SORPTION OF BORON AND CHROMIUM ONTO SOLIDS OF ENVIRONMENTAL SIGNIFICANCE: IMPLICATIONS FOR SAMPLING AND REMOVAL IN WATER TREATMENT

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ABSTRACT

The chemistry, analysis, treatment, and occurrence of boron and chromium are of high interest since they are under consideration for revised MCLs in potable water. As a starting point to guide regulatory decision-making, a comprehensive review of boron in relation to potable water was undertaken. That work demonstrated that there were not proven cost-effective options for boron treatment.

In preparation for a national survey of boron and chromium occurrence, it was discovered that existing analytical protocols sometimes '"missed" much of the total chromium that was present in water. It was determined that this was due to incomplete dissolution of particulates during routine Standard Method analysis of drinking water at pH 2.0. A more rigorous hydroxylamine digestion was developed and applied to circumvent this limitation.

In relation to treatment, it was determined that sodium carbonate softening at pH 10.3 is a viable method of removing various inorganic contaminants including chromium from drinking water sources. The nationwide survey revealed that removals varied widely and were dependent on solution composition. Median removal of chromium was 92%. Linear and nonlinear empirical models were fit to crudely estimate the removal of various contaminants in the presence of other elements that are typically removed in the softening process (i.e. calcium, magnesium, silicon, iron, and aluminum). Boron was removed to a much lesser extent (median removal 2%) in this study, consistent with the general result of the literature review that enhanced treatments will be required for this contaminant.

Modified precipitative softening was examined as a potentially attractive option to remove boron from natural waters. It was discovered that in some cases when magnesium and silicon were present, and if the pH was 10.8 ± 0.2, very high levels of boron removal (up to 90%) could be achieved versus 10% typically observed for conventional processes. This can be exploited to remove boron in waters naturally containing high levels of magnesium and silicon, or by adding supplemental amounts of either magnesium or silicon when one constituent is deficient.

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AUTHOR'S PREFACE

Each chapter of this dissertation is a separate manuscript that is formatted according to the specifications of the journal to which it was submitted. Chapter 1, "Boron in the Environment", has been published in *Critical Reviews in Environmental Science and Technology*. Chapter 2, "Determination of Total Chromium in Environmental Water Samples", has been published in *Water Research*. Chapter 3, "Precipitative Removal of As, Ba, B, Cr, Sr, and V using Sodium Carbonate", has been reviewed by and resubmitted to the *Journal of Environmental Engineering*. Chapter 4, "Enhanced Silicon and Boron Removal during Precipitative Softening", will be submitted to the Journal of Environmental Engineering.

Although each chapter is a separate manuscript, this dissertation is organized to explain phenomena related to boron and chromium removal from natural waters. Each manuscript stems from an aspect of boron and/or chromium chemistry that was uncovered during the completion of American Waterworks Association Research Foundation Project 2759, "Occurrence Survey for Boron and Hexavalent Chromium". Chapter 1 is a thorough review of boron chemistry, occurrence, health effects, regulations, and treatment techniques. Chapter 2 describes an alternative digestion method for environmental water samples to better determine total chromium concentration. Chapter 3 details occurrence data for various elements (including boron and chromium) obtained during this survey and further describes how their removal during precipitative softening can be modeled using a linear or nonlinear regression technique. Chapter 4 describes in detail how silicon and boron can be removed from natural waters during a precipitative softening process.

CHAPTER I: BORON IN THE ENVIRONMENT

Jeffrey L. Parks and Marc Edwards

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ABSTRACT: Boron has recently come to the attention of the USEPA as a possible contaminant worthy of regulation but questions must still be addressed before a regulatory determination can take place. This paper reviews current knowledge about boron as it pertains to water treatment and the environment so that informed decisions can be made regarding regulations and direction of future research. Specifically, this paper summarizes boron chemistry, boron occurrence, health effects of boron, existing guidelines and regulations concerning boron, and methods for removing boron from drinking water.

INTRODUCTION

Recently boron has come to the forefront as a possible drinking water contaminant that could be regulated in the next few years (EPA, 2003). The basis for possible regulation is a 1992 EPA Drinking Water Health Advisory for boron. A lifetime human health advisory of 0.6 mg boron /L for drinking water was deemed appropriate based on findings in a study by Weir and Fisher.(EPA, 1992; Cantilli, 1991; Weir and Fisher, 1972). The value of 0.6 mg/L was calculated using Equation (1):

$$HA = \{(NOAEL) * (BW) / (UF) * (QTY)\} * RSC \tag{1}$$

where NOAEL = no observed adverse effect level = 8.8 mg/kg/day

BW = body weight = 70 kg for adult

UF = uncertainty factor = 100 (assumed)

QTY = quantity of water consumed per day = 2 L/day for adult

RSC = relative source contribution, assumed at 20%.

Before regulatory determination can take place, however, more information is required. At what level is boron a health concern in humans? What are the current levels of boron in our nation's groundwater and surface drinking water sources? What are effective methods for removing boron from water?

Even without more stringent EPA regulations, boron removal from water sources will be necessary in the near future. With the worlds fresh water sources dwindling, attention is turning to seawater as a drinking water supply. In addition to its high salinity, seawater has an average boron concentration of 5 mg/L. Even though this level of boron may not acutely affect human health, its removal is essential if this water is to be used for irrigation. Likewise, in re-use and recharge applications of fresh water, boron can accumulate to troublesome levels.

BORON CHEMISTRY AS IT RELATES TO WATER TREATMENT AND THE ENVIRONMENT

A basic understanding of boron chemistry is essential in developing treatment methods for boron removal from a water source. This section describes boron’s atomic and physical properties, how boron is found in nature, current and potential uses of boron, and its reactivity in a variety of environmental circumstances. Finally, current analytical techniques for boron measurement are described.

A. Atomic and Physical Properties.

Boron has an atomic number of 5 and is located on the periodic table in Group IIIA. Its quantum number is 1s22s22p1. Boron is different from other elements in Group IIIA because there is no simple way for it to complete its valence shell. Boron has only three valence electrons and is often thought of as 'electron deficient' because three single bonds would still leave the boron atom with only six electrons in its valence shell (as opposed to the eight electrons required for a full valence shell). To compensate for this deficiency, boron often uses hydrogen atoms to 'bridge' between two boron atoms. These are called 'three-center bonds' because they extend over three nuclei but contain only a single pair of electrons (Brady and Humiston, 1978).

Boron has only two stable boron isotopes in nature. These have an atomic mass of 10 and 11 and occur in roughly a 20:80 ratio leading to an average atomic mass of 10.81 g/mol (Power and Woods, 1997). In some circumstances this fact may be used to identify water sources by their boron isotope ratio; i.e. different water sources invariably have slightly different isotope ratios and when these waters mix, the resultant isotope ratio will be between the two original ratios proportionately (e.g. Davidson and Bassett, 1993; Vengosh et al., 1994).

In nature, essentially all boron is in the trivalent (+3) oxidation state. Unlike its neighbor aluminum, however, boron does not exist as a trivalent cation under conditions found in nature but is always found bound to oxygen (Holleman and Wiberg, 2001). Also, unlike aluminum, boron can only form covalent bonds because of its small size and high ionic potential (Brady and Humiston, 1978).

Boron normally has a coordination number of 3 or 4 in naturally occurring compounds (Holleman and Wiberg, 2001). In boric acid and its salts, boron has a coordination number of 3 since it is bound to three oxygen atoms. The coordination number is also three in boron trifluoride, BF_3. Boron can also combine with four fluorine atoms to form the tetrafluoroborate anion, BF_4^-. In this compound, boron has eight electrons in its valence shell and a coordination number of 4.

B. Chemistry in Nature.

In nature boron is found in the form of boric acid, borate (i.e. salt of boric acid), or as a borosilicate mineral (Holleman and Wiberg, 2001). Boric acid, H3BO3 (or B(OH)3), behaves as a weak Lewis acid in aqueous solution (Power and Woods, 1997).

It accepts hydroxide ion from water and releases a proton into solution according to the following equilibrium equation (Ka = 5.8x10-10; pKa = 9.24 @ 25 °C) (Dean, 1987):

$$B(OH)_3 + H_2O <=> B(OH)_4^- + H^+ \qquad (2)$$

Boric acid dissociation as a function of pH; above pH 9.24 the anion, $B(OH)_4^-$, is predominant, while below pH 9.24 the uncharged species is predominant.

Boric acid is soluble in water (5.5 g / 100 g solution at 25 °C) and its solubility increases with temperature (Waggott, 1969). At concentrations below 0.02 M (216 mg/L as B) only the mononuclear species $B(OH)_3$ and $B(OH)_4^-$ are present. Polynuclear ions or ringed structures can exist at higher concentrations but these will not be discussed here due to their perceived rarity in nature (Power and Woods, 1997).

C. Industrial Uses of Boron.

Boron has many uses worldwide. The principal industrial uses of boron compounds are in the production of fiberglass insulation, borosilicate glass, and detergents. Other uses include fertilizers, metallurgy, and nuclear shielding (Power and Woods, 1997).

Boron is used in the fiberglass and glass industries because of its mechanical qualities. Boron oxide lowers the expansion coefficient in glass and therefore borosilicate glass has an increased shock resistance. Boron also gives glass increased mechanical strength and increased drawing quality that is especially useful in the manufacture of fiberglass (Woods, 1994).

Boron is used in the manufacture of detergents and bleaches as well. Boron in the form of sodium perborates is added to detergents as a bleaching agent. The hydrolysis of sodium perborate forms the hydroperoxide ion. This is only effective at temperatures above 60 °C unless an activator is present. It also has been added to diaper pails and to animal litter to reduce odor since it prevents the formation of ammonia by inhibiting the urease enzyme (Woods, 1994).

Boron has varied uses as a result of its nuclear properties. Elemental boron is used in alloys for nuclear reactor control rods because of its large neutron capture cross section (Waggott, 1969). This same property has led the medical establishment to use ^{10}B in a procedure known as boron neutron capture therapy in the treatment of cancer patients (Hawthorne, 1993).

A recent innovation utilizing boron is the fuel cell as patented by Millennium Cell, Inc. Sodium borohydride is dissolved in water and passed over a catalyst producing liquid borax and hydrogen gas. The hydrogen can then be used in a fuel cell where it is converted into electricity and water. The borohydride fuel cell's advantage is that hydrogen is produced on demand and there is no need to store it as is the case with other fuel cells. An obvious drawback is the need to recycle the borax back into its borohydride form (ABC News, 2001). Currently, Rohm and Haas is the only producer of sodium borohydride in the United States. A fairly complex reaction sequence is utilized in borohydride production, including converting boric acid to trimethylborate (TMB), converting sodium to sodium hydride, and then reacting the TMB and sodium hydride to make sodium borohydride (Mannsville Chemical Products Corp., 1999). Still, some designers believe this may be a viable technology in the next decade (Avril, 2002).

D. Reactivity of Boron.

Volatilization. Volatilization of boron is insignificant at ambient temperatures. However, boric acid does co-evaporate with moisture from seawater to form borate aerosols in the atmosphere (Argust, 1998). While earlier reports suggested that this was a major source of boron in the atmosphere, the study of Savenko (1977) suggested that much less boron is from this source than previously suspected. Nevertheless, this co-evaporation or co-distillation of boron is important. Although the amount of boron in the distillate is a function of concentration in the feed, at the mg/L level the distillate can contain as much as 25-30% of the borate initially present in the feed water (Wong, 1984). Boron concentrations in a steam phase in equilibrium with water can also be quite high (Ellis and Mahon, 1977).

Precipitation. No solubility products could be readily found for solids containing Al^{3+}, Fe^{3+}, Fe^{2+}, Ca^{2+}, Mg^{2+}, K^{+}, Na^{+}, Cu^{+}, or Cu^{2+}. This is most likely because complexation is not significant; indeed, boron buffers are often used in metal complexation studies for this reason. It has been noted, however, that the solubility of calcium borate is approximately 600 mg/L of boron (Lapp and Cooper, 1976). Solubility product constants can be calculated for several hydrated boron-containing minerals from data presented in Mattigod (1983) (Table 1-1). Using these solubility product constants in conjunction with MINEQL, a mineral solubility and equilibrium program, it was determined that no boron-containing solids (from those listed in Table 1-1) precipitate at levels up to 1000 mg/L calcium, 1000 mg/L magnesium, and 5 mg/L boron (Schecher, 1998).

Coprecipitation with calcium carbonate. Coprecipitation of boron with calcium carbonate is dependent on the form of $CaCO_3$ (aragonite v. calcite) as well as the salt (NaCl) and magnesium concentrations. Boron is more easily coprecipitated with aragonite than with calcite. Magnesium influences whether aragonite or calcite is formed (aragonite is favored in the presence of magnesium). Boron coprecipitation decreases in aragonite with increasing NaCl concentration and increases in calcite with increasing NaCl concentration (Kitano et al., 1978).

