REMOVAL OF TRACE INORGANIC
CONSTITUENTS BY CONVENTIONAL
WATER TREATMENT PROCESSES

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TRACE INORGANIC CONSTITUENTS OF WATER

Definitions

For purposes of classification, the principal constituents of water (Table 1) may be separated according to their concentrations in natural waters.

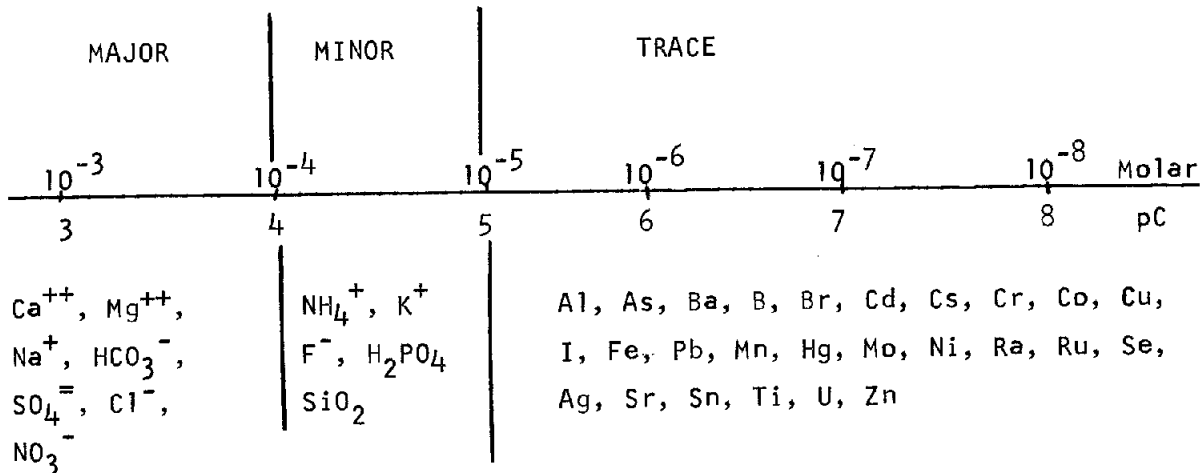| MAJOR	MINOR	TRACE		
10^{-3}	10^{-4}	10^{-5}	10^{-6}	10^{-7}	10^{-8} Molar
3	4	5	6	7	8 pC
Ca^{++}, Mg^{++}, Na^{+}, HCO_3^{-}, $SO_4^{=}$, Cl^{-}, NO_3^{-}	NH_4^{+}, K^{+} F^{-}, H_2PO_4 SiO_2	Al, As, Ba, B, Br, Cd, Cs, Cr, Co, Cu, I, Fe, Pb, Mn, Hg, Mo, Ni, Ra, Ru, Se, Ag, Sr, Sn, Ti, U, Zn		

Figure 1. Classification of Inorganic Aqueous Constituents

The "major inorganic constituents" of water may be defined as those constituents which are commonly found in concentrations in excess of 10^{-4} moles/liter.

The "minor inorganic constituents" may be defined as those constituents found in the concentration range of $10^{-4}M$ to $10^{-5}M$. This classification might include iron in ground waters ($Fe^{++} = 0.5$ mg/ℓ = $10^{-5}M$), but not in surface waters ($Fe^{++} = 0.05$ mg/ℓ = $10^{-6}M$), for example.

"Trace inorganic constituents" might then be defined as any constituent present in concentrations less than $10^{-5}M$. This category is the largest in terms of numbers of constituents. It includes those "trace metals" which are of concern because of their toxicity to humans, plants

TABLE 1

ATOMIC WEIGHTS OF PRINCIPAL AQUEOUS CONSTITUENTS

Name	Symbol	Atomic No.	Atomic Weight
Aluminum	Al	13	26.98
Arsenic	As	33	74.92
Barium	Ba	56	137.3
Boron	B	5	10.81
Bromine	Br	35	79.90
Cadmium	Cd	48	112.40
Caesium	Cs	55	132.90
Calcium	Ca	20	40.08
Carbon	C	6	12.01
Chlorine	Cl	17	35.45
Chromium	Cr	24	52.00
Cobalt	Co	27	58.93
Copper	Cu	29	63.54
Fluorine	F	9	19.00
Hydrogen	H	1	1.01
Iodine	I	53	126.90
Iron	Fe	26	55.84
Lead	Pb	82	207.2
Magnesium	Mg	12	24.31
Manganese	Mn	25	54.94
Mercury	Hg	80	200.5
Molybdenum	Mo	42	95.9
Nickel	Ni	28	58.70
Nitrogen	N	7	14.01
Oxygen	O	8	16.00
Phosphorus	P	15	30.97
Potassium	K	19	39.09
Radium	Ra	88	226.02
Ruthenium	Ru	44	101.0
Selenium	Se	34	78.9
Silicon	Si	14	28.08
Silver	Ag	47	107.87
Sodium	Na	11	22.99
Strontium	Sr	38	87.62
Sulfur	S	16	32.06
Tin	Sn	50	118.6
Titanium	Ti	22	47.9
Uranium	U	92	238.03
Vanadium	V	23	50.94
Zinc	Zn	30	65.38

and sensitive aquatic life forms.

The regulatory limits which are placed on the concentrations of toxic trace inorganic constituents in water supplies are generally in the range of 10^{-6}M to 10^{-7}M. These levels of concentration are three to four orders of magnitude less than those of the major aqueous constituents. As a resul the detection and analysis of these constituents with accuracy and precision is difficult. This difficulty is compounded by attempting to automate analyses for monitoring or regulating water quality.

