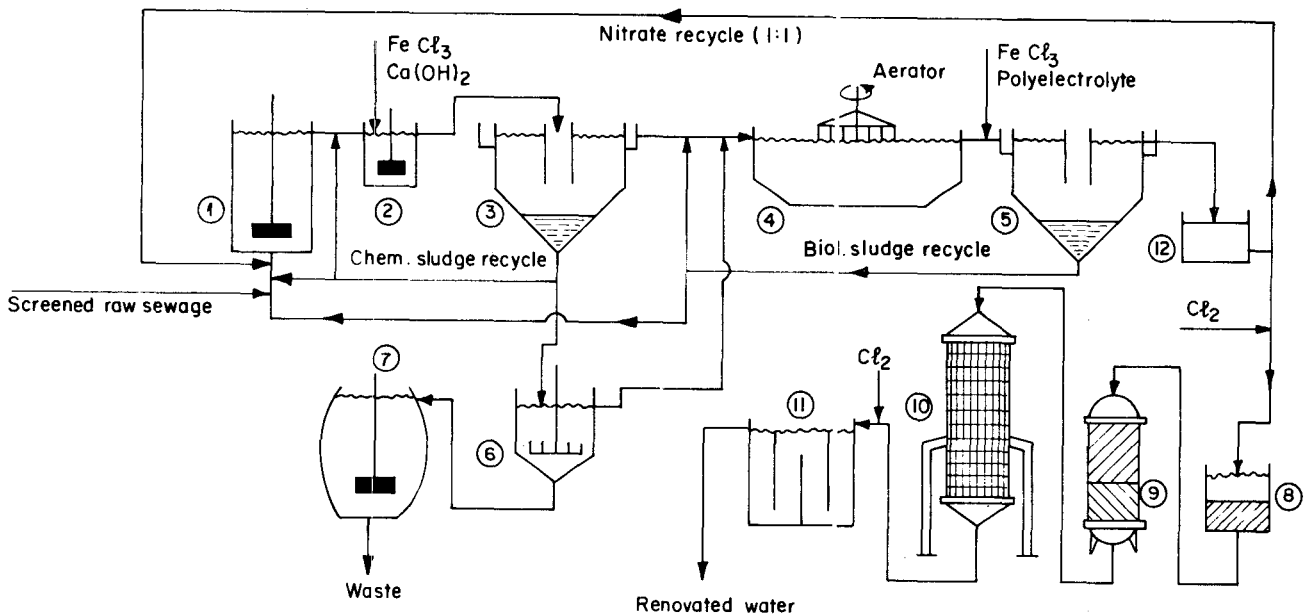
### Stage 1: Denitrification

Screened raw sewage is pumped to a 16 m<sup>3</sup> reactor at a flow rate of 2,4 m<sup>3</sup>/h, along with recycled streams from succeeding stages, consisting of nitrified effluent, chemical organic sludge, and waste activated sludge. The flow rate of recycled nitrified effluent is controlled at a ratio of 1:1, which effectively reduces the final nitrate concentration to about 12 mg/l as N. (Further reduction in the nitrate concentration can be achieved by increasing the recycle ratio of the nitrified effluent.) The recycled sludges serve as a source of carbon and micro-organisms for the purpose of partial biological denitrification.

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**TABLE 2**  
**PRINCIPAL FORMS IN AQUEOUS SOLUTION, MAIN INDUSTRIAL SOURCES AND TOXIC EFFECTS**