Complex formation. There is little or no information in the environmental literature on complexes between boron at the mg/L level and environmentally important cations such as Al^{3+}, Fe^{3+}, Fe^{2+}, Ca^{2+}, Mg^{2+}, K^+, Na^+, Cu^+, or Cu^{2+}.

Fluoride is commonly added to drinking water to prevent tooth decay in the general population. As discussed previously, boron forms soluble complexes with the fluoride ion. This fluoroborate complex takes between 1 - 2 hours to form completely at pH 3.5 - 5. Up to 16% of the fluoroborate ion is lost during storage, possibly due to volatilization (Wood and Nicholson, 1995). We believe that a possible mechanism for this loss is the transformation of the fluoroborate ion to boron trifluoride, an extremely volatile gas with a boiling point of -99.9 °C (Holleman and Wiberg, 2001).

Boron is known to form soluble complexes with organic polyhydroxyl compounds either present naturally or added to water specifically to complex boron (Akiga et al, 1996; Mackin, 1986; Smith et al., 1995; Matsumoto et al., 1997), and a host of bio-molecules in mammalian tissues and fluids (Woods, 1996). With respect to organic matter, the extent of natural boron complexation is believed to be about 20% or less in natural waters (Mackin, 1986), and boron is released during organic matter oxidation which occasionally leads to inverse relationships between dissolved oxygen and dissolved boron in the water column (Shirodkar and Singbal, 1992).

Sorption. Boron adsorbs to many different mineral and solid surfaces forming weak, labile bonds. For example, boron can sorb weakly to kaolinite and illite clay, and to sewage sludge, with a maximum sorption density of 31 mg B / g for these sorbents (Banerji, 1969). Such reactions are an important control on the concentration of boron in soils (Evans and Sparks, 1983; Goldberg and Glaubig, 1985 and Goldberg et al., 1993), and a review of the literature indicates a maximum sorption density of about 0.047 mg B / g soil (Gupta et al., 1985). A study by Su and Suarez (1995) indicates boron can also form inner-sphere complexes with various minerals. These include aluminum and iron hydroxides, allophane, and kaolinite. Quartz and calcite, however, showed little or no ability to adsorb boron from solution (Su and Suarez, 1995).

Accessible interlayers in 2:1 phyllosilicates are important in boron adsorption. A study by Hatcher et al (1967) concluded that the major species responsible for boron adsorption are freshly precipitated aluminum hydroxide ($Al(OH)_3$) and related hydroxy-aluminum materials. In a study by Sims and Bingham (1967) montmorillonite that had been treated to remove hydroxy-aluminum had low boron retention. These authors point out importance of Fe or Al species present as interlayer materials, coatings or impurities and of access of B to interlayer positions as necessary for maximum B retention.

Large quantities of boron can also be adsorbed to diopside, tremolite, and enstatite, all minerals with no iron or aluminum present. This suggests that magnesium-hydroxy coatings could be active sorption sites. Magnesium hydroxide ($Mg(OH)_2$) has significant ability to remove boron from solution and this ability is not altered by aging.

The authors also concluded that boron was possibly incorporated into the crystalline structure of $Mg(OH)_2$ (Rhoades et al., 1970).

E. Analytical Techniques for Boron Measurement.

Many colorimetric methods have been used to measure boron concentrations. These include the curcumin method, the carmine method, and the azomethine H method among others (Standard Methods, 1998; Shanina et al, 1967). While these are well suited for field analysis, their detection limits cannot approach those of more sensitive emission spectroscopy methods such as ICP-ES, ICP-MS, or thermal neutron capture gamma ray spectroscopy. Detection limits for boron on ICP-MS have been reported as low as 0.05 ppb (Malhotra et al, 1996). In ultra-pure water analysis a boron detection limit of 1.4 ng/L was reported (Darbouret and Kano, 2000). Typical detection limits for ICP-ES are 1 ppb. Miyazaki and Bansho (1986) report an ICP-ES detection limit of 0.35 ppb when combined with solvent extraction. They extracted boron from the water with 2,6-dimethyl-4-heptanone (DIBK) containing 2-ethylhexane-1,3-diol. They also reported a 'memory' effect when using a glass spray chamber and therefore used a Teflon spray chamber. Approximately 100 seconds were required for the boron signal to decay to the background level (Miyazaki and Bansho, 1986).

An inexpensive field technique for boron measurement is a fluoroborate ion-selective electrode (Wood and Nicholson, 1995). Its practical detection limit is reported as 0.35 mg/L; however boron concentrations as low as 0.001 mg/L (1 ppb) can be determined from a curvilinear calibration graph. This work was performed specifically on the fluoroborate ion however, and therefore its application to waters with boric acid has not been quantified.

OCCURRENCE OF BORON IN THE ENVIRONMENT

This section describes various sources of boron in the environment and summarizes national and worldwide data on boron occurrence in drinking water sources. Food as a source of boron is also described.

A. Sources/Mechanisms for Boron Release into Environment.

Boron can enter the environment in a variety of ways. It is naturally present in many silicate minerals and is therefore found in many soils. At least 200 minerals contain boron but only a few are of commercial importance (Table 1-2). Only borax (tincal), kernite, colemanite, and ulexite are mined extensively (Lyday, 2000). The mean concentration of boron in the earth's crust is 10 µg/g. Shale can have concentrations as high as 100 µg/g which means dissolved boron has been in seawater throughout history (Evans and Sparks, 1983). Many factors affect the boron concentration in soils, including soil type and pH. Boron concentration is higher in clay and loam than in sandy soils (Gupta, 1967). Excessive liming of soil can make boron less available to plants at higher pH (Gupta and Macleod, 1981; Berger and Truog, 1945; Peterson and Newman, 1976). No explanation is given for this phenomenon, but the authors state that it is due to soil pH rather than the amount of calcium. Also, much of the total boron in soil is held by organic matter and is released by microbial action (Evans and Sparks, 1983). Weathering of boron-containing minerals and soils releases boron into water.

The ocean contains on average 4.6 mg B/L but can range between 0.52 mg/L in the Baltic Sea to 9.57 mg/L in the Mediterranean Sea (Argust, 1998) and some of this boron can partition into the atmosphere. It is estimated that oceans are responsible for 65 - 85% of all atmospheric boron (Anderson et al., 1994). Boron-containing minerals often occur in areas with a history of volcanism and therefore boron can enter the atmosphere from volcanoes and geothermal ducts (Coughlin, 1998). This boron in the atmosphere makes its way into rainwater and can eventually be introduced into a drinking water source. These are only some of the mechanisms by which boron is naturally incorporated into the world's drinking water sources.

Various studies (Boyd and Walley, 1972; Carriker and Brezonik, 1978; Jahiruddin et al., 1998) indicate that boron concentration increases with proximity to seawater. This is due to the co-evaporation of boric acid moisture from seawater to form borate aerosols in the atmosphere as discussed previously (see “Reactivity of Boron: Volatilization”) and their subsequent condensation in rainwater.

A study by Jahiruddin et al. (1998) showed that there was no apparent relationship between the soluble boron concentration in surface waters in Scotland and sediment boron concentrations in those same water bodies. These results were suggested to show soluble boron in surface water does not originate primarily from mineral sources.
Boron also enters the environment from a number of anthropogenic activities. Over 4 million metric tons of boron (as boron oxide) were produced in 2000. Of this, about 546,000 metric tons was produced in the United States (Figure 1-1). Major domestic uses

of boron were for glass (76%) and detergents (7%), while worldwide consumption leaders were glass products (54%) and detergent products (12%) (Figure 1-2). Other uses include metal alloys, fire retardants, and chemical fertilizers (Lyday, 2000). Of these, the vast majority of boron that enters drinking water sources originates in detergents and fertilizers. One researcher has estimated as much as 50% of boron in wastewater effluent comes from detergents (Dyer and Caprara, 1997).

B. Occurrence in the United States.

Various surveys have been performed to determine the distribution of boron in United States waters. In 1969 the United States Public Health Service conducted a survey of 969 community water systems and found a 99th percentile boron concentration of 1.0 mg/L; i.e., 99% of all waters tested had boron concentrations less than 1.0 mg/L. The maximum level encountered was 3.28 mg/L (Coughlin, 1998). In 1987 the National Inorganics and Radionuclides Survey reported a mean boron concentration of 0.15 mg/L for 989 public water supplies tested. The maximum level encountered in this survey was 4.0 mg/L (Coughlin, 1998).

The most comprehensive database for water quality data in the United States is the EPA's STORET database. This database was developed in the 1960's to store data from some 700,000 monitoring stations and was used until the 1990's. A modernized version had been developed and was released in March of 1999. Data from the former database is still available but will be reviewed for quality requirements before it is placed into the new system. New data is required to have quality assurance information but users should not assume the data are more accurate than they actually are. The accuracy of the data is solely dependent on the data provider and the test methods that were employed (EPA, 1999).

The majority of the data included in the STORET (STOrage and RETrieval) database comes from west of the Mississippi River. Table 1-3 contains a summary of boron concentrations in U.S. waters as reported in the STORET database from 1984 to 1993 (Dyer and Caprara, 1997). From this table one can see that the nationwide average boron concentration is 0.076 mg/L. However, this value could be highly skewed since 91% of the data was collected in just 14 states and 54% of the data was from Illinois alone.

C. Worldwide Occurrence.

Data for worldwide boron levels in drinking water are scarce. Coughlin presents data from several occurrence studies around the world and these are summarized in Table 1-4 (Coughlin, 1998). The data from Chile are unusually high due to the fact that there is an abundance of boron-containing minerals present. In fact, soil concentrations of 900 ppm boron have been measured (Coughlin, 1998).

D. Boron in Food.

Food is the primary source of boron that is ingested by humans. A recent study indicates that the average adult in the United States consumes about 1 mg of boron per day in their diet (Meacham and Hunt, 1998). The richest sources of boron include fruits and nuts. Wine is also a major contributor. Typical values of boron content in foods are shown in Table 1-5 (Rainey and Nyquist, 1998). As one can see from this data, an individual's boron intake is determined by his or her dietary habits in addition to the levels of boron in drinking water and can vary widely.

HEALTH EFFECTS OF BORON

This section describes the effects boron has on living organisms in our environment. This includes plants, microorganisms, animals, and humans.

A. Plants.

There is a small range between boron deficiency and boron toxicity in plants. Boron has been shown to play a role in carbohydrate metabolism, sugar translocation, pollen germination, hormone action, normal growth and functioning of the apical meristem, nucleic acid synthesis, and membrane structure and function (Howe, 1998). Symptoms of boron deficiency include discontinuance of root and leaf growth, bark splitting, retardation of enzyme reactions, reduced pollen germination, and even death (Versar, Inc., 1975; Wells and Whitton, 1977; WHO, 1998). The initial stages of boron toxicity in plants include yellowing of leaf tips progressing into the leaf blade. Death of chlorotic tissue occurs followed by leaf loss. This ultimately results in a loss of photosynthetic capacity and a loss in plant productivity (Lovatt and Dugger, 1984; WHO, 1998).

Boron deficiency may occur in heavy-textured soils with high pH because under these conditions boron is readily adsorbed (Howe, 1998). Boron toxicity may also occur in boron-rich soils or in soils that have been exposed to boron-contaminated irrigation waters or the excess application of boron-rich fertilizers, sewage sludge, and fly ashes (Nable et al., 1997). Some plants are more sensitive to boron than others. Sensitive plants can tolerate irrigation waters with only 0.3 mg/L boron while very tolerant plants may be able to survive where 4 mg/L boron irrigation water is used (Keren and Bingham, 1985).

B. Microorganisms.

Toxicity thresholds (TTs) were determined for various microorganisms in a study by Bringmann and Kuhn (1980). They found that the bacteria, *Pseudomonas putida*, had a TT of 290 mg/L boron. Toxicity threshold was defined as the concentration at which the inhibitory action of a chemical leads to a >3% difference in the quantity of organisms versus a control group. The green alga, *Scendesmus quadricauda*, had a TT of 0.16 mg/L, while the protozoan, *Entosiphon sulcatum*, had a TT of 0.28 mg/L (Bringmann and Kuhn, 1980).

Activated sewage treatment was not affected by a boron concentration of 20 mg/L (Howe, 1998). Banerji (1968), on the other hand, observed a significant decrease in chemical oxygen demand (COD) removal at concentrations greater than 10 mg/L on aerobic activated sludge biological treatment. Banerji (1968) observed no effects on settling at concentrations below 100 mg/L boron while other researchers observed activated sludge settling problems at a concentration of 0.05 mg/L (Banerji et al., 1968). Banerji (1969) also observed a two-fold reduction in the endogenous respiration of activated sludge at a boron concentration of 100 mg/L (Banerji, 1969).