Concentrations of Trace Inorganic Constituents in Natural Waters

Surface waters of the United States have been analyzed in the laboratories of the U.S. Environmental Protection Agency in Cincinnati, Ohio.[1] The summary presented in Table 2 gives averages of the concentrations of trace metals found in filtered samples of U.S. surface waters when "detectable" amounts of the indicated metal were present. These averages are strongly biased towards the high side because the "not detectable" samples were not included in the averaging. However, the data serve to indicate the upper level, order-of-magnitude concentrations of these trace constituents.

For purposes of comparison, Table 2 lists the USPHS Drinking Water Standards where they apply to trace inorganic constituents. The comparison indicates that, where arsenic and cadmium are found in surface waters, they are likely to be close to the limits set by the drinking water standards.

The data from Table 2 are plotted on Figure 2 to show the relative abundance of the trace metals. Of the seven highly toxic metals, arsenic is the most abundant. No data were available for selenium, however.

TABLE 2

TRACE METALS IN U. S. WATERS
(After Kopp and Kroner, 1969)

Trace Metal	Concentrations		1962 USPHS Standards µg/ℓ	Effect on Domestic Water Use
	µg/ℓ	Molar		
13 Al	74	2.7×10^{-6}	-	-
33 As*	64	9×10^{-7}	50	Toxic to humans
56 Ba	43	3×10^{-7}	1000	Toxic to humans
4 Be	0.2	2×10^{-8}	-	-
5 B	101	9.3×10^{-6}	1000	Plant toxicity
48 Cd*	9.5	8×10^{-8}	10	Toxic to humans
24 Cr*	9.7	1.9×10^{-7}	50	Toxic to humans
27 Co	17	3×10^{-7}	-	-
29 Cu	15	2×10^{-7}	1000	Staining, taste
26 Fe	52	9×10^{-7}	300	Staining, taste
82 Pb*	23	1×10^{-7}	50	Toxic to humans
25 Mn	58	1×10^{-6}	50	Staining
80 Hg*	(< 0.1)	$< 5 \times 10^{-9}$	5	Toxic to humans
42 Mo	68	7×10^{-7}	-	-
28 Ni	19	3×10^{-7}	-	-
34 Se*	-	-	10	Toxic to humans
47 Ag*	2.6	2×10^{-8}	50	Toxic to humans
38 Sr	217	2.5×10^{-6}	-	-
23 V	40	8×10^{-7}	-	-
30 Zn	64	1×10^{-6}	5000	Taste

*Highly toxic metals

The trace metals are grouped in Figure 2 according to their general significance. Group I, which includes aluminum, iron, manganese, molybdenum and beryllium are considered relatively non-toxic. Group II consists of those metals which are of interest because of their toxicity to plants (boron, nickel, vanadium) or aquatic organisms (zinc, copper, cobalt). The members of this group are not thought to be toxic to humans at the concentrations found in natural waters.

Group III consists of those elements for which the U.S. Public Health Service (USPHS) has promulgated standards. For purposes of comparison, the USPHS limits which would constitute grounds for rejection of the water supply are plotted on the right side of the scale. The comparison shows that arsenic, when found in U.S. surface waters, may exceed these limits. The levels of cadmium, similarly, may approach the USPHS limits set for cadmium. In general, the concentrations of chromium, silver, lead and barium found in U.S. surface waters are well below the established limits.

It appears that mercury is almost in a class by itself with respect to the extremely low limit proposed and concentrations observed. Owing to the low concentrations found in aqueous solution, little data on mercury is available, whereas because of the difficulties in analyzing for selenium, little background information is available for that element.

Toxic Metals-Aqueous Ionic Forms

As shown in Table 3, of the seven toxic trace metals (arsenic, cadmium, chromium, lead, mercury, selenium, and silver), three are principally found as anions in aqueous solution. The remainder are cations.