Metal	Principal forms in aqueous solution	Main industrial sources	Toxic effects
Arsenic	Trivalent; anion Pentavalent; anion	Insecticides, fertilizers; detergents.	Potential carcinoger; chronic toxicity from accumulation in body; ingestion of high levels causes neuropathy, vascular injury, skin cancer. Inorganic form more toxic than organic form. Trivalent form more toxic than pentavalent form.
Barium	Divalent; cation	—	Muscle stimulant; toxic to heart, blood vessels and nervous system.
Cadmium	Divalent; cation	Metal plating; photography	Associated with cardiovascular disease; causes nausea and vomiting; accumulates in liver and kidneys; recognised carcinogen.
Chromium	Hexavalent; anion Trivalent; cation	Metal plating; dyestuff mfr.	Hexavalent form causes nausea and ulcers on long-term exposure. Hexavalent form most likely form found in drinking-water. Trivalent form harmless.
Lead	Divalent; cation	Motor fuel; batteries	Accumulative body poison; causes anaemia, brain damage, paralysis.
Mercury	Divalent; cation Monovalent; cation Organic complexes	Chlorine mfr; pesticides; fungicides	Highly toxic to humans; causes stomatitis, tremors, chest pains; emotional disturbances.
Selenium	Tetravalent; anion Hexavalent; anion	Copper refining	Has both adverse and beneficial effects, depending on amount consumed. Chronic exposure causes dermatitis and gastro-intestinal disturbances.
Silver	Monovalent; cation	Metal plating; photography	Causes darkening of the skin (argyria) at fairly low concentrations. Once adsorbed is held indefinitely in the tissues.



**KEY**

- |                           |                            |                          |                              |
|---------------------------|----------------------------|--------------------------|------------------------------|
| 1. Denitrification        | 4. Nitrification           | 7. Anaerobic digestion   | 10. Active carbon adsorption |
| 2. Chemical mixing        | 5. Secondary clarification | 8. Roughing filtration   | 11. Final chlorination       |
| 3. Chemical clarification | 6. Sludge thickening       | 9. Dual media filtration | 12. Flow division            |

*Figure*  
*Schematic diagram of pilot-scale (60 kl/d) integrated wastewater treatment/water reclamation plant*

### Stages 2 and 3: Chemical mixing and clarification

Ferric chloride (75 mg per ℓ of raw sewage) and lime are mixed and fed to the reactor outflow, the pH being controlled at 7.8. Sludge is drawn continuously from the chemical clarifier and split into three equal streams, one returning to the denitrification reactor, one returning to the chemical mixing tank, and one being wasted to the thickener (stage 6), prior to anaerobic digestion (stage 7). The waste sludge serves as a reserve source of carbon during periods of weak sewage strength.

### Stages 4 and 5: Nitrification and secondary clarification

An aeration pond and a secondary clarification unit together serve as an activated sludge process stage. A further 10 mg of ferric chloride per ℓ of raw sewage, along with 0.7 mg/ℓ polyelectrolyte, are added at the clarification stage to improve the settleability of the activated sludge and to further reduce the turbidity of the effluent to below 2 nephelometric turbidity units (NTU).

### Stages 8 and 9: Filtration

Effluent from the secondary clarifier is prechlorinated and passed through a roughing filter (sand), then through a dual media filter (sand and anthracite), to give an effluent with a turbidity of less than 0.6 NTU.

### Stages 10 and 11: Active carbon adsorption and final chlorination

The filtered effluent is polished by passing it through a single active carbon column and by the application of chlorine for final disinfection.

## Experimental

Two separate solutions (one containing cadmium, chromium, mercury, arsenic and selenium, and the other silver, lead and barium) were prepared by dissolving suitable concentrations of the metal salts in tap water. The use of separate solutions was necessary in order to avoid precipitation between the lead and the chromium salts. These solutions were then continually pumped, on separate days, to the feed solutions to the various stages, to produce the feed concentrations shown in Table 3.

Details of the various investigations carried out on the individual unit processes of the system, as well as on the system as a whole, are given in Table 4. Addition and sampling times were selected so that 'plateau' levels of effluent concentration would be attained for each unit process.