C. Aquatic Organisms.

The acute toxicity of boron to various fish has been the focus of a number of studies. The most sensitive freshwater fish identified thus far is the rainbow trout (Oncorhynchus mykiss). Initial studies in reconstituted water indicated a LOEC (lowest observed effect concentration) of 0.1 mg/L. The LOEC is the lowest observed concentration at which there is a significant increase in the frequency of an adverse reproductive or developmental effect in comparison to a control group. Subsequent tests in natural waters (with boron amendments) however, indicated that the LOEC ranged from 1.1 to 1.73 mg/L. Major trout hatcheries commonly use waters containing up to 1 mg/L boron with no apparent problems (Butterwick et al., 1989; Howe, 1998).

A recent study by Pillard et al. (2002) evaluated the toxicity of boron to the mysid shrimp (*Americamysis bahia*) in saline water. This species was chosen because it is the most common marine invertebrate required in whole effluent toxicity (WET) tests and it has proven to be more sensitive to ion toxicity than other WET organisms. Pillard et al. (2002) observed a NOAEC (no observed adverse effect level) of 275 mg/L boron in water with a salinity of 10 ppt (parts per thousand) and 170 mg/L boron in water with a salinity of 20 ppt (Pillard et al., 2002). The NOAEL is the highest concentration at which there is not a significant increase in the frequency of an adverse reproductive or developmental effect in comparison to a control group (The NOAEL can differ significantly from the LOEC depending on the magnitude of the concentrations tested).

D. Animals.

Boron is nutritionally important to animals. Boron has been found to enhance the maturation of the growth plate in the long bones in chicks (Hunt, 1994). Boron has also influences brain activity in mature rats (Penland and Eberhardt, 1993). In rats, a lack of boron has also decreased the absorption of calcium, magnesium, and phosphorus (Hegsted et al., 1991). Another study substantiated this finding by discovering that boron supplementation to boron deficient chicks increased femur calcium, phosphorus, and magnesium concentrations (Hunt, 1994).

A study on rabbits indicated boron is not able to penetrate intact skin but is readily absorbed through broken skin (Draize and Kelly, 1959; Moore, 1997).

Many studies have been made on rats, mice, rabbits, ducks, and dogs (e.g., Price et al., 1990; Price et al., 1994; Fail et al., 1990; Fail et al., 1991; Price et al., 1991; Smith and Anders, 1989; Weir and Fisher, 1972; Weir and Fisher, 1966) and are summarized extensively in Moore (1997). Moore concluded that a NOAEL of 9.6 mg B/ kg body wt./day was appropriate based on developmental toxicity in rats, the most sensitive organism in the studies reviewed. Data indicated NOAELs for female and male reproductive toxicity were 24 and 17 mg/kg body wt./day, respectively (Moore, 1997).

E. Humans.

Boron has not been established to be an essential element in the human diet because a specific biochemical function for it has not been identified (Nielsen, 1997). However, there is strong circumstantial evidence that this may be the case. Boron is important in the metabolism and utilization of calcium in humans (Nielsen, 1994). Other benefits of boron include improvement of brain function, psychomotor response, and the response to estrogen ingestion in postmenopausal women (Nielsen, 1994). There is evidence that boron plays a role in healthy bones and joints (Newnham, 1994). The Newnham study and various others (Havercroft and Ward, 1991; Shah and Vohora, 1990; Travers et al., 1990) illustrate that boron can be effective in preventing and treating various forms of arthritis.

A skin irritation study similar to the Draize and Kelly (1959) study on rabbits was conducted on humans in 1998 and resulted in a similar conclusion. Wester et al. (1998) determined that 0.1 to 0.2% of applied borates (either boric acid, borax, or disodium octaborate) absorbed through human skin. Treatment of the skin with sodium lauryl sulfate (SLS), a known skin irritant, resulted in a slight increase on boron absorbed but not enough to be statistically significant.

No human studies are available that effectively assess developmental toxicity. Harchelroad and Peskind (1993) reported that the oral ingestion of 250 g of boric acid by a woman in her second trimester of pregnancy had no effect on her offspring. Her blood boron level was 7.9 mg/L five hours after ingestion and decreased to 0.42 mg/L after 28 hours.

Several studies detail the elimination of boron in urine. In one study 98.7% of an injected 600 mg dose of boric acid was eliminated in the first 5 days (Jansen et al., 1984a; Moore, 1997). Oral doses have also been shown to be almost entirely eliminated in the urine. Janson et al. (1984b) found that 92 to 94% was eliminated in the first 4 days; and more than 50% was excreted in the first day.

Studies indicate that most soft tissues in the human body contain similar levels of boron to that in blood. Bone tends to have a higher amount, as well as fingernails, toenails, and hair (Forbes et al., 1954; Abou-Shakra et al., 1989).

Murray (1995) critically reviewed existing toxicologic and pharmacokinetic data on boron and made a risk assessment regarding human health. He used the NOAEL value of 9.6 mg B/kg/day determined by Price et al (1994) along with an average body weight of 60 kg and various uncertainty factors to determine the acceptable daily intake of boron to be 18 mg B/day (Murray, 1995).

CURRENT REGULATIONS AND GUIDELINES GOVERNING BORON

A. EPA Contaminant Candidate List (CCL)

The United States Environmental Protection Agency (USEPA) is required by the Safe Drinking Water Act (SDWA) to establish a list of contaminants to assist in setting priorities for its drinking water program. This list, called the Candidate Contaminant List (CCL), was published in 1998 and includes boron (EPA, 2003). Boron, however, was not selected as a priority for regulatory determination due to insufficient data and information on treatment options.

B. World Health Organization Guideline

The World Health Organization (WHO) did not address boron in its 1958, 1963, or 1971 International Standards for Drinking-Water. In 1984 the WHO determined that no action was required for boron. However, in 1993 the WHO established a health-based guideline of 0.3 mg/L for boron. This value was raised to 0.5 mg/L in 1998 primarily because the treatment technology at that time precluded the ability to achieve 0.3 mg/L in areas with high natural boron levels. Furthermore, in 2000 it was decided to leave the guideline at 0.5 mg/L until data from ongoing research becomes available that may change the current view of boron toxicity or boron treatment technology (WHO, 2003).

C. European Union

The European Union is currently comprised of 15 countries in Europe and is in the process of accepting 13 additional eastern and southern European countries. The European Union established a value of 1.0 mg/L for boron in 1998 for the quality of water intended for human consumption (Council of the European Union, 1998).

D. Canada

The interim maximum acceptable concentration (IMAC) for boron in Canada is 5 mg/L. The Canadians have established this value on the basis of practical treatment technology. They believe available technologies are inadequate to reduce boron concentrations to less than 5 mg/L. They will review this IMAC periodically as new data becomes available (Health Canada, 2002).

E. New Zealand

New Zealand has established a drinking water standard for boron of 1.4 mg/L. This maximum acceptable value (MAV) was calculated using a Tolerable Daily Intake (TDI) approach which identifies the dose below which no major adverse health effects are likely to occur from a lifetime consumption of two liters of water per day (New Zealand Ministry of Health, 2000).

TREATMENT OF BORON-CONTAINING WATERS

Boron must be removed from waters for various reasons and, as described previously, boron concentration is regulated in some areas. Boron levels of interest range from a few µg/L to several grams per liter depending on the specific industry (Table 1-6). This section describes the wide range of existing water treatment technologies that have been tested or utilized for boron removal.

A. Precipitation

Removal of contaminants by direct precipitation is very advantageous for treatment of drinking water or wastewater. For example, in comparison to coagulation where 10-100 moles of sorbent such as $Fe(OH)_3$ or $Al(OH)_3$ solids are commonly formed per mole contaminant removed (i.e., McNeill and Edwards, 1997), direct precipitation can typically remove closer to 0.3 to 3 mole contaminant per mole cation added. This higher efficiency directly translates to lower overall costs because both chemical costs and sludge volumes are reduced. On the other hand, many contaminants are too soluble to be removed by precipitation, whereas virtually any level of contaminant removal can be obtained by sorption if enough surface area is provided (assuming appropriate pH and water composition conditions can be maintained) (Edwards and Benjamin, 1989). For these reasons, low solubility metal borate precipitates would be very useful to water treatment if they existed, although the cationic component of the solid must obviously be safe for human consumption if used in drinking water applications.

Unfortunately, it does not appear that suitable low solubility compounds have ever been identified to date for inorganic borate. Magnesium borate [$Mg_3(BO_3)_2$] is listed as "insoluble" (Dean, 1987). While deserving of future study given that boron and magnesium are naturally present at 4.5 and 1350 mg/L in seawater, respectively, formation of this compound may not remove boron from drinking water to levels less than 1 mg/L at reasonable pHs. Calcium borate is also among the less soluble borates, and in one study addition of 10 g/L gypsum to water completely removed 1 mg/L boron to below detection (Gupta and Chandra, 1972). This is such a high solids dose, however, that grams per liter of soluble Ca^{+2} and SO_4^{-2} must be added to the drinking water to remove the boron, which would be unacceptable, as would the resulting sludge production. Moreover, it is not clear that the mechanism of removal was precipitation in the Gupta study. Another reference cites formation of low solubility compounds between zirconium and boron, but no solubility products were provided (Pilipenko et al., 1990), nor is it known if the term "low solubility" in the study meant μg/L, mg/L or g/L levels of soluble boron in equilibrium with the added zirconium.

Of course, given that g/L levels of boron have been of concern in certain cases, direct precipitation has its role in removal of boron from water (Table 1-7). For example, it has been reported that either activated alumina plus lime, or MgO plus lime, could remove between 60-80% of the boron from a 1-10 g/L initial borate solution (Recepoglu and Beker, 1991). Of course, this leaves hundreds of mg/L level of boron in the finished water, and is therefore not suited to achieving proposed drinking water standards. In general, it is believed that direct precipitation is not effective at reducing boron below 200 mg/L (Pilipenko et al., 1990).

There is one recent intriguing report in the literature that suggests some lower solubility boron compounds exist, but it was not peer reviewed and it even seems contrary to other observations in the literature that will be discussed later. That is, careful reading of Japanese patent literature suggests that dosing of 10 mg/L alum to seawater decreased soluble boron from 4.15 down to 0.93 mg/L (Minegichi and Katagiri, 1997), and a solid purportedly formed which could be removed by a 0.1 µm pore size filter. Dosing a similar amount of iron was not effective, suggesting that some kind of aluminum borate solid was forming. It is instructive to calculate the stoichiometry of the reported reaction. Assuming a molecular weight of 333 mg/L alum per mole aluminum (this will vary slightly dependent on waters of hydration in the solid), the 0.03 mM Al^{+3} added precipitated 0.3 mM boron from seawater. This ratio, if it were true, would suggest that some kind of alumino-borate solid that contained other cationic constituents must have formed. This issue deserves additional research.

B. Inorganic Sorption

Boron removal by sorption onto activated alumina, bauxite, $Mg(OH)_2$, $Fe(OH)_3$, activated carbon, $Al(OH)_3$, calcite, or combinations of these solids formed in situ during coagulation and softening has been reported (Table 1-7). With a few possible exceptions in which operating details were not provided, boron is not strongly sorbed by the sorbents commonly formed in drinking water treatment. Consequently, gram per liter levels of sorbents must be formed or added to remove significant amounts of boron, as opposed to the mg/L levels typically employed for some other contaminants in drinking water such as arsenic (McNeill and Edwards, 1997). Chemical costs and sludge handling costs rise in proportion to the adsorbent dose, so this immediately raises concerns regarding the economic feasibility of these approaches.

For many sorbents, optimum removal is often at pH 6-9 (Choi and Chen, 1979), which is the pH range at which significant anionic boron may be present (pKa = 9.24). This pH is also low enough that OH^- in water may not be able to out-compete borate for surface sites. Generally speaking, sorption is only slightly impacted by levels of sulfate and silica present in natural waters (Choi and Chen, 1979). In treatment of geothermal waters, however, which contained several hundred mg/L of silica, the first 3 moles of Mg^{+2} added/mol silica was completely consumed by reactions with silica. Thereafter, the added $Mg(OH)_2$ solid was able to react with the 24 mg/L boron present, and removals as high as 33% were achieved if 8 moles of $Mg(OH)_2$ were added per mole silica (Recepoglu and Beker, 1991). With respect to treatment of wastewaters, addition of $Mg(OH)_2$ solids at a molar ratio of 20:1 removed more than 90% of boron initially present at 500 mg/L, leaving behind 50 mg/L soluble boron. Boron appears to be capable of forming polymeric surface complexes on sorbents, but only at equilibrium levels well above 1 mg/L (Su and Suarez, 1995).