Complexation of these metals with inorganic and organic ligands may increase their solubility. An example is mercury which is converted, in
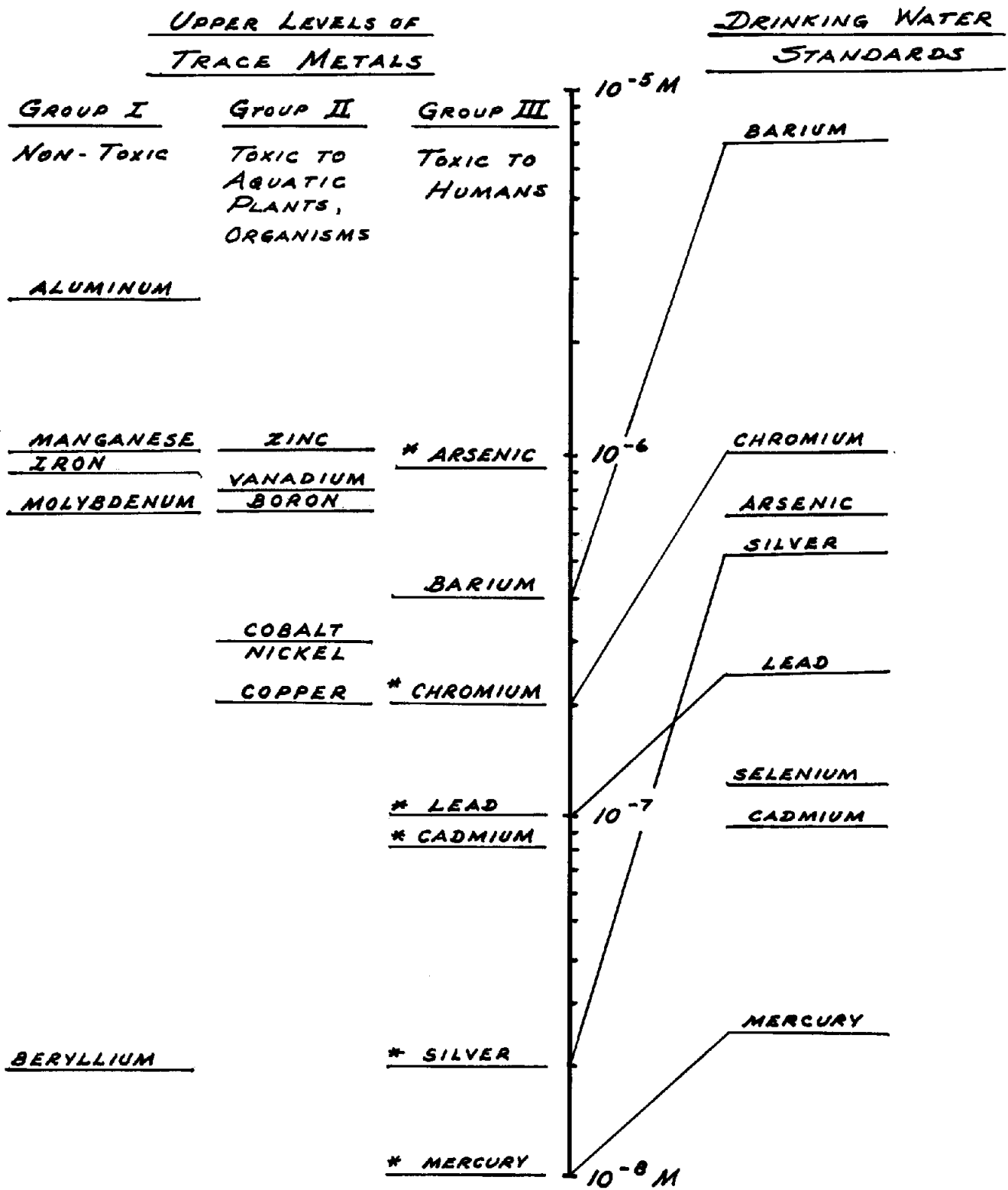
FIGURE 2. TRACE METAL CONCENTRATIONS

TABLE 3

SOURCES AND AQUEOUS IONIC SPECIES OF TOXIC TRACE METALS

Toxic Metal	Principal Aqueous Ionic Forms	Sources Mineral	Man-Made
33 As	AsO_2^- (AsIII), arsenite AsO_4^{-3} (AsV), arsenate	FeAsS As_2S_3 AsO_2 $FeAs_2$ As_4S_4	herbicides, fertilizers, detergent presoaks
48 Cd	Cd^{+2}	$CdCO_3$ CdS CdO	electroplating, photography
24 Cr	Cr^{+3} (CrIII) CrO_4^{-2} (CrVI) chromate $Cr_2O_7^{-2}$ (CrVI) dichromate	$PbCrO_4$ $Fe_2Cr_2O_4$	metal plating, industrial dyes, ink
82 Pb	Pb^{+2}	PbO, PbS $PbCO_3$ $PbSO_4$	auto and boat fuel, ammunition
80 Hg	Hg_2^{+2}, mercurous Hg^{+2}, mercuric CH_3Hg^+, methylmercury	HgS, HgO HgCl	Manufacturing of chlorine, electronics, pesticides, fungicides
34 Se	SeO_3^{-2} (SeIV) selenite SeO_4^{-2} (SeVI) selenate	trace constituent of metal sulfide ores	smelting of copper
47 Ag	Ag^+	Ag_2O, Ag Cl Ag_2S, AgF	electroplating, food and beverage processing

part, to methylmercury, an organic complex, by methanogenic bacteria in anoxic waters and sediments. This complex is transported more rapidly through the aquatic food chain than mercurous or mercuric ion.

The mineral sources of the trace metals are of interest because the removal of metals from water by precipitation processes frequently involves the reversal of the equilibrium which put the metal into solution initially. The mineral sources are predominantly metal oxides, carbonates and sulfides. All of these become less soluble with increasing pH.

Six of the toxic trace metals, the exception being chromium, react readily with sulfides and sulfur groups.

Relative Significance

Based on their ionic form, the concentrations observed in U. S. surface waters and the relative toxicity of the trace metals as judged from the USPHS limits, some subjective estimates can be made of the relative significance of the trace metals in the aqueous system (Table 4). Arsenic and cadmium, because of their relative abundance, and mercury, because of the possible formation of organic complexes, are atop the list.

Trace Metals in Ground Waters

Studies of the concentrations of trace metals in natural waters generally concentrate on surface waters. The rationale is that the surface waters are more subject to contamination from industrial wastes, mine drainage, and atmospheric contaminants than ground waters. As a result, there is far less information on the quantities of trace constituents in ground water than seems necessary for the adequate assessment of the levels of exposure to trace constituents from drinking ground water. It is true, of course,

Table 4

RELATIVE SIGNIFICANCE OF TRACE METALS

IN SURFACE WATER SOURCES

1. Arsenic   -- observed concentrations high with respect to
                   USPHS limits

2. Mercury   -- possibility of organic complexation leading to
                   extremely high toxicity

3. Cadmium   -- observed concentrations high with respect to
                   USPHS limits

4. Selenium   -- lack of adequate information on concentrations
                   in U. S. waters

5. Lead   -- high toxicity, but observed concentrations within
                   USPHS limits

6. Chromium   -- observed concentrations well within USPHS limits

7. Silver   -- extremely low concentrations observed

8. Barium   -- relatively low toxicity; low concentrations observed

that the large majority of the population of North America drinks water derived from surface water supplies. Ground water supplies are very numerous, serving many smaller communities. This tends to compound the problem of sampling and analysis.