TABLE 3  
COMPOSITION AND METAL CONCENTRATIONS  
OF FEED SOLUTIONS

Solution No.	Composition	Metal valency	Metal concentration in feed solution (µg/ℓ)
1	Cd(NO <sub>3</sub> ) <sub>2</sub> ·4H <sub>2</sub> O	II	900
	CrO <sub>3</sub>	VI	4 500
	HgCl <sub>2</sub>	II	150
	As <sub>2</sub> O <sub>3</sub>	III	150
	SeO <sub>2</sub>	IV	150
2	AgNO <sub>3</sub>	I	900
	Ba(NO <sub>3</sub> ) <sub>2</sub>	II	4 500
	Pb(NO <sub>3</sub> ) <sub>2</sub>	II	4 500

TABLE 4  
EXPERIMENTAL DETAILS

Stage	Nominal Retention time	Addition time	Sampling frequency
Complete process	22 h	26 h	Every hour for 4 h after 26 h from start of addition
1. Denitrification	3½ h	2 h	Every 20 min for 7 h
2,3. Chemical mixing and clarification	25 min	1 h	Every 10 min for 2 h
4. Nitrification	11½ h	3 h	Every 30 min for 7 h after 11 h from start of addition
5. Secondary clarification	25 min	1 h	Every 10 min for 3 h
8,9. Roughing and dual media filtration	30 min	1 h	Every 10 min for 2 h
10. Active carbon adsorption	1¼ h	2 h	Every 20 min for 5 h
11. Final chlorination	4 h	2 h	Every 30 min for 7 h

TABLE 5  
ANALYSIS TECHNIQUES

Element	Technique	Wavelength (nm)	Detection limit ( $\mu\text{g}/\text{l}$ )
Cadmium	Direct flame absorption — air-acetylene flame	228,8	5
Chromium	Direct flame absorption — air-acetylene flame	357,9	25
Lead	Direct flame absorption — air-acetylene flame	217,0	25
Silver	Direct flame absorption — air-acetylene flame	328,1	5
Barium	Direct flame absorption — nitrous oxide-acetylene flame (sample 5) concentrated by evaporation)	553,6	50
Mercury	'Cold vapour' generation	253,7	1
Arsenic	Hydride generation — nitrogen-hydrogen flame	193,7	2
Selenium	Hydride generation — nitrogen-hydrogen flame	196,0	2

Samples for metal analysis were collected at suitable intervals (Table 4) from the unit process under investigation, and were contained in 250 ml wide-mouthed glass reagent bottles sealed with plastic-lined bakelite caps. Each sample was preserved by the addition of 2,5 ml of concentrated AR grade nitric acid.

The concentrations of the various metals in the samples were determined by means of atomic absorption spectrophotometry as shown in Table 5 (U.S. Environmental Protection Agency, 1979).

In addition, during the investigation on the system as a whole, 250 ml samples were also collected for analysis for: Kjeldahl, ammonia, nitrate and nitrite nitrogen, total and orthophosphate, sulphate, and chemical oxygen demand (COD). These samples were preserved by the addition of 0,25 ml of a 40 g/l solution of mercuric chloride. Analysis for these determinands was carried out by automated colorimetric techniques (NIWR, 1974).

Owing to the presence of significant quantities of particulate matter, it was necessary, prior to analysis, to filter samples collected from the denitrification, chemical clarification, and nitrification units (stages 1,2/3,4). Therefore, in the case of these sets of samples, the analysis results are indicative of the composition of the clarified effluent only.

## Results and Discussion

### Capability of the System as a Whole to Remove Toxic Metals

The average concentrations of metals determined in samples taken from various stages of the plant, during a 4-hour period after the attainment of process equilibrium, are presented in Table 6.

With the exception of barium, concentrations of all the metals were reduced to values below their respective atomic absorption detection limits ('complete' removal) at or before the

TABLE 6  
ANALYSIS RESULTS (METALS) FROM INVESTIGATION OF THE CAPABILITY OF THE SYSTEM AS A WHOLE TO REMOVE TOXIC METALS

Metal	Average concentration ( $\mu\text{g}/\text{l}$ )						
	Feed	1	2/3	4	5	8/9	10 11
Cadmium	900	14	<5	71	<5	<5	<5
Chromium	4 500	30	<25	395	<25	<25	<25
Silver	900	<5	<5	<5	<5	<5	<5
Lead	4 500	100	<25	300	<25	<25	<25
Barium	4 500	650	500	870	230	90	75 80
Mercury	150	<1	<1	<1	<1	<1	<1
Arsenic	150	11	3	18	<2	<2	<2
Selenium	150	4	4	11	2	<2	<2