Nearly all of the above studies illustrate that conventional coagulation processes using alum or ferric will not be highly effective in removing boron. This finds some support in the literature. For example, in 1996, a consulting company sampled a few treatment plants in England (Table 1-7), and found that boron removal was always less than 28% (Borax Consolidated Ltd., 1996) with typical removal below 10%. Likewise, undetectable levels of boron removal were obtained from alum and ferric doses of 40-100 mg/L in wastewater applications at pH 5.5 or 8 (Waggott, 1969). Numerous other studies mention that they attempted coagulation, but that it was not effective (i.e., Bansal, 1980). Softening processes have some promise, but there is currently no proof that they can be effective at reasonable chemical doses, and in fact, some evidence suggests that they will not be useful. For instance, Waggott (1969) tested very high dose lime softening (263-400 mg/L) as a means of removing boron from wastewater effluent. No information was presented as to the concentrations of $CaCO_3$ or $Mg(OH)_2$ solids formed, or final pH for that matter, but removal of 1.6 mg/L B was between 0-16% at all conditions tested. These observations are consistent with fundamental studies of boron removal by calcite formation in seawater (Kitano et al., 1978)-- even formation of gram per liter levels of $CaCO_3$ would only remove < 0.05 mg/L boron from seawater.

In contrast, a Mg^{2+} assisted lime softening process has been cited as effective in reducing B to less than 0.2 mg/L in wastewater re-use applications, although the initial B level, chemical doses or other operational details were not provided (Idelovitch et al., 1980). If the study of Wong (1984) is any indication, it seems likely that the chemical doses used by Idelovitch were high. For example, in the Wong study, 87% of a 1.2 mg/L B solution was removed by dosing 1.2 g alum/liter with an even greater lime dose at pH 12.0 (Wong, 1984). Sodium aluminate gave 65% removal at a dosage of 1.1 g/liter also at pH 12 in the same study. Addition of sodium aluminate and lime together during softening reportedly remove 90% of boron from seawater, whereas each chemical alone is not capable of this level of removal, but again, information on chemical doses was not provided and the original references could not be obtained (Lapp and Cooper, 1976). In summary, in every case where boron removal was effective during softening, greater than gram per liter levels of sorbents had to be formed as calcite, $Mg(OH)_2$ or other unknown compounds, and when high removal was reported data on doses were not provided. No one has ever reported information on boron removal from conventional softening processes at drinking water treatment plants.

Hydrous cerium oxide (HCO) has been found to be suitable for the sorption of boron from geothermal waters. Boron uptakes increase with adsorption temperatures above 100 °C and can reach a level of 1.0 mmol/g at 200 °C (Hayashi et al., 1991).

C. Ion Exchange and Other Organic Sorbents

Some observations have been made regarding boron removal by strong acid and strong base ion exchange resins. Removal by sorption to boron specific resins, activated carbon and cellulose are discussed in a separate sub-section below.

Strong Base and Strong Acid Resins. Given that boron is very weakly acidic, it is not surprising that it is removed within strong base anion exchange resins. Most experience with boron removal using this technology has been obtained in the semiconductor industry, where boron is a dopant and even μg/L concentrations in the cleaning solution must be strictly controlled. Interestingly, researchers have discovered that while silica was previously believed to be the first ion to breakthrough strong base resins in ion exchange processes, boron actually breaks through well before silica when it is present (Malhotra et al., 1996). This is problematic because the boron breakthrough cannot readily be detected by conductivity only. Indeed, chromatographic peaking of previously removed boron has led to plant toxicity when strong base ion exchange was used in irrigation water (Paul, 1974).

Boron removal by strong base resins has also been exploited in the nuclear power industry, where maintaining precise control over pressurized water reactors is critical (Brown, 1980; Lou et al. 1999). Boron removal by strong base resins is insignificant at pH 5 but is substantial at higher pH (Wong, 1984). While the capacity for boron removal can be increased by impregnating the resin with citric acid (Ristic and Rajakovic, 1996) because its selectivity is the least of any common chemical in water, strong base exchange resins are not likely to be cost effective in boron removal from drinking water. Contrary to expectations given boron's anionic or neutral character, some incidental removal of boron has been noted to occur in cation exchange resins, but specifics were not provided (Wong, 1984).

Boron-Specific Resin, Activated Carbon and Cellulose. Industries interested in removing boron from water have long sought specificity in removal. Several types of resins are reported to be boron specific including Diaion CRB 02, Purolite S 108, and Amberlite IRA-743. New resins that might improve removal characteristics have been under development since at least 1971 (Grinstead and Wheaton, 1971; Maeda et al., 1995; Bicak and Senkal, 1998). While the literature cites small scale pilot testing and some preliminary cost data, especially for removal of boron that had passed through reverse osmosis and electrodialysis plants in potable water production (i.e., Song and Huang, 1987), it is unknown if any full scale applications of this technology are in use for drinking water treatment, or even wastewater treatment for that matter. Sahin (1996) has established that the optimum pH for boron removal by Amberlite IRA-743 is observed at pH = 8 and that 95% removal efficiency can be obtained when waters contain high levels (50 - 1600 mg/L) of boron (Sahin, 1996).

The vast majority of research conducted to date on use of these resins is based on studies at the Kilzidere-Turkey geothermal power plant and other areas in Turkey where boron is actively mined. At the geothermal plant, the water under consideration has a pH of 9.3, extremely low hardness (total Ca and Mg < 0.5 mg/L), and extremely high silica (415 mg/L SiO_2), sulfate (700 mg/L), and alkalinity (> 1500 mg/L as $CaCO_3$). In this water, the sulfate and silica and other dissolved salts do not appear to influence resin performance significantly, nor does pH over the range typically encountered in drinking water treatment. While two stages of regeneration are typically necessary for boron specific resin, including 4% H_2SO_4 to desorb the boron followed by 4% NaOH to neutralize the acid from step one, it has been shown that regeneration with acid alone is feasible in some particularly high alkalinity water (Roberts, 1971; Okay et al., 1985). This produces a substantial cost savings.

After considering the value of the boron recovered from the resin in the Turkish research, a calculation was performed suggesting that the process is somewhat less expensive than $Mg(OH)_2$ dosing for this particular water, but details of the calculation were not presented (Okay et al., 1985). It has been stated that recovery of boric acid from regeneration solutions is not cost effective if the water treated contains less than 1 g/L (Pilipenko et al., 1990). If this is true, resource recovery from regenerant solutions in drinking water applications is likely to be difficult, if not impossible, given that drinking waters typically contain less than 2 mg/L B. Pilipenko (1990) further notes that boron specific resins are unlikely to work well in drinking waters due to their greatly reduced capacities at the mg/L level, but no strong arguments were made for this point of view.

Recently, French researchers have tested Amberlite IRA-743 in two drinking water sources (Simonnot et al., 2000). Data from that study indicated that the resin was fairly specific for boron, and that the bed volumes treated before complete breakthrough was about equal to 2000 divided by the mg/L boron concentration in the influent. Thus, at 5 mg/L influent boron, 100% breakthrough occurred at 400 bed volumes, whereas at 1 mg/L influent boron breakthrough was at about 2000 bed volumes. The authors noted that this was a promising technology, but even more questions were raised in this work than were answered. These include 1) concern over chemical or biological degradation of the resin, and its useful lifetime, 2) high operating costs and initial costs (i.e., \$850 - \$1350/ft^3 of resin in 2003, depending on manufacturer), and studies suggesting that the resin may be fouled by solids (Lapp and Cooper, 1976), 3) what to do with the large volume of regenerant with concentrated boron, and 4) concern over the high pH of water produced during treatment.

The last two concerns raised by Simonnot et al. (2000) are noteworthy. Disposal of residuals often accounts for as much as 90% of treatment costs in drinking water for contaminants such as arsenic (Frey et al., 1998), and this issue has never been considered in any previous cost analysis of the boron specific resins. This is because the solutions treated previously contained relatively high influent levels of boron, producing a highly concentrated regenerant from which the researchers believed boron could be recovered as a resource. As noted above, this might not be possible in drinking water. Alternatively, as in the case of desalination applications, the boron-containing brine can be discharged to the ocean. Simonnot et al. (2000) also noted that use of the resin dramatically changed the character of the water that was treated. In fact, even for a moderately buffered water source (68 mg/L as $CaCO_3$), effluent pH was as high as 11. Rinsing the resin with a buffered solution can solve this problem, however the primary concern is the volume of regenerants that are required. Moreover, the resin has not yet been approved for use in drinking water applications.

Activated carbon, strong base resins impregnated with citric acid, and columns packed with cellulose have all been tested as a means of removing boron (Table 1-8). The capacity of these materials is very low, even through 90%+ removal is possible at low column run times or if gram per liter levels of carbon is dosed. For this reason, these sorbents are unlikely to be economically applied to drinking water treatment.

D. Membrane Filtration

Nanofiltration, reverse osmosis, and electrodialysis reversal have been tested in boron removal (Table 1-9). It should be noted at the outset that none of these technologies is routinely used in drinking water treatment due to their very high cost. Moreover, as this review notes, even these advanced technologies have extreme difficulty in removing boron by themselves, and often require enhancements before they can effectively remove boron.

For example, electrodialysis reversal has been cited as removing 96% of boron from water by manufacturers (Ionics, 1995), however the one test on drinking water led to nearly undetectable removal (Nicolai et al., 1996). If the water is highly mineralized or if pH is below about 8.2, it appears that treatment efficiency falls off dramatically.

Under circumstance of low total dissolved solids (TDS) and boron, greater than 96.6% removal of boron was possible at four ultra-pure water systems tested, but this was after reverse osmosis or softening of the water as pretreatment (Hernon et al., 1999).
It is well known that single stage reverse osmosis (RO) cannot typically meet WHO guidelines of 0.5 mg/L boron in seawater (Table 1-9), and “extra treatment” of such water to meet these guidelines has been the subject of considerable research. The rejection of boron depends on pH, so it is possible to obtain good removals using RO at very high pH, but under circumstances that are atypical of drinking water treatment and under conditions where scaling is a major problem. Nanofiltration by itself does not remove detectable levels of boron from water.

Several types of assisted or enhanced RO treatment have been tested. For instance, if two or three stage RO is used, pH can be raised after hardness ions are removed in stage 1, allowing better removal of boron due to the higher pH while avoiding scaling due to calcite or $Mg(OH)_2$ precipitation (Magara et al., 1998). Alternatively, researchers have tested the dosing of chemicals that complex boron before the membrane process. The general idea is that, by producing a dissolved boron compound that has a charge or a larger molecular size, rejection of boron by the membrane will be improved to acceptable levels. Smith et al. (1995) found that dosing >1 g/L polymer before a nanofiltration membrane led to >80% boron removal, but these levels of polymer are hundreds or thousands of times higher than are used in drinking water. Likewise, dosing of cellulose can enhance boron removal by RO (Choi and Chen, 1979). Finally, Japanese patent literature suggests that addition of >3.5 mole fluoride per mole boron will increase RO rejection efficiency to more than 98%, presumably by formation of borofluorate complexes (Akiga et al., 1996). Ironically, use of existing equilibrium constants suggests that the levels of fluoride dosed were completely insufficient to form these complexes, so either the available complexation constants are wrong, or an alternative explanation for the improved removal is necessary.

E. Phytoremediation

The use of plants to lower boron levels in soil has received some study. Banuelos et al. (1993) found that Indian mustard (*Brassica juncea*), tall *fescue (Festuca arundinacea*), Birdsfoot trefoil (*Lotus corniculatus*), and kenaf (*Hibiscus cannibinus*) reduced extractable soil boron by as much as 52% (Banuelos et al., 1993). Poplar trees have been used in New Zealand to lower boron levels in a sawdust pile leachate from 1.87 mg/L to < 0.80 mg/L in less than two years (Robinson et al., 2003).

CONCLUSIONS

As the world's water demand increases more attention will be given to the oceans and brackish water as sources of drinking water. Studies have shown that 18 mg B/day has no adverse effects on human health (Murray, 1995) and the average human consumes about 1 mg B/day in their diet (Meacham and Hunt, 1998). This leaves 17 mg B/day that could be consumed in drinking water without adverse effects. Therefore, for an average consumption of 2 L/day, drinking water boron concentration could be as high as 8.5 mg/L without adversely affecting human health. Since seawater has a boron concentration less than this, at first glance there would appear to be no reason for removing boron from seawater. However, this boron concentration is much too high for the water to be used for irrigation. While we do not see a need for boron regulation in drinking waters based on results from existing studies, the world still has a need for better boron removal techniques.