Ground waters are often highly mineralized and, on occasion, exhibit very high concentrations of trace constituents. In addition, ground water aquifers, once contaminated, tend to remain contaminated for a long period of time. On the other hand, ground waters tend to be neutral in pH or slightly alkaline and, where carbonate deposits are present in the aquifer, they are high in alkalinity. This would serve to limit the solubility of trace metals such as lead, cadmium, mercury, silver, zinc, cobalt, as carbonates or oxides. Reducing conditions which result in the reduction of sulfates to sulfides would, similarly, result in the limitation of the solubility of metal sulfides. The deposition of metal sulfides in anoxic sediments explains the occurrence of toxic metals along with pyrites in coal deposits.

Conventional Water Treatment Processes

Treatment for removal of trace metals from water supplies is uncommon. Rarely have water treatment plants been designed with the removal of a specific trace metal in mind. In cases where gross contamination of a water supply has been observed, an alternate supply has generally been developed. The supplies involved have generally been small.

In the case of a major water supply system, however, it is not generally economic, if even possible, to develop a major new water supply source. In the event of increasing trace metal concentrations or owing to the

development of more stringent standards, therefore, existing treatment plants may have to be altered or augmented to provide for trace metal removal. Hopefully, modifications of chemical additions in conventional water treatment may be adequate to obtain a sufficient degree of removal of these elements.

The processes commonly used for water purification are listed in Table 5, "Conventional Water Treatment Processes." Most surface waters receiving treatment in North America are dosed with an aluminum or iron coagulant. The water is then flocculated, settled and filtered. Chlorination for disinfection is a process common to the treatment of water from all sources. However, the marginal dosages employed hardly classify chlorination as an oxidative process.

Softening by chemical precipitation (lime, soda ash) and ion exchange are processes employed chiefly for the treatment of ground waters. Only a fraction of the waters on the North American continent are treated for the reduction of hardness.

A still smaller fraction of the water supply of North America is treated for the removal of iron and manganese. In these cases however, oxidants, such as oxygen, chlorine and potassium permanganate are frequently employed. Often, the pH is increased to hasten the kinetics of the oxidative processes.

Finally, activated carbon is used, frequently on an intermittent or seasonal basis, for the adsorption of organic substances which cause taste, odor or color. Water supplies derived from eutrophic lakes and reservoirs commonly require this treatment.

As an approximation then, conventional water treatment can be considered to be coagulation, sedimentation and filtration possibly employing aluminum or iron salts, coagulant aids, chlorine, activated carbon and lime. The

Table 5

CONVENTIONAL WATER TREATMENT PROCESSES

1. Coagulation and filtration

    (a) Aluminum sulfate

    (b) Iron salts

    (c) Coagulant aids (clays, silica, polyelectrolytes)

2. Precipitation with lime (CaO) and soda (Na_2CO_3)

3. Oxidation using chlorine (Cl_2), oxygen (O_2), potassium permanganate ($KMnO_4$) or ozone (O_3)

4. Ion exchange, sodium cycle

5. Activated carbon sorption

latter is frequently used as a post-treatment to increase the pH so that the treated water will be close to saturation equilibrium with respect to calcium carbonate.

Mechanisms of Trace Metal Removal

Considering the processes employed in water purification, trace metal removal might be effected during conventional treatment by a number of mechanisms. These are listed in Table 6.

Freshly precipitated hydrous aluminum and iron oxides provide a large and active surface for the adsorption of trace amounts of metals. The capacity for adsorption is often strongly dependent upon pH; increasing with increased pH for many metals. Optimum conditions for the adsorption of most trace metals have not yet been clearly determined.

The precipitation of trace elements, principally as metal oxides and carbonates, would be enhanced by increased pH. This effect, in part, may account for the observed strong pH dependency of some adsorption pehnomena. A combination of pH adjustment and coagulant addition may serve to give a high degree of metal removal.

Difficulties with the removal of certain metals from drinking waters (notably, iron and manganese) have been attributed to the presence of organic complexes. Reportedly, the organo-metallic complexes may increase metal solubility, interfere with adsorption, prevent agglomeration and interfere with removal by filtration. Oxidation of the organic substances in the water by large dosages of chlorine, potassium permanganate or ozone may serve to eliminate inferences with the removal of the metal by conventional water treatment processes.

Table 6

POSSIBLE MECHANISMS FOR REMOVAL OF TOXIC TRACE METALS
BY CONVENTIONAL WATER TREATMENT PROCESSES

1. Sorption on incipient precipitates of hydrous aluminum, ferric

    or manganese oxides; sorption on clays or sediments

    removed during coagulation and filtration.

2. Precipitation as oxides, carbonates, sulfides or phosphates

    following the addition of lime (CaO) or soda (Na_2CO_3).

3. Oxidation, possibly of organic complexes, followed by

    precipitation.

4. Ion Exchange, cationic.

5. Adsorption on activated carbon, removal of metallo-organic

    complexes.

While ion exchange may be effective in the removal of both cationic and anionic constituents of water, the process is not widely used in water treatment. It is relatively costly for large installations. Moreover, a large amount of brine residue is produced through regeneration of the ion exchange media.