secondary clarification stage. Complete removal of mercury and silver and removal of almost all of each of the other metals, with the exception of barium, was effected at the first (denitrification) stage. The concentration of barium was reduced at the secondary clarification stage to around 200  $\mu\text{g}/\text{l}$ , and further reduced at the polishing stages to approximately 80  $\mu\text{g}/\text{l}$ , a concentration well below the maximum contaminant level of 1 000  $\mu\text{g}/\text{l}$ . The denitrification unit (stage 1) proved to be the most significant stage of the process for metal removal. The anaerobic conditions generated in this unit caused a considerable portion of the sulphates present to be reduced to sulphides, with resultant precipitation of heavy and other metals, and, in particular, reduction of hexavalent chromium to the relatively harmless trivalent form. Recycling of sludges

from the chemical and secondary clarification units (stages 3 and 5) would also result in the introduction of lime and ferric chloride to the denitrification unit. Thus the metal removal by mechanisms taking place in stages 3 and 5 can also occur in the denitrification unit. Some of the metals subsequently reappeared in the effluent from the nitrification stage, which may have been due to metals present in the sludge carried over to that stage either being reoxidised and dissolved or being converted to a very fine particulate or colloidal form. Some metals, especially mercury, lead and silver, will adsorb onto the natural turbidity in the water (Sorg, 1978), while others have been shown to be precipitated on mixing with raw sewage (Funke, 1975), so it is quite possible that a considerable quantity of the metals added to the feed water to stage 1 would be removed in this fashion.

Analysis of samples collected at the same time as those for the metal analysis, for Kjeldahl, ammonia, nitrate and nitrite nitrogen, total and orthophosphate, sulphate, and COD (Table 7), showed that the normal performance of the plant was not adversely affected by the continued presence, for 26 hours, of these toxic metals. Similar analyses carried out for several weeks after the addition of the metals revealed no detrimental after-effects on the capability of the system to produce water of a high quality.

### Capability of Individual Unit Processes to Remove Toxic Metals

The average plateau concentrations of metals determined in samples collected during the investigation into the capability of individual unit processes to remove toxic metals are shown in Table 8. The results show that, in some cases, individual unit processes can act as additional safety barriers against toxic metal contamination, should one or more of the preceding units cease to function normally, for example, as a result of overloading.

As has already been shown, the denitrification stage effectively removed all the silver and mercury and almost all of the other constituents, with the exception of barium.

Cadmium, chromium, mercury and arsenic were completely removed at the chemical mixing/clarification stages, while the remaining metals, again with the exception of barium, were almost completely eliminated. Chemical coagulation studies (Sorg, 1978) have demonstrated that the removal mechanisms involved may be either one or a combination of precipitation, co-precipitation and adsorption. (Many metals form insoluble hydroxides and carbonates, and will precipitate from solution. Some metals will co-precipitate with iron hydroxide, while others may form iron-metal complexes. As previously

TABLE 7  
ANALYSIS RESULTS (OTHER DETERMINANDS) FROM INVESTIGATION OF THE CAPABILITY OF THE SYSTEM AS A WHOLE TO REMOVE TOXIC METALS

Determinand (Average conc. in µg/l)	1. (Cd, Cr, Hg, As, Se)								2. (Ag, Ba, Pb)							
	Feed	Stage							Feed	Stage						
		1	2/3	4	5	8/9	10	11		1	2/3	4	5	8/9	10	11
Total Kjeldahl-N	85	38	38	3.8	1.8	1.9	1.7	1.5	93	40	19	3.0	1.6	1.5	1.1	0.9
Ammonia-N	54	23	23	1.2	<0.2	<0.2	<0.2	<0.2	31	20	18	1.0	<0.2	<0.2	<0.2	<0.2
Nitrate-N	0.2	<0.2	<0.2	12	11	11	10	11	0.2	0.3	<0.2	13	12	11	14	10
Nitrite-N	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Total-P	7.6	1.4	0.3	<0.2	<0.2	<0.2	<0.2	<0.2	9.2	0.7	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
Ortho-P	6.2	0.8	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	7.6	0.6	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
Sulphate (SO <sub>4</sub> )	110	78	70	64	67	62	61	61	100	69	67	66	65	65	64	64
COD	300	63	42	28	19	20	13	13	350	53	30	29	15	18	11	<10