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Table 1-1. Solubility Product Constants for Various Boron-Containing Minerals

Mineral	**K_{sp}**	**Solubility Reaction**
Pinnoite	2.5E-05	$Mg[B_2O(OH)_6] + H_2O = Mg^{2+} + 2B(OH)_4^-$
Inderite	1.4E-17	$Mg[B_3O_3(OH)_5]\cdot 5H_2O = Mg^{2+} + 3B(OH)_4^- + H^+ + H_2O$
Colemanite	2.9E-18	$Ca[B_3O_4(OH)_3]\cdot H_2O + 4H_2O = Ca^{2+} + 3B(OH)_4^- + H^+$
Inyoite	2.9E-18	$Ca[B_3O_3(OH)_5]\cdot 4H_2O = Ca^{2+} + 3B(OH)_4^- + H^+$
Borax	3.3E-26	$Na_2[B_4O_5(OH)_4]\cdot 8H_2O = 2Na^+ + 4B(OH)_4^- + 2H^+ + H_2O$
McAllisterite	1.3E-46	$Mg[B_6O_7(OH)_6]\cdot 4.5H_2O + 7H_2O = Mg^{2+} + 6B(OH)_4^- + 4H^+$
Nobleite	1.7E-48	$Ca[B_6O_9(OH)_2]\cdot 3H_2O + 10H_2O = Ca^{2+} + 6B(OH)_4^- + 2H^+$

Table 1-2. Boron-Containing Minerals of Commercial Importance

Mineral	Chemical Compostion	% Boron
Boracite	$Mg_6B_{14}O_{26}Cl_2$	19.30
Colemanite	$Ca_2B_6O_{11}\cdot 5H_2O$	15.78
Datolite	$CaBSiO_4\cdot OH$	6.76
Hydroboracite	$CaMgB_6O_{11}\cdot 6H_2O$	15.69
Kernite	$Na_2B_4O_7\cdot 4H_2O$	14.90
Priceite	$Ca_4B_{10}O_{19}\cdot 7H_2O$	15.48
Proberite	$NaCaB_5O_9\cdot 5H_2O$	15.39
Sassolite	H_3BO_3	17.48
Szaibelyite	$MgBO_2\cdot OH$	12.85
Tincal (borax)	$Na_2B_4O_7\cdot 10H_2O$	11.34
Tincalconite	$Na_2B_4O_7\cdot 5H_2O$	15.16
Ulexite	$NaCaB_5O_9\cdot 8H_2O$	13.34

Source: Lyday, 2000

Table 1-3. Summary of Boron Levels in Selected States

		Boron concentration in mg/L			
State	*Total Samples*	*10 %ile*	*50 %ile*	*90 %ile*	*Max.*
U.S. STORET	55,416	0.010	0.076	0.387	150.0
Arizona	1,673	0.100	0.100	0.170	2.1
California	6,421	0	0.105	0.449	140.0
Colorado	1,979	0.010	0.102	0.302	0.860
Idaho	519	0.028	0.080	0.170	0.330
Illinois	30,116	0.050	0.050	0.112	2.625
Michigan	159	0.010	0.055	0.347	1.000
Montana	1,571	0.010	0.140	0.610	81.0
Nevada	234	0.024	0.105	0.784	73.0
New Mexico	1,930	0.100	0.100	0.616	150.0
North Dakota	2,398	0.070	0.228	0.519	17.0
Oklahoma	515	0.030	0.170	0.440	1.100
Oregon	1,394	0.03	0.030	0.268	6.300
Utah	835	0.037	0.070	0.316	3.893
Wyoming	634	0.015	0.097	0.262	1.200

Table of STORET database: 1984 - 1993; selected states account for 91% of the data
Source: Dyer and Caprara, 1997

Table 1-4. Summary of Maximum Boron Levels in Selected Countries

Region/Country	Description	Maximum B Concentration (mg/L)	Source
Canada	Surface Water	2.9	Coughlin, 1998
Chile	Drinking Water	15.2	Barr et al, 1993
Germany	Surface Water (1974)	2.0	Butterwick et al, 1989
Sweden	Surface Water (1972)	1.046	Butterwick et al, 1989
United Kingdom	Surface Water (1980)	0.822	Butterwick et al, 1989

Table 1-5. Boron Concentrations in Various Foods

Food Category	Boron Content (μg/100 g)	Food Category	Boron Content (μg/100 g)
Raisins	2200	Bananas	135
Peanuts	1700	Peas, green	130
Peanut Butter	1450	Beans, string	120
Wine	610	Spaghetti sauce, tomato sauce	120
Peaches	530	Coleslaw, cabbage	120
Grapes	490	Beef stew	120
Peas, cowpeas, field peas	460	Potatoes	110
Cereals, ready to eat	450	Lettuce	105
Beans, dried, cooked	400	Pizza	76
Beans, lima	370	Orange Juice	72
Apples	360	Spaghetti, tomato-based sauce	65
Potato chips	325	Tomatoes, tomato juice	63
Grape Juice	300	Fish and shellfish	54
Applesauce	280	Sandwiches, with meat (inc. hamburgers)	51
Pears	280	Bread and rolls, white	46
Oranges	260	Corn	46
Broccoli	250	Rice	32
Fruit cocktail	240	Coffee	29
Carrots	230	Chicken	27
Onions	190	Ice cream, milk desserts	22
Apple Juice	180	Milk	18
Cantaloupe	180	Fruit-flavored drinks	16
Spinach, collards, turnip greens	180	Cola drinks	13
Chili con carne	170	Beer	12
Soups, meat based	140	Tea	9

Source: "Daily boron intake from the American diet" by Rainey et al., 1999

Table 1-6. Review of industries and scenarios where boron removal is of interest.

Type of Water	Initial boron conc.	Cause of Concern
Ultrapure water	< 0.5 mg/L	Significant levels of boron pass through strong base de-ionizers, distillation and RO units. Particular problem in semiconductor industry where precise control of B doping is required.
Geothermal	10-100 mg/L	Release of boron to receiving water can exceed mg/L level in streams, limiting exploitation of geothermal resource.
Nuclear	> 3 g/L	Boron concentration is varied to control rate of core reactions. Boron is very effective in neutron capture, and leakage represents a significant problem.
Landfill Leachate	1-10 mg/L	Indicator of leachate plume and extent of potential groundwater contamination.
Coal power plants/fly ash	3-100 mg/L	Ash pond water and cooling pond water contain high levels of boron. About 25% of the boron is carried over in this water during evaporative purification, preventing re-use as potable water.
Irrigation Water	> 1 mg/L	Removal may be necessary to prevent crop damage. May also need to be leached or immobilized in soil to recover land for agriculture in some cases.
Seawater Evaporation Brine	g/L	Boron co-precipitates with $Mg(OH_{)2}$, decreasing the melting point and preventing resource recovery
Desalination	5 mg/L	Several countries have limit on B in drinking water in the tenths of mg/L range. Cannot be achieved by normal RO.
Sewage	1-3 mg/L	Boron in detergents adds to wastewater loads, and might inhibit bacterial activity and exceed mg/L levels in streams
Drinking Water Treatment	< 1 mg/L	If boron exceeds mg/L level, could inhibit plant growth.

Table 1-7. Boron Removal by Conventional Sorption, Softening or Co-Precipitation

Technology	Water Tested	Mass or Percentage Removal	Comment	Reference
Softening	Seawater	Insignificant	Batch test of calcite precipitation	Kitano et al., 1978
	Wastewater	0%	Bench Test	Waggott, 1969
	Wastewater with 1.2 mg/L B	50%	Original reference could not be obtained, secondary reference cited. Mg^{2+} addition required.	Idelovich et al., 1980 and Nicoli et al., 1996
Alum/Ferric Coagulation	Wastewater	0%	No removal at high doses	Waggott, 1969
	Unk.	90%	Alumina/lime/soda ash process. Original reference could not be obtained.	Lapp and Cooper, 1976
	Drinking waters in England with up to 0.5 mg/L B	< 28%	No information provided on coagulant doses or pHs. Typical removal < 10%	Borax Consolidated Ltd., 1996
	Wastewater	0	Bench Test	Waggott, 1969
	Seawater	< 4%	10 mg/L Ferric Chloride with sand filter	Minegichi and Katagiri, 1997
Coagulants	Synthetic waste, 5 g/L B	Little or no B removal	13 coagulants reportedly tested	Bansal, 1980
Coagulation	4 hard waters in England	< 28%	Full-scale treatment. < 10% removal typical.	Borax Consolidated Ltd., 1996
Other sorbents				
- Bauxite	Unknown	50%	Bench Test	Choi and Chen, 1979
- MgO	Synthetic waste > 100/mgL B	50-90%	Expensive. Final sludge contained 3.5% B by weight. > 50 mg/L boron left in water.	Okay et al., 1985
	Synthetic water > 20 mg/L B	50-60% removal	> 5 mg/L B left in water	Nicoli et al., 1996
		50%	Waters with about 30-90 mg/L initial B.	Nicoli et al., 1996
-12 inorganic sorbents	36 g/L sulfate and 1.5 g/L B	< 1%	Removed up to 6.5 mg/B/g sorbent.	Ooi et al., 1996

Table 1-8. Boron Removal by Sorption to Organic Matter or Ion Exchange

Technology	Water Tested	Mass or Percentage Removal	Comment	Reference
Activated Carbon	Synthetic waters with 5-100 mg/L B	up to 90%	Batch Tests. Doses exceeding 100 g/L carbon necessary to obtain high removal or low initial boron. Very poor adsorbent.	Choi and Chen, 1979
Impregnated Resin	28-100 mg/L B in DI water	>95%	Impregnation of citric acid increases capacity, but capacity is low	Ristic and Rajakovic, 1996
Cellulose	Unk.	90%	Columns with influent containing 30-100 mg/L B. Very low capacity	Choi and Chen, 1979
Ion Specific Resin: Diaion CRB 02 Purolite S 108 Amberlite IRA-743 or XE-243	Kizildere geothermal field work. Very low hardness, high silica and sulfate, 30 mg/L B.	>97%	Resin insensitive to virtually all anions including silica, SO_4^{-2}, Ca^{+2}. Tested up to 3 regeneration cycles, and could be regenerated with H_2SO_4 alone due to high alkalinity geothermal water. Acid regenerant can be re-used.	Badruk et al., 1999(a); Beker et al., 1996; Okay et al., 1985; Beker, 1999; Recepoglu and Beker, 1991
	RO permeate with 1.8 mg/L B	>99%	pH of produced water with H_2SO_4 regeneration alone was < 4.5 for 600 Bed volumes.	Nadav, 1999
	2 tapwaters	>99%	Could treat about 400 bed volumes when influent contained 3 mg/L B. pH control difficult. Went as high as 11 after NaOH regeneration.	Simonnot et al., 2000

Table 1-9. Boron Removal by Reverse Osmosis, Nanofiltration, Electrodialysis Reversal, or Enhanced Versions of these Processes

Technology	Water Tested	Mass or Percentage Removal	Comment	Reference
EDR	Unk.	96%		Ionics, 1995
	Unk.	75%		Pilipenko et al., 1990
	Drinking water	0%	Poor removal attributed to lower pH of 8.2 and presence of salts.	Nicoli et al., 1996
	NaCl solutions (unknown composition)	27-89%	Better percentage removal at higher pH, if salt concentration < 0.2 g/L, and at lower initial B concentrations.	Melnik et al., 1999
RO	Unk.	25-88%	High mineral waters, synthetic seawater	Pilipenko et al., 1990; Fukunaga et al., 1997; Prats et al., 2000
	Synthetic waste > 5 g B/L	46%	Synthetic radioactive wastewater.	Bansal, 1980
	Seawater	43-78%	Survey of 8 operating RO plants. Percent rejection decreased with lower salinity.	Magara et al., 1996
Nanofiltration	Unk.	Minimal	Specifics not repeated	Nicoli et al., 1996
Assisted RO	Seawater	>70	If higher pH or cellulose dosed	Minegichi and Katagiri, 1997
	RO permeate	40-100%	Best removal at pH 10.5	Prats et al., 2000
	RO permeate	>98%	If F- complexes are preformed, >3.5 mol F- for every mol B. Avoids scaling.	Akiga et al., 1996
	RO permeate	>90	pH raised to above 9 after 1st RO membrane to avoid scaling of second stage	Sawada et al., 1996; Magara et al., 1998
Assisted Nanofiltration	Synthetic waste 10 mg B/L	>80%	Addition of > 1 gram per liter N-methyl-D-glucamine polymer to enhance removal	Smith et al., 1995

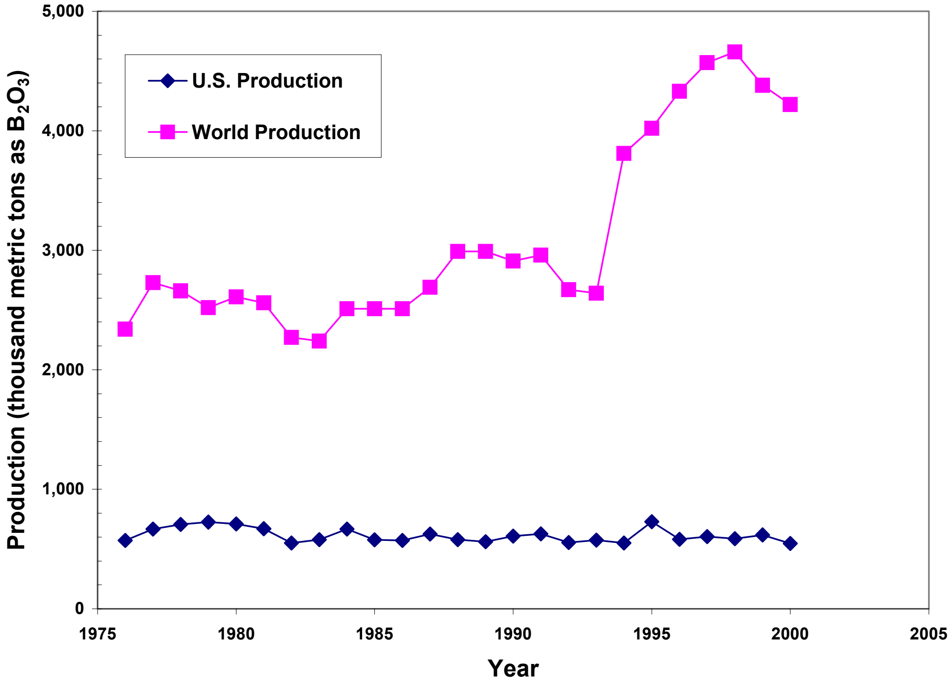

Figure 1-1. U.S. and worldwide historical production of boron (as boron oxide)