The addition of powdered activated carbon to existing water treatment plants is generally convenient and inexpensive. Adsorption of the organometallic complexes by the carbon might serve to enhance metal removal.

Some potential removal techniques for groups of trace metals in conventional water treatment plants are enumerated in Table 7.

Table 7

POTENTIAL REMOVAL TECHNIQUES FOR

GROUPS OF TRACE METALS

Cations | Potential Removal Techniques

Cations

Cd^{+2}

Hg^{+2}

Pb^{+2}

$Ag+$

Potential Removal Techniques

(a) Adjustment of pH

-- addition of lime (CaO)

(b) Addition of carbonate

-- addition of soda ash (Na_2CO_3)

(c) Adsorption on hydrous aluminum

or iron oxides, clays, silts,

silica, polyelectrolytes, manganic

oxides, etc.

Anions

AsO_2^-, AsO_4^{-3}

CrO_4^{-2}, $Cr_2O_7^{-2}$

SeO_3^{-2}, SeO_4^{-2}

Adsorption on hydrous aluminum

or iron oxides, clays, other

sorbents.

Organic Complexes

CH_3Hg^+, $(CH_3)_2Hg$

$(CH_3)_3As$

etc.

(a) Oxidation of organic substances

followed by precipitation or

adsorption

(b) Adsorption on powdered activated

carbon

REMOVAL OF ARSENIC BY CONVENTIONAL WATER TREATMENT PROCESSES

Laboratory studies of the removal of arsenic by adsorption on hydrous iron and aluminum oxides have indicated that trace concentrations of arsenic can be substantially reduced by conventional water treatment methods.[2] These studies employed a radioisotopic tracer, As^{74}, to follow the removal of arsenic (V) following coagulation with iron and aluminum salts.

Arsenic has been most frequently introduced into aqueous water systems in the form of the herbicide arsenite, As (III), because the reduced form of arsenic is more toxic to aquatic plant life than the oxidized form.

In the presence of aqueous oxygen, the arsenite is ultimately oxidized to arsenate, As(V). Since concentrations encountered in surface waters range up to 50 μg/ℓ, the initial concentration of arsenic used in testing was adjusted to 50 μg/ℓ. Coagulation with aluminum and iron sulfates at pH reactions ranging from 5 to 8 was conducted in a laboratory jar stirrer apparatus. Final separation of solids was accomplished by membrane filtration.

The results of the arsenic removal studies indicated that iron was more effective than aluminum in forming a hydrous oxide which removed arsenic (V), but both coagulants could be quite effective under proper conditions (Figures 3,4). Arsenic removal was somewhat dependent upon coagulant dosage and more strongly dependent upon pH. Arsenic removal was best at pH reactions at or below 7.0. This was taken as an indication that the ionic species present may have influenced adsorption (Figure 6).