TABLE 8  
ANALYSIS RESULTS FROM INVESTIGATION OF THE CAPABILITY OF INDIVIDUAL UNIT PROCESSES TO REMOVE TOXIC METALS

Metal	Average 'plateau' concentration (µg/l)								
	Feed	Stage							
		1	2/3	4	5	8/9	10	11	
Cadmium	900	20	<5	140	40	30	<5	300	
Chromium	4 500	50	<25	700	1 600	4 100	800	1 600	
Silver	900	<5	20	20	100	90	<5	230	
Lead	4 500	50	50	1 000	400	<25	<25	2 000	
Barium	4 500	600	600	600	500	1 000	120	2 300	
Mercury	150	<1	<1	<1	<1	4	2	140	
Arsenic	150	10	<2	9	30	4	<2	25	
Selenium	150	4	6	11	23	4	10	3	

mentioned, some metals will readily adsorb onto the turbidity in the water.)

Significant quantities of the metals passed through the nitrification and secondary clarification stages of the process. Mercury alone was effectively removed, again probably due to adsorption.

All of the lead, along with all but a few micrograms per l of mercury, arsenic and selenium was eliminated, probably by adsorption mechanisms, at the filtration stages, but this process proved to be particularly ineffective for barium and hexavalent chromium removal.

As expected, active carbon treatment also proved to be an effective barrier against the passage of toxic metals, particularly cadmium, silver, lead, mercury and arsenic. Most of the barium and selenium were also removed by this process. There are several ways by which active carbon treatment may effect trace metal removal. For example, the presence in the carbon of oxygen and sulphur as impurities can result in the formation of oxide and sulphido groups at the carbon surface. The oxide groups can act as weak-acid cation exchangers, while the sulphido groups may cause the carbon to exhibit chemisorptive behaviour towards metals. Secondly, nucleation sites for the precipitation of metals from solution are provided at the carbon surface. Adsorption of organo-metallic complexes from solution is also possible (Singer, 1974). Only hexavalent chromium was not effectively removed at this stage. This may have been due to the fact that the pH of the feed water to the active carbon unit is between 7 and 8, whereas Sorg (1979) has shown that granular active carbon is effective for hexavalent chromium removal only within a pH range of 5 to 6.

The final (chlorination) stage did not play a significant part in the removal of these metals.

It is quite possible that the presence of the metals in different forms or valency states, as well as variations in the operating conditions (for example, pH or temperature), could alter, to varying degrees, the removal efficiency of specific unit processes. However, the overall effectiveness of the system for the removal of these toxic metals should not be significantly affected.

## Conclusions

The overall effectiveness of an integrated wastewater treatment/water reclamation system for the removal of continuous loads of toxic metals, in particular those listed in the U.S. Environmental Protection Agency *National Interim Primary Drinking Water Regulations*, has been shown. In addition, certain unit processes in the system have been shown to be capable of acting as additional safety barriers against toxic metal contamination in the event of overloading or malfunction of preceding units. The most significant processes for trace metal removal were the denitrification, chemical mixing/clarification, and active carbon treatment stages.

Operational and economic advantages of this system, as well as its ability to produce water of acceptable microbiological quality, have been reported previously (Van Vuuren and Taljard, 1979). Other investigations carried out concurrently with the one described in this paper have also demonstrated the effectiveness of the system for the removal of continuous loads of phenols and toxic inorganic anions (Siebert, 1981) and 19 potentially hazardous organic micropollutants (Van Rensburg

*et al.*, 1980).

Therefore, for the possible alleviation of water shortages in the future, the preparation of a high quality water directly from raw sewage by means of integrated wastewater treatment/water reclamation processes, can be regarded, from economic, operational and health standpoints, as an entirely feasible undertaking.

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