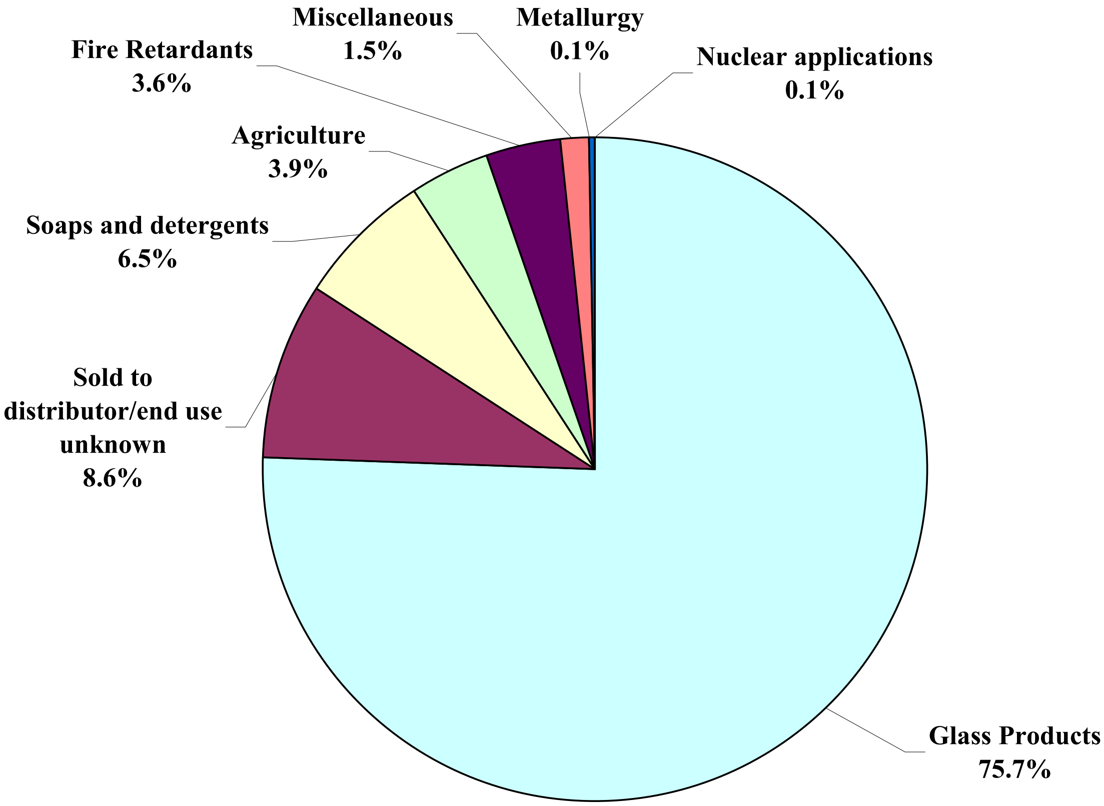

Figure 1-2. Year 2000 U.S. consumption of boron by end use

CHAPTER II: DETERMINATION OF TOTAL CHROMIUM IN ENVIRONMENTAL WATER SAMPLES

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ABSTRACT

It is often desirable to quantify both dissolved Cr(VI) and total Cr in samples accurately. Various protocols are now being utilized to quantify the amount of total chromium in natural waters and each of these has possible interferences. This study describes the shortcomings of each method when particulate iron is present in a water sample, and a more rigorous digestion protocol is tested. Data from bench studies as well as a field survey of 21 water utilities are presented. Additionally, field data from several hundred water utility samples are presented to illustrate the potential for incomplete recovery of total chromium using accepted protocols.

INTRODUCTION

Two oxidation states of chromium are important in natural waters: Cr(VI) and Cr(III). Each has a unique chemistry and behavior; for example, Cr(VI) is believed to be a carcinogen in humans while Cr(III) is actually a micronutrient (Katz et al, 1993). As total Cr and Cr(VI) may be regulated differently, it is necessary to quantify both Cr(VI) and total Cr in samples accurately. In the paragraphs that follow, existing sampling protocols are described, some practical chemistry aspects of chromium in the environment are reviewed, and potential deficiencies in current analytical approaches are anticipated.

Existing Sampling Protocols. There are several EPA and Standard Method procedures relevant to sampling and quantification of chromium in environmental samples (Table 2-1). Drinking water sample preparation/preservation protocols are described in Standard Method 3030 while a method for alkaline digestion of soil samples for chromium is given by EPA SW846 Method 3060A (Standard Methods, 1998; EPA 2000). EPA Methods 1669/1639, for the sampling of ambient water for chromium, were adapted from techniques developed for seawater (EPA 1996a; EPA 1996b).

It is important to understand sample pre-treatment protocols in Standard Method 3030A (Figure 2-1). To review the key steps, the pH is adjusted to 2.0 or less in the field and the turbidity of the drinking water sample is measured upon receipt in the lab. The sample is later digested with nitric acid according to Standard Method 3030E (if turbidity exceeds 1.0 NTU) and analyzed with an approved instrument such as ICP-MS, ICP, or

Graphite Furnace AA. If the turbidity is below 1.0 NTU the sample may be analyzed without digestion (Standard Methods, 1998).

Standard Methods (1998) states in 3030A that, for further verification on the necessity of sample digestion, a comparison can be made between digested and undigested samples to ensure comparable results. Standard Method 3030D gives details on which digestion procedure should be used in various situations but fails to make a recommendation in the case of chromium. Additionally, Standard Method 3030D recommends using the least rigorous digestion method that provides consistent results but fails to rank the methods accordingly.

Particulate Chromium in Environmental Samples. Both Cr(III) and Cr(VI) can strongly sorb to iron hydroxide solids forming particulate Cr(III) and Cr(VI) in water (Dzombak and Morel, 1990)(Figure 2-2). This reaction is routinely exploited in industry to remove mg/L levels of both Cr(VI) and Cr(III) from wastewaters using iron coagulants and materials such as iron oxide coated sand (Edwards et al, 1989; Bailey et al, 1992). For purposes of this paper we operationally define three fractions of chromium in association with iron hydroxide as follows:

(1) "Soluble" chromium passes through a 0.45 μm pore size filter,
(2) "Sorbed" chromium is the fraction of chromium that is chemisorbed to the iron hydroxide, but which could be released in either acidic or basic solution without complete dissolution of the iron hydroxide solid,
(3) "Fixed" chromium is the fraction of chromium associated with the iron hydroxide that is not released unless the solid is completely dissolved.

Each of these fractions can occur for Cr(III) and/or Cr(VI).

The types of iron hydroxide particles that might be encountered in drinking water sources are varied. Fresh iron hydroxide particles formed by coagulation and Fe^{2+} removal can be easily dissolved in relatively weak acid (Davis et al, 2002). However, older iron hydroxide that might be present on corroded pipes, in sludge after aging, or present in turbidity from soil is much more difficult to dissolve (Rushing et al, 2003). Our extensive experience in drinking water analysis suggests that digestion in 5% nitric acid or HCl/hydroxylamine is necessary to dissolve many types of iron particles. It is only in unusual circumstances that exposure to a pH 2 solution will completely dissolve iron particles and boiling in 5% nitric acid for 12 hours is often insufficient. This is implicitly recognized in Standard Methods (1998), which recommends that hydroxylamine be used for conversion of Fe(III) to Fe(II) in samples where iron must be quantified. Hydroxylamine is not, however, one of the options listed for preliminary treatment of samples in Standard Method 3030.

Practical and Conceptual Basis for Anticipated Problems with Total Chromium Analysis. Certain sampling and analytical problems are anticipated if particles are present in environmental samples. For instance, Standard Method 3500-Fe advises caution when sampling water with particles, since the bottle must be shaken vigorously before a representative sample is removed for analysis. It also mentions that colloidal iron may adhere to sample containers. Although no method is cited to detect problems with colloidal iron attachment, it is stated that the problem can be acute for plastic bottles and that acid should be used at the time of sample collection to minimize deposition on container walls (Standard Methods, 1998). Obviously, if iron particulates/colloids contain sorbed or fixed chromium (see Figure 2-2), untimely settling and sorption of these particles could cause problems with Cr analysis. Particles can also interfere in analytical protocols by plugging nebulizers, and particulate Cr may give a smaller signal than the soluble Cr used to standardize the instrument. For example, previous research by Zhang and Koropchak (1999) using ICP-ES or ICP-MS in conjunction with thermospray sample introduction is based on the fact that particulate Cr is not significantly detected in samples compared to soluble Cr.

Field experiences have suggested that there is a significant problem with current procedures. Eaton et al. (2001) and Davis (2000) found that for many samples of California drinking water samples the total Cr concentration was apparently less than soluble Cr(VI) (Figure 2-3). Since this is clearly impossible, if soluble Cr(VI) measurements are accurate as is currently believed, the result strongly implies that some Cr(VI) has to be "lost" during determination of total Cr. Eaton et al. (2001) found that addition of hydrogen peroxide to the samples in question improved total Cr recovery. Other data collected by Edwards et al. (1998) in a survey for arsenic in U.S. drinking water also indicated there could be problems with total Cr determination. For 66 waters collected, soluble Cr was determined in samples after filtration in the field, and this result was compared to total Cr recovered after an 'in-the-bottle' acid digestion containing an unfiltered, unacidified sample. Over 60% of these samples had soluble Cr greater than 120% of the total Cr (Figure 2-3).

Mechanistically, these apparently impossible results are actually anticipated when considering the interaction between chromium and iron hydroxide particles. To illustrate, consider a solution in which 2 mg/L fresh iron hydroxide particles are in a sample containing either 5 ppb Cr(III) alone or 5 ppb Cr(VI) alone. Existing models (Dzombak and Morel, 1990) can be used to predict Cr sorption onto fresh iron hydroxides for a range of pH. If the iron hydroxide does not dissolve, the models predict that Cr(VI) will be virtually 100% soluble above pH 8.0, but from pH 2-6 less than 10% of Cr(VI) is soluble (Figure 2-4). In other words, for this illustrative sample adjusted to pH 2 (according to approved EPA protocol), it is predicted that about 90% of the Cr(VI) would be present on the particulate iron if it did not dissolve. As pH drops down further below 2, the percentage of Cr(VI) that would be soluble is predicted to increase from about 10 up to 90%, but there is always Cr(VI) sorbed to the iron hydroxide that is present.

Note that this example could also explain aspects of the Eaton et al. (2001) monitoring results in California. Since soluble Cr(VI) is determined after adjusting the sample to pH 8 or above and then filtering, for the illustrative sample in the presence of iron hydroxide, 5 μg/L Cr(VI) would pass the filter and be quantified as Cr(VI) using the ion chromatography method (Figure 2-4). However, if the same sample were "preserved" by acid addition to pH 2.0, less than 0.5 μg/L of the Cr(VI) would be soluble assuming the iron hydroxides were not dissolved. The remaining 90% of the Cr(VI) would be associated with particles causing potential problems with recovery.

The improvement in recoveries brought about by hydrogen peroxide is consistent with this hypothesis. We note that even in water saturated with oxygen, Cr(III) is thermodynamically favored over Cr(VI). Thus, when a water is acidified Cr(VI) may be reduced to Cr(III). The driving force for Cr(VI) reduction to Cr(III) increases with lower pH. Recent work (Pettine et al, 2002) proved that Cr(VI) reduction is catalyzed in acidic solution by H_2O_2. In other words, addition of peroxide is expected to increase the rate of

Cr(VI) reduction to Cr(III) at low pH since the rate of reduction can be quite slow in the absence of a reductant such as ferrous iron or hydrogen sulfide. According to Figure 2-4, if such a change occurred, the shift from Cr(VI) to Cr(III) speciation would tend to release Cr to the water since Cr(III) does not sorb as readily to iron particles at lower pH.

Given the troublesome field experiences described above and the anticipated problems with existing analytical methods, experiments were designed to rigorously evaluate current approved protocols for the determination of total chromium in ambient water samples. Special attention was devoted to waters containing significant amounts of iron. Alternative protocols were also tested that might result in improved recovery of total chromium when iron particles are present.