Removal of Mercury by Conventional Waters Treatment Processes

Investigations of the removal of mercury from water utilized the radio-tracer, Hg^{203}, in form of mercuric, Hg(II), chloride.[3] Adsorbents
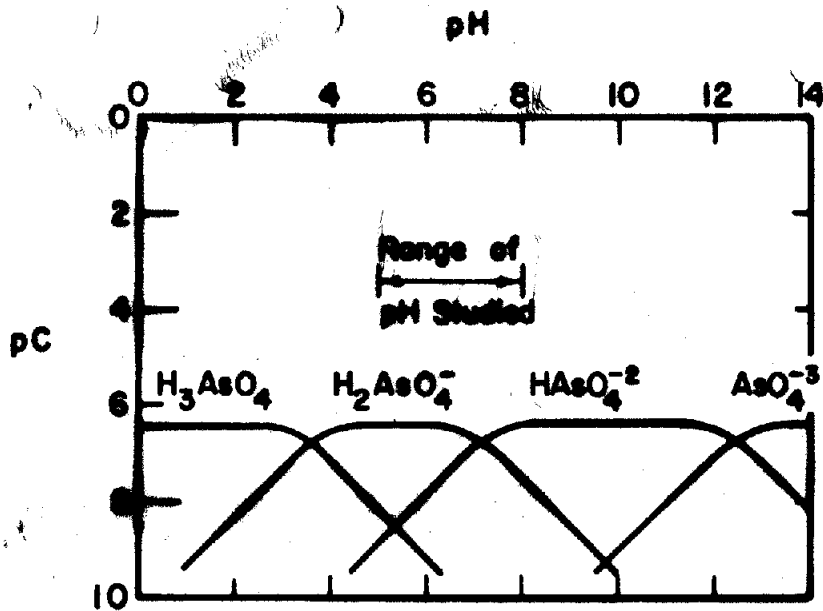
Figure 1. Distribution of Arsenic V
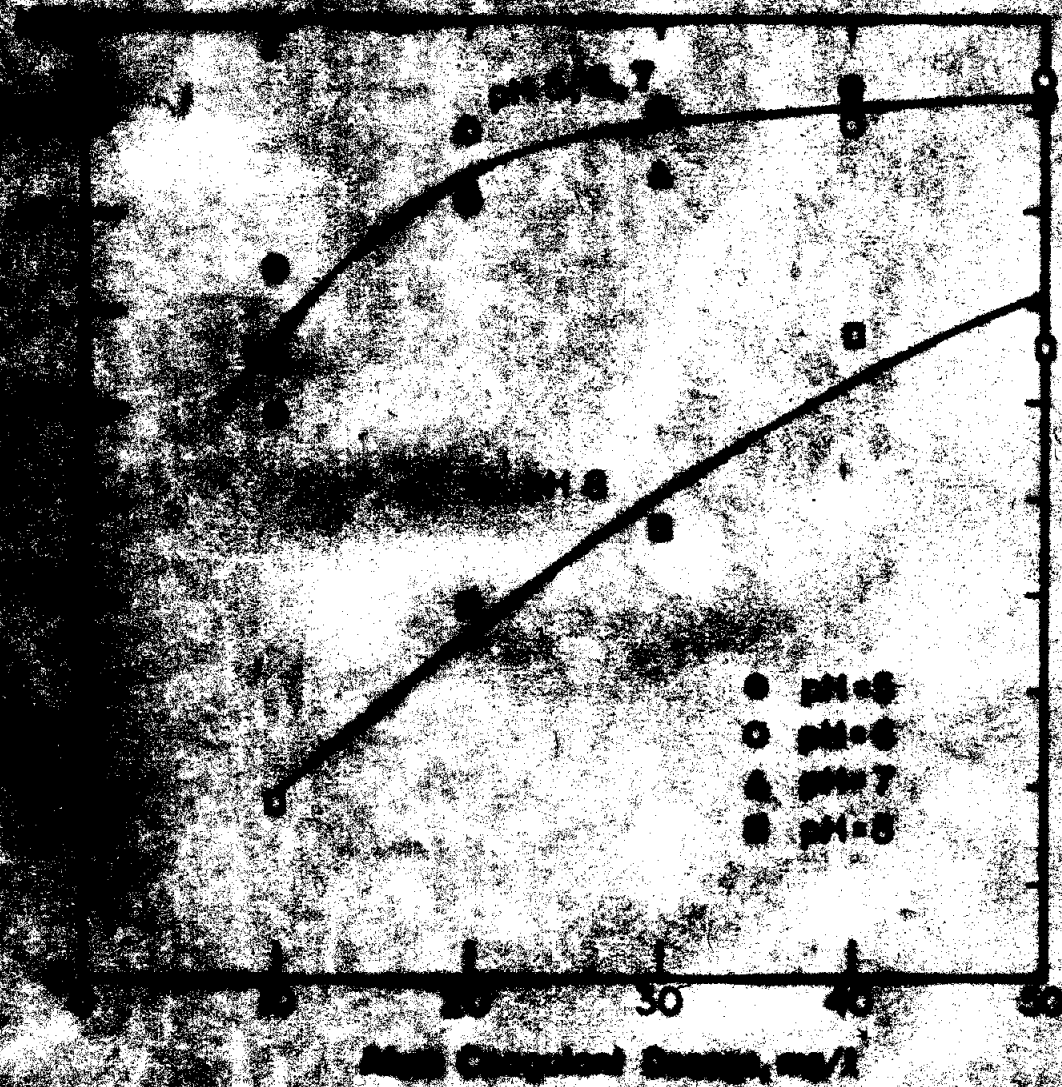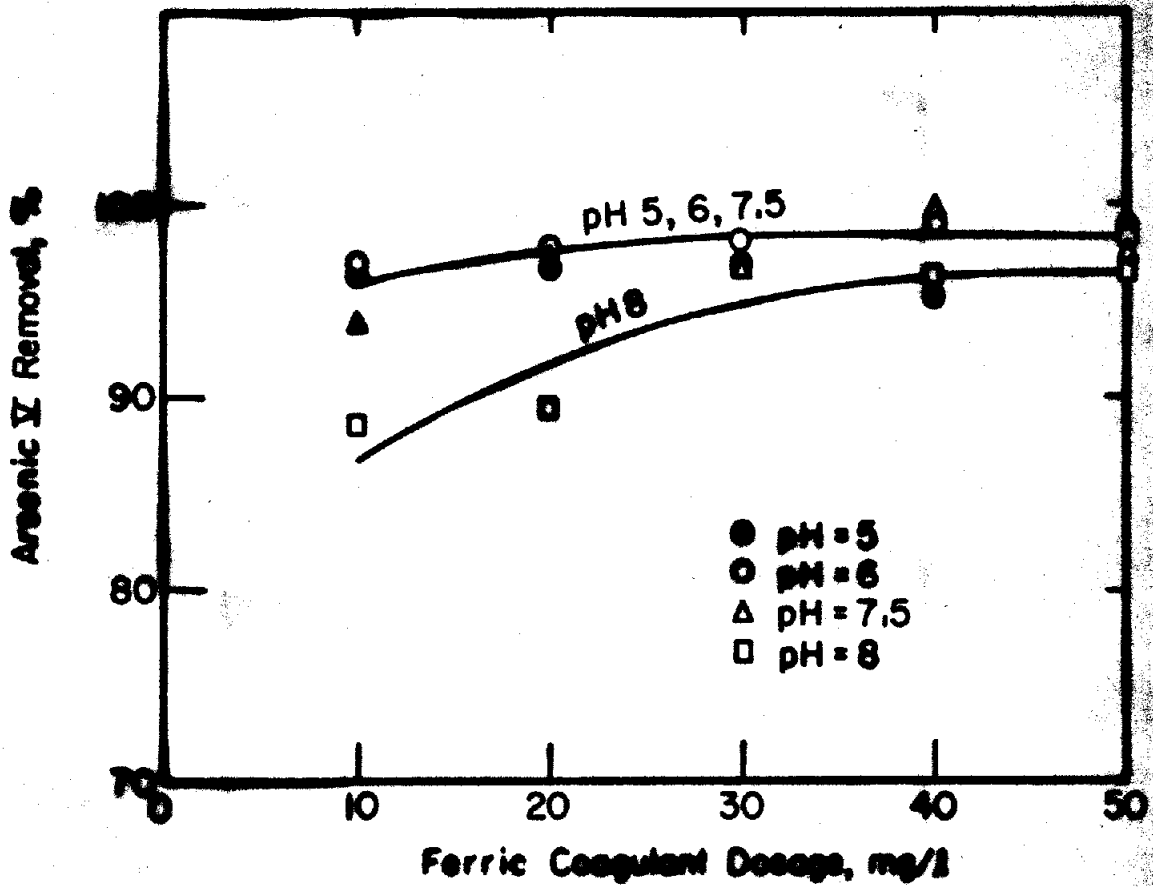Species in 6.7 x 10⁻⁷ M Solution
(50 µg/1) of Arsenic Acid