EXPERIMENTAL MATERIALS AND METHODS

Bench scale tests were performed to evaluate materials (i.e., sample bottles, filters, preservative) for possible contamination and the effect of various iron particulates on several digestion and analytical protocols. Additionally, a field survey of 21 water treatment plants was executed to rigorously evaluate the above hypotheses regarding problems in total chromium recovery using standard techniques.

Analytical Methods. Samples were analyzed for total chromium using an Agilent 7500c ICP-MS in helium collision mode according to EPA Method 200.8 (EPA 1994). Samples were analyzed for Cr(VI) using a Dionex DX-320 system with an AD25 UV-Vis detector according to EPA Method 1636 (EPA 1996c). Iron was analyzed using an

Agilent 7500c ICP-MS with an octopole reaction system. Hydrogen gas was utilized as a reaction gas to minimize the interference with ^{56}Fe from ^{40}Ar^{16}O.

Testing of Preservation and Storage. Past researchers have shown that chromium can be lost from solution upon storage (Gilbert et al., 1973; Shendrikar et al., 1974). Therefore, the initial phase of QA/QC evaluated chromium sorption to high density polyethylene (HDPE) bottles and nylon syringe filters. Six HDPE bottles were filled with distilled water. Sodium carbonate was added to each for a final concentration of 12 mM and nitric acid was added to three (3) of these bottles for a final acid concentration of 2%. These preservation conditions are the same as those utilized for chromium in the field survey described later. Twenty μg/L of either Cr(III) or Cr(VI) was added to one acid-preserved and one base-only preserved bottle. Samples were taken at various times and analyzed without filtration. Samples were also taken from the "control" bottles (i.e. those without chromium spikes) and filtered through a 0.45 μm pore size nylon syringe filter.

Sorption was insignificant for bottles spiked with Cr(VI) for both acid- and base-preserved waters. However, chromium recovery from a bottle spiked with Cr(III) and adjusted to high pH (ca. 10.5) was only 40% after 20 days. This loss is attributed to sorption onto the bottle since no filtration took place before acidification and analysis. No chromium was leached from the bottles or filters in any of the solutions.

Further tests were conducted to assess Cr(III) sorption to nylon filters at high pH. At pH 8.5, no Cr(III) was lost to the filter but at pH 12.5 about 30% was lost. A 2% nitric acid solution was immediately passed through the filter used at pH 12.5 and all of the lost chromium was recovered. This proves that a major part of the Cr(III) was lost to the filter and not to the bottle at higher pH. This trend is again consistent with expectations of lower solubility of Cr(III) at higher pH. However, in terms of the Standard Method protocol, the key point is that neither Cr(VI) or Cr(III) was lost to the bottles or filters when the samples were acid preserved.

Bench Study of Iron Particulates in Synthetic Water. Since iron particles were expected to be a possible contributor to poor total chromium recoveries, several experiments were designed to investigate their fate in various methods. Synthetic waters were prepared at pH 5 and pH 8.4—these pH values are considered relatively low and high for natural water. Ferric iron was then dosed (final concentration of 5 mg/L as Fe) to the water along with a predetermined amount of sodium hydroxide to maintain the desired pH. After 30 minutes chromium was added in the form of Cr(III) (40 ppb) and Cr(VI) (40 ppb). Solids formed during this experiment were termed “preformed,” since the ferric hydroxide particulate was formed before the chromium was added.

An identical set of samples was prepared in which the ferric hydroxide particulate was formed after the chromium had been spiked into the water. The iron particles in these formed with chromium already present in the water, and the solids are designated “in-situ.” It was expected that chromium might be more difficult to recover from this type of particulate since it could be incorporated into the solid structure as fixed Cr (Figure 2-2) or a Fe(III)-Cr(III) hydroxide precipitate (Sass and Rai, 1987). Aliquots of each sample were collected and digested according to the protocols described in Table 2-2.

Field Survey. Sample kits were assembled and mailed to 21 water treatment plants across the United States. The kits consisted of eight (8) HDPE bottles containing various preservatives. Some bottles also contained matrix spikes of either Cr(III) or Cr(VI). Bottle descriptions are listed in Table 2-3, along with sample treatment protocols followed in the field and then in the laboratory.

RESULTS AND DISCUSSION

Bench Study of Iron Particulates in Synthetic Water. The solutions containing "in situ" and "preformed" iron hydroxide solids synthesized at pH 5 had initial turbidities less than 1 NTU (0.35 and 0.80, respectively), while both waters at pH 8.4 had turbidities of 1.4 NTU. Standard Method 3500-Fe (1998) recommends a hydroxylamine digestion to measure total iron in an environmental sample. Therefore, it was anticipated that the hydroxylamine digestion procedure (Table 2-2) would give the highest recoveries for Cr since it dissolves the iron particulates, thereby releasing any "fixed" chromium. Recoveries of total chromium per the hydroxylamine digestion procedure were indeed the highest and ranged between 90% and 104%. Iron recoveries in these samples were also high at 89% to 97%. In comparison, without the addition of hydroxylamine, recoveries of chromium were as low as 21% for the peroxide digestion and as low as 83% for hot HNO_3 digestion (Standard Method 3030E). Chromium recoveries by Standard Method 3030E were significantly lower ($P < 0.0032$) than for hydroxylamine digestion. This proves the validity of our key hypothesis even for fresh iron hydroxide.

Per the standard EPA protocol for total chromium determination (described above), the waters with turbidity less than 1 NTU could have been acidified to pH < 2 and analyzed directly. Following this procedure the recovery of chromium was 85% for the "preformed" water (by comparison, using Standard Method 3030E chromium recovery was also 85%). For the "in situ" water, recovery of total Cr could not be accurately determined on the ICP-MS due to an interference with the ICP-MS analysis for chromium. Interference from particulate material in the sample is the most likely cause as described earlier. Iron recovery from the pH 5 "preformed" water was only 92% using Standard Method 3030E and is consistent with expectations based on earlier discussion.

Strictly following EPA protocol, a Standard Method 3030E nitric acid digestion was required for the pH 8.4 samples (turbidities = 1.4 NTU). The recovery of total chromium was 83% - 89% while iron recoveries were 76% ("preformed") and 91% ("in situ").

From this experiment it is clear that following the EPA protocol could lead to at least a slight underestimation of the amount of total chromium in a water sample with fresh iron hydroxide. A fairly large amount of particulate material can be present in a water sample even if turbidity is less than 1 NTU. If this material contains iron, chromium may be adsorbed to the particles or it may be fixed such that it will not be released into solution at pH 2. In addition, Standard Method 3030E cannot always dissolve even relatively fresh iron hydroxide in samples with turbidity above or below 1 NTU. In some instances even filtration and acidification cannot remove all particulate matter that may cause problems (Figure 2-5). In such cases hydroxylamine digestion led to improved recovery of both chromium and iron.

Field Survey Results

The results from the field survey are presented in Table 2-4. The data includes type of water, pH, turbidity, alkalinity, as well as soluble and total iron and chromium concentrations.

Matrix Spike Recoveries. Excellent recoveries (range: 88% - 105%) of Cr(III) spikes were obtained from the acid preserved samples. Hexavalent chromium matrix spike recoveries were also excellent (range: 94% - 108%; except for a single sample with 0% recovery). The sample with 0% recovery of Cr(VI) contained 7 mg/L soluble iron. After acid digestion 98% of the total chromium matrix spike was recovered from this sample. We consider it likely the low recovery of Cr(VI) in this sample was due to rapid ferrous iron reduction of the Cr(VI) spike to Cr(III) and it does not indicate a problem with the method. Indeed, it merely confirms that the aqueous environment of the original sample is incompatible with the presence of Cr(VI) (James et al., 1995). These results would normally be cited as confirming that there is not a problem with the standard sampling and analytical protocol. However, further analysis of digested samples as described below demonstrated that there were actually serious problems with the protocol.

Aliquots of the acid preserved samples were digested by a variety of procedures as detailed in Table 2-2. In most cases the hydroxylamine digestion results were highest. If it is assumed that the hydroxylamine digestion recovers all iron and chromium, a

Percent Recovery Error can be established in comparison to the hydroxylamine procedure:

$$\%\ \text{Recovery Error} = \frac{(\text{Total Metal by Hydroxylamine - Total Metal by Procedure 'X'})}{(\text{Total Metal by Hydroxylamine})} \times 100\%$$

There is a relationship between the error in total chromium recovery and the particulate iron present in a water sample. Particulate iron is defined as the difference between iron recovered by the hydroxylamine procedure (total iron) and the soluble iron in the sample preserved at pH 2 and filtered in the lab. At plants with particulate iron less than 30 ppb, the percentage error of the 3030E method was low compared to the hydroxylamine digestion (Figure 2-6a). In contrast, neither total chromium nor soluble chromium (VI) was completely recovered from plants with large amounts of iron particulate present (>30 ppb) when comparing Standard Method 3030E with the hydroxylamine digestion (error range: 13-100%; median = 70%) (Figure 2-6b). Hydrogen peroxide did not appear to enhance recovery (error range: 33-100%; median = 76%) when used alone.

How can the poor recoveries of Standard Method 3030E be reconciled with the excellent recovery of chromium matrix spikes to the same samples? Recall that the chromium species present in the real water samples may be different from the soluble chromium spiked to the water samples. For instance, chromium in the original sample may be trapped inside well-aged crystalline solids and the acid digestion would not release it (Figure 2-2), similar to previous results with fixed chromium in the lab. Insoluble Cr(III) or Cr(VI) may have been present, dissolution of which is either thermodynamically or kinetically limited. For instance, barium chromate, $BaCrO_4$, (K_{sp}

1.6×10^{-10}) might be present and could bias Cr(VI) results if it did not dissolve (James et al, 1995). In any case, both modeling and experimental data clearly show that Standard Method 3030E cannot recover a significant portion of the chromium present in many environmental samples when iron is present, and current monitoring data for total Cr based on this method may be biased low, especially for samples containing measurable amounts of iron. In some cases none of the Cr is recovered with standard procedures.

Anticipated Problems with EPA Method 1669. While we did not utilize EPA Method 1669, problems can be anticipated by direct extension of our results. In this cumbersome field method Cr(III) is sorbed to a previously prepared iron hydroxide solid surface from a water sample. The iron solid is dosed from a suspension at pH 8. The water sample/iron hydroxide mixture is then filtered, and the filter is preserved in concentrated nitric acid. The Cr(III) is assumed to quantitatively sorb to the iron and be trapped on the filter, and it is further assumed that no Cr(VI) is sorbed to the iron. Chromium is analyzed after the collected solids on the filter have dissolved (EPA, 1996a; EPA, 1996b). One problem is that for a drinking water of relatively low pH a portion of the Cr(III) will be soluble in the presence of the added iron hydroxide (Figure 2-4). EPA Method 1669 was developed for the determination of Cr(III) in seawater, which is strongly buffered at pH > 8.0. It would clearly be problematic for a low-pH groundwater. Likewise, at least some Cr(VI) would sorb to iron at lower pHs, and therefore would be quantified as Cr(III) by the procedure. Finally, if "fixed" chromium is present in the solids, it might not be dissolved by this procedure. Results from Method 1669 for Cr should therefore be viewed with these possible problems in mind.

Bioavailability. These results may also have direct implications for Cr(VI) bioavailability in drinking water. If these waters are representative, we speculate Cr(VI) that is soluble in samples could sorb to iron hydroxide particles present in the acidic stomach. Uptake of Cr(VI) may be less than anticipated in such circumstances.

CONCLUSIONS

Two types of error have been identified in determination of total chromium using standard techniques, and each of them can arise from interactions with iron particles that are present in many ambient waters, and which are recalcitrant to dissolution in weak (pH 2) or strong (5%) acid digestion.

(1) If a sample collected in the field is acidified to slightly less than pH 2.0, soluble Cr(VI) can sorb to iron particles if they are present. These particles can be lost from solution by a variety of mechanisms (attachment to the sides of the container or sedimentation in test tubes), and the Cr(VI) recovery can approach 0%.

(2) Chromium in samples can be present in a “fixed” form. This refers to Cr associated with particles that is not solubilized during a nitric acid digestion. This type of Cr will not be recovered by Standard Method 3030E; however, a much greater portion of this chromium is recovered by hydroxylamine digestion.

We recommend that an acid-preserved and a base-preserved sample be acquired if total chromium and soluble Cr(VI) concentrations are desired. The base-preserved sample can be filtered and analyzed directly by IC to determine a soluble Cr(VI) concentration. The acid-preserved sample should be digested in the bottle according to the hydroxylamine procedure in this work or its equivalent regardless of turbidity. The resulting solution can then be analyzed directly for total chromium or analyzed after centrifugation or filtration.