Figure 3. Removal of Arsenic V by Adsorption
on Hydrous Ferric Oxide

such as hydrous aluminum and iron oxides, polyelectrolytes, activated carbon, kaolinite and montmorillonite clay were used in studies of the coagulation, sedimentation and filtration of water containing from 5.8 to 50 µg/ℓ of mercuric ion.

The initial study of mercury removal explored the effect of allowing prolonged periods of time, up to 36 hours, to elapse following the addition of the mercuric ion to tap water at pH 8.5 prior to the start of the coagulation process. There was a progressive increase in removal of mercury upon filtration. This was taken as evidence of the slow, progressive precipitation or agglomeration of a mercury salt. The results are shown in Figure 6.

The addition of aluminum and iron coagulants enhanced the removal of mercury, possibly either through adsorption or by hastening the agglomeration of the precipitated mercury salt.

The addition of carbon, clays, and polyelectrolytes also enhanced removal, but the removal with all coagulants and adsorbants was highly variable. Optimum removal with the iron coagulant was obtained at pH 8.

From the results of the study, it was concluded that the mercuric ion, freshly added to solution at pH 8.5, slowly hydrolyzed to form a colloid which could be removed by membrane filtration. Coagulants and adsorbants enhanced removal indicating that conventional water treatment processes might achieve partial, but inconsistent, removals of mercury.

SUMMARY

Methods for the alteration or adaptation of conventional water treatment processes to effect the removal of trace inorganic constituents are being sought.[4] Owing to the low concentrations of the trace constituents required by the drinking water standards, adsorption phenomena play a major role in
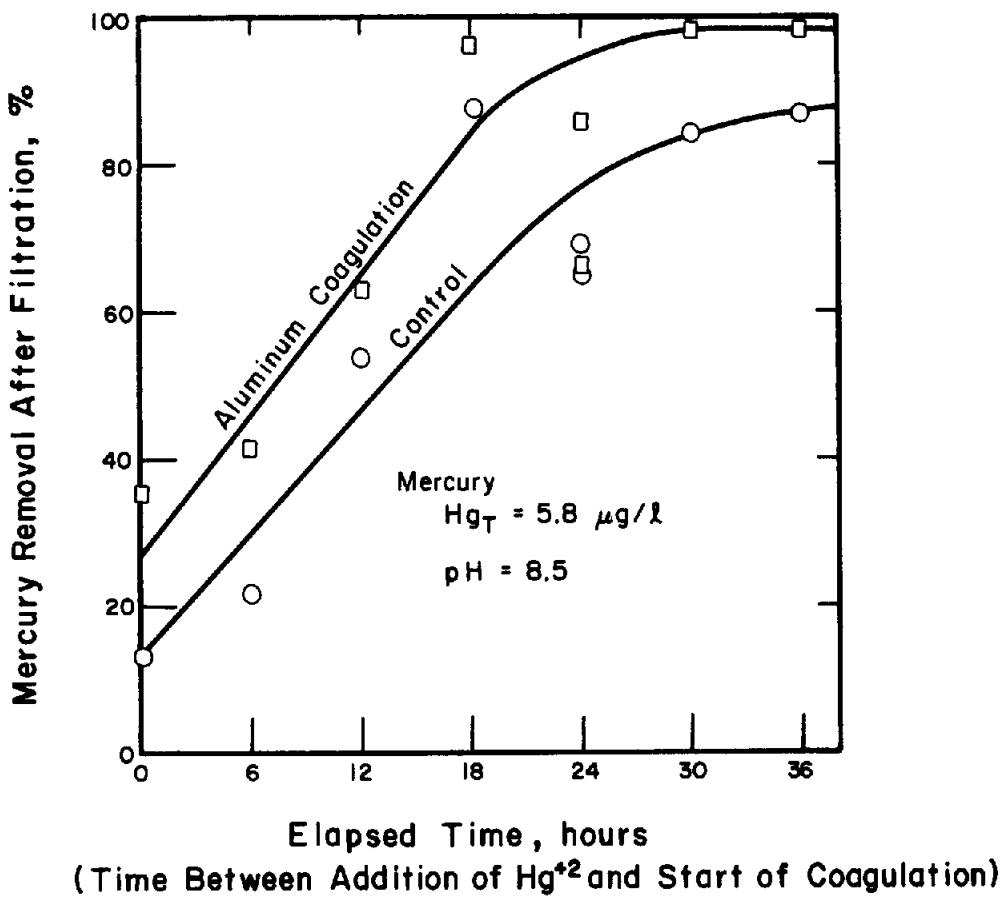
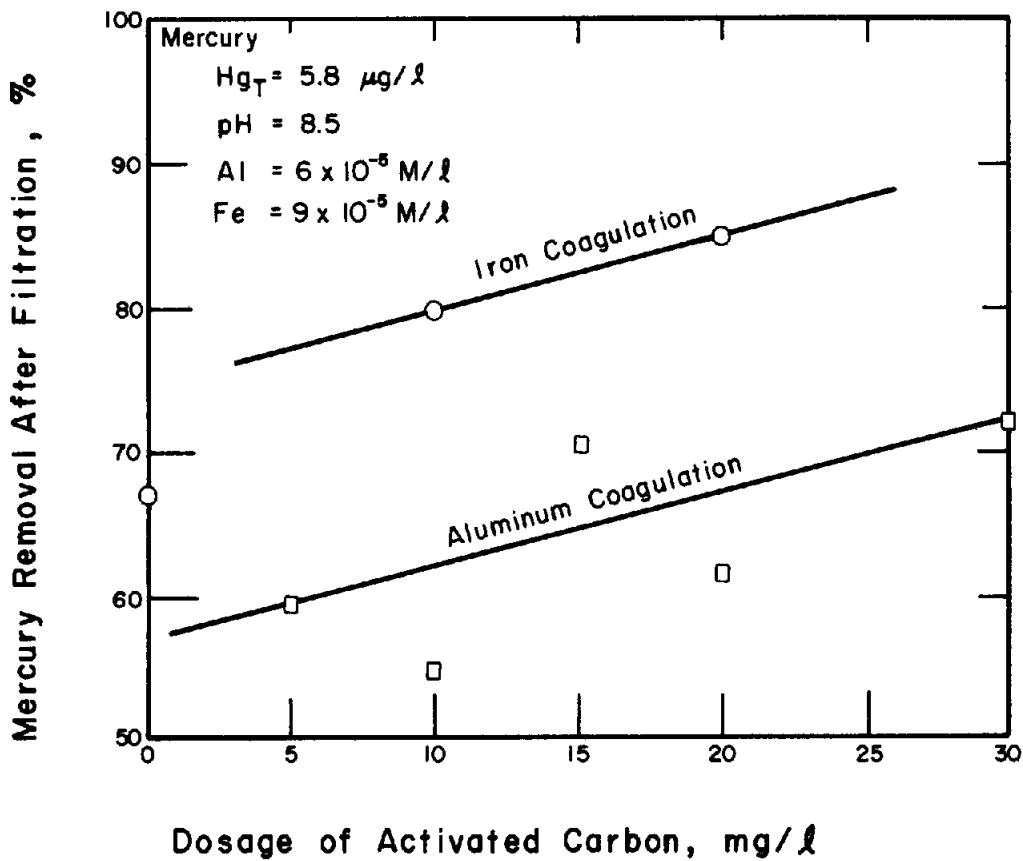FIG. I   REMOVAL OF MERCURY AS A FUNCTION OF TIME

FIG. 2   INFLUENCE OF ACTIVE CARBON ON THE REMOVAL
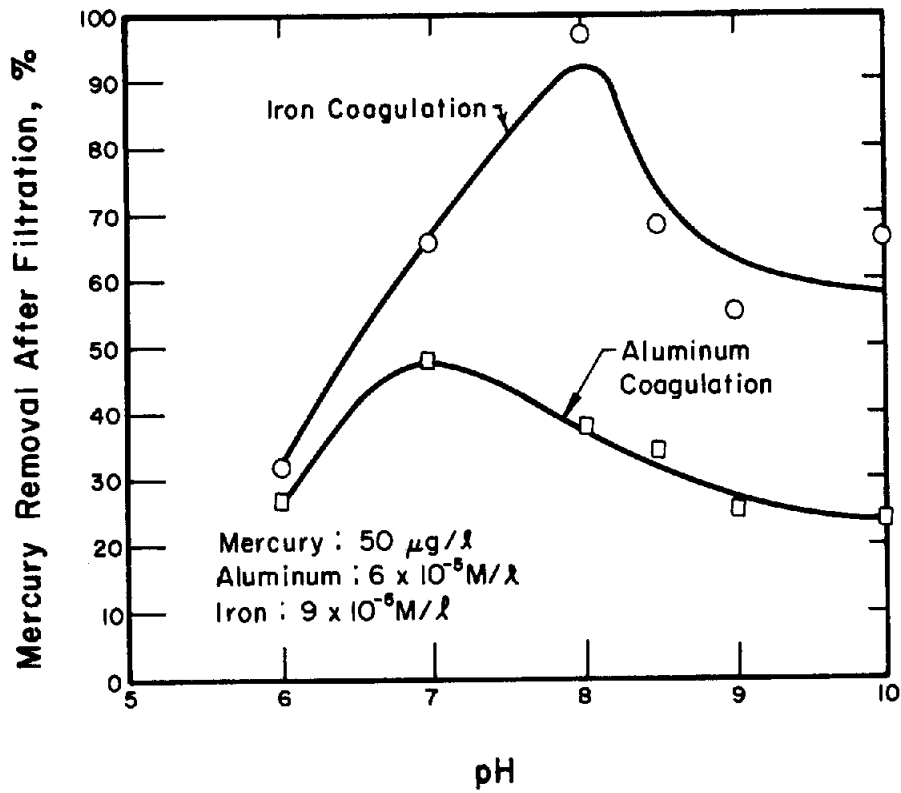OF MERCURY BY COAGULATION

FIG. 3   INFLUENCE OF pH ON REMOVAL OF MERCURY BY
COAGULATION

removal processes. Optimum conditions for the removal of one trace constituent may not correspond to optimum conditions for the removal of another trace constituent. At this time, there are no clearly defined and well-tested process modifications for the removal of trace constituents. However, there is evidence that conventional methods of water treatment (coagulation and filtration) provide partial removal of trace constituents.

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