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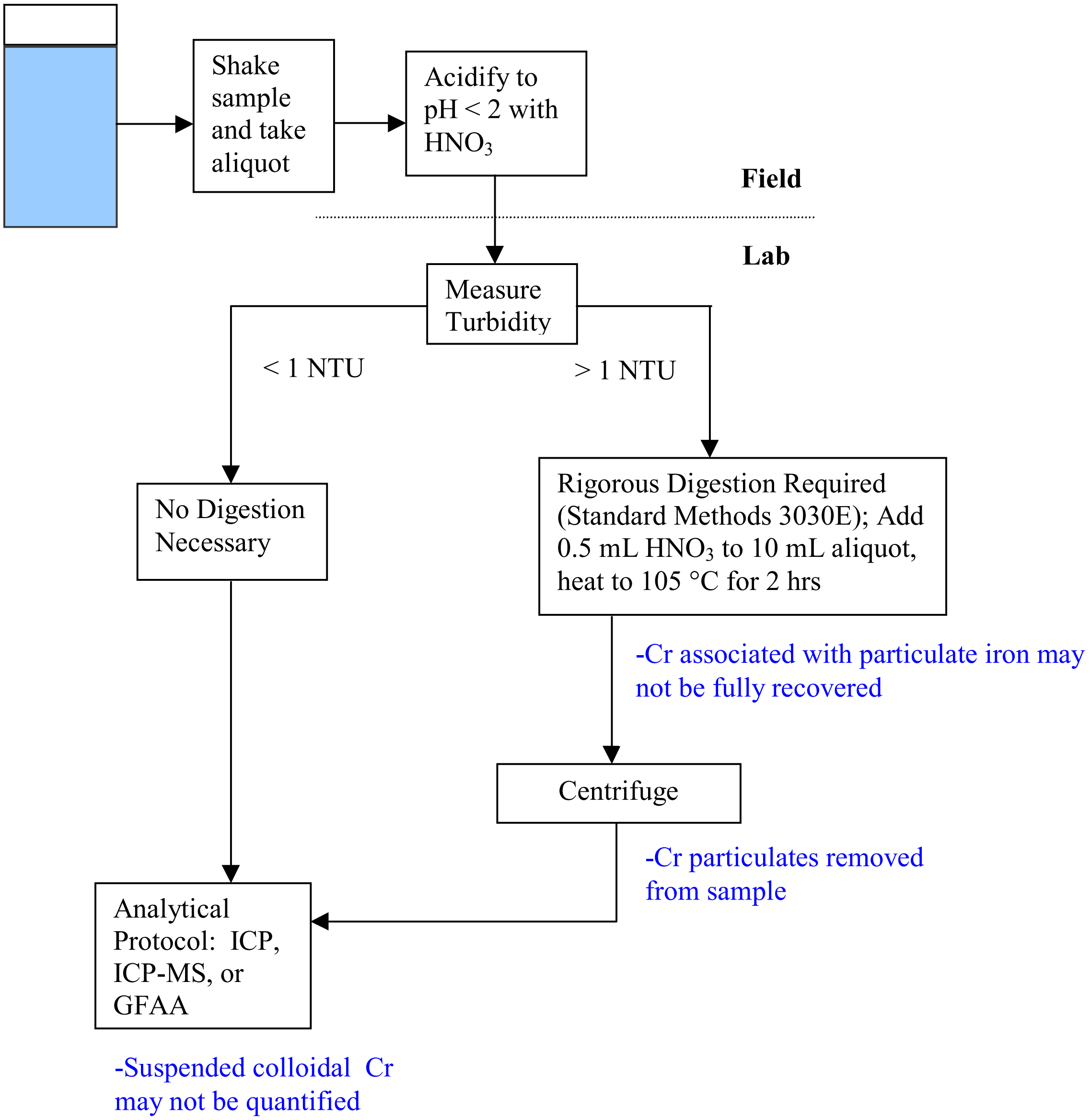

Figure 2-1. EPA Sampling Protocol for Total Chromium and Sources of Possible Error

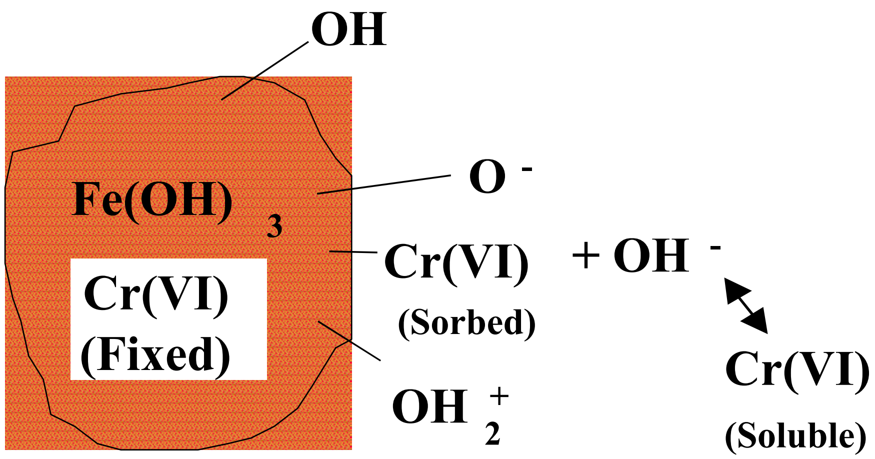

Figure 2-2. Possible forms of chromium(VI) in solution in the presence of iron particles. Cr(VI) can be in solution (soluble), Cr(VI) can stick (sorb) to the surface of iron oxide particles, or Cr(VI) can be held deep inside the iron in a form we term "fixed" Cr.

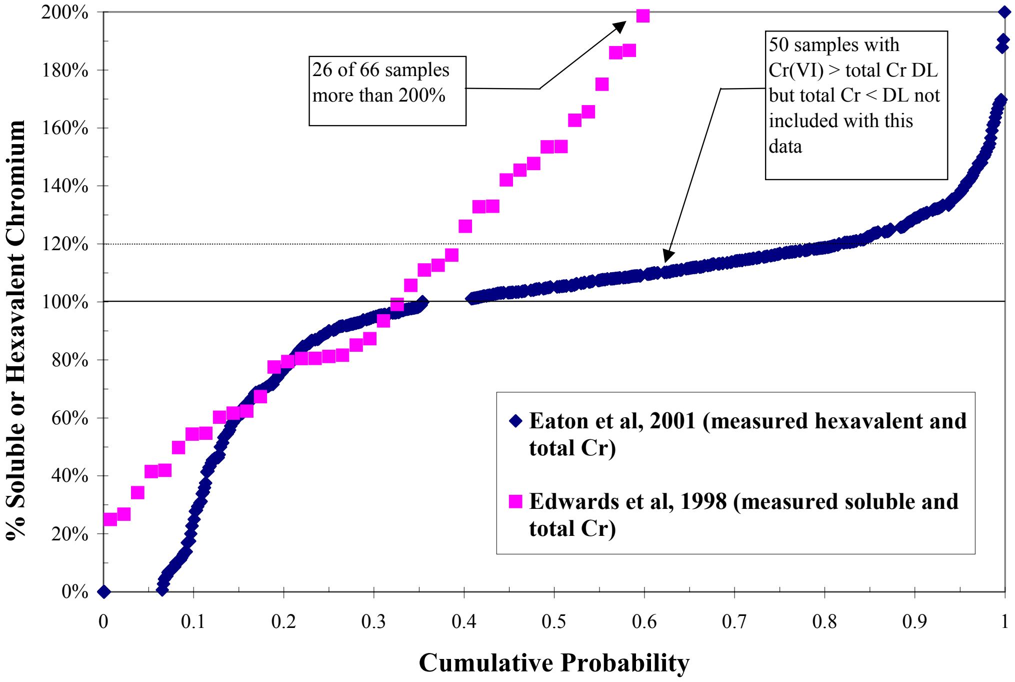

Figure 2-3. Eaton et al. (2001) data showing percent of chrome present in samples as hexavalent chromium when analyzed per Standard Methods 3030 without hydroxylamine digestion. Note that nearly 20% of the samples show recoveries for hexavalent chromium that are >120% of the total chromium. Also shown, Edwards et al. (1998) data showing percent of soluble chrome present in samples analyzed without hydroxylamine digestion.

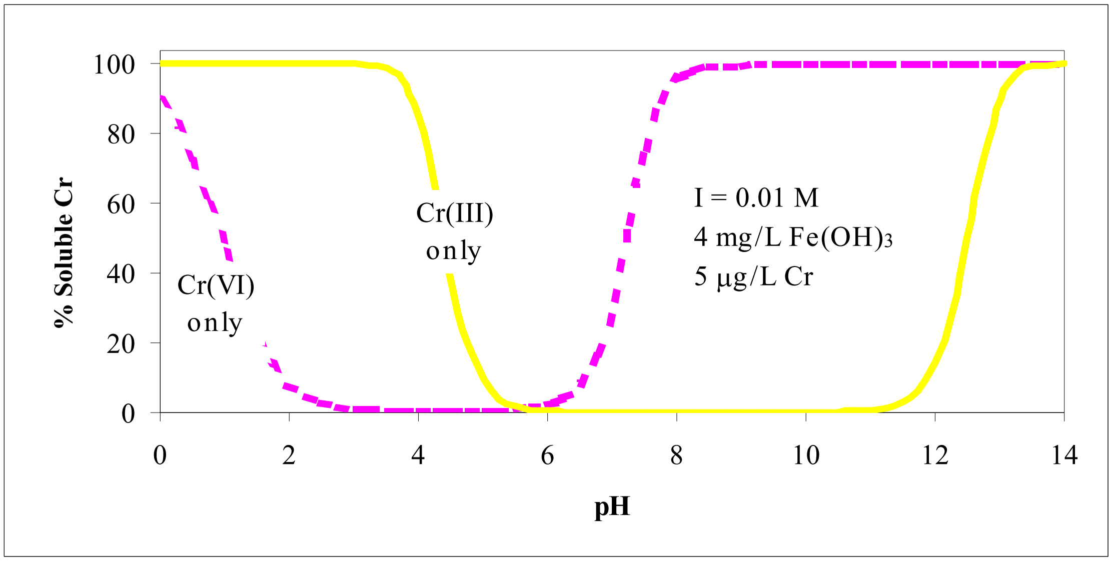

Figure 2-4. Model prediction of soluble Cr(III) and Cr(VI) in a drinking water sample in the presence of iron particles (4 mg/L $Fe(OH)_3$ is about 2 mg/L particles as Fe) using diffuse layer model of Dzombak and Morel (1990).

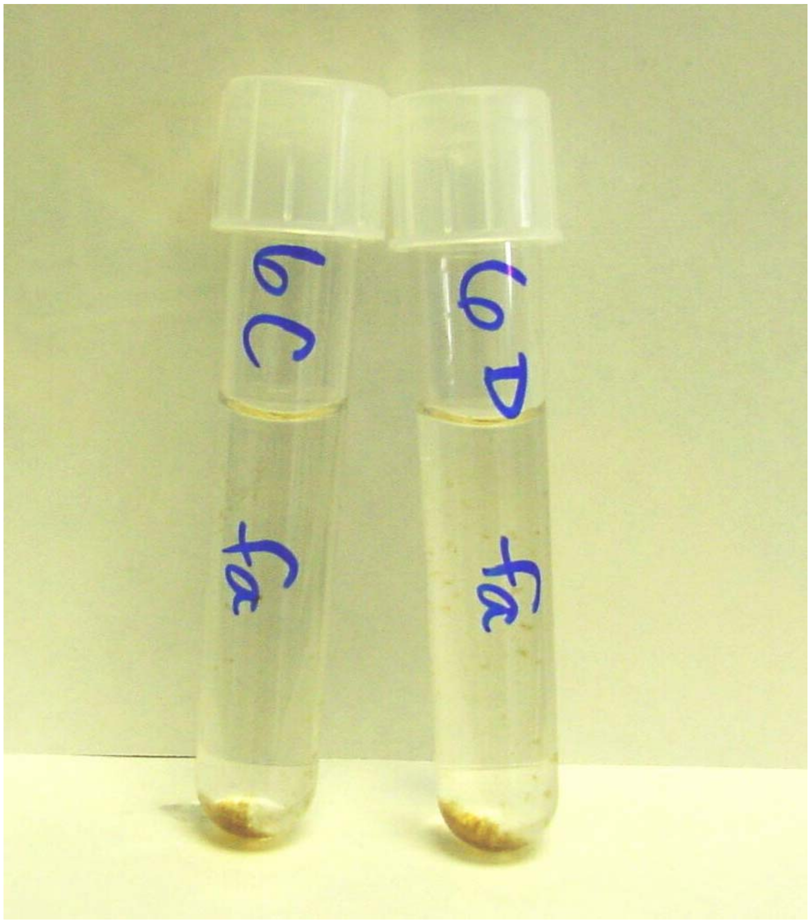

Figure 2-5. Iron hydroxide solids that originally pass through a 0.45 μm pore size filter can settle or stick to containers – sometimes this is visually apparent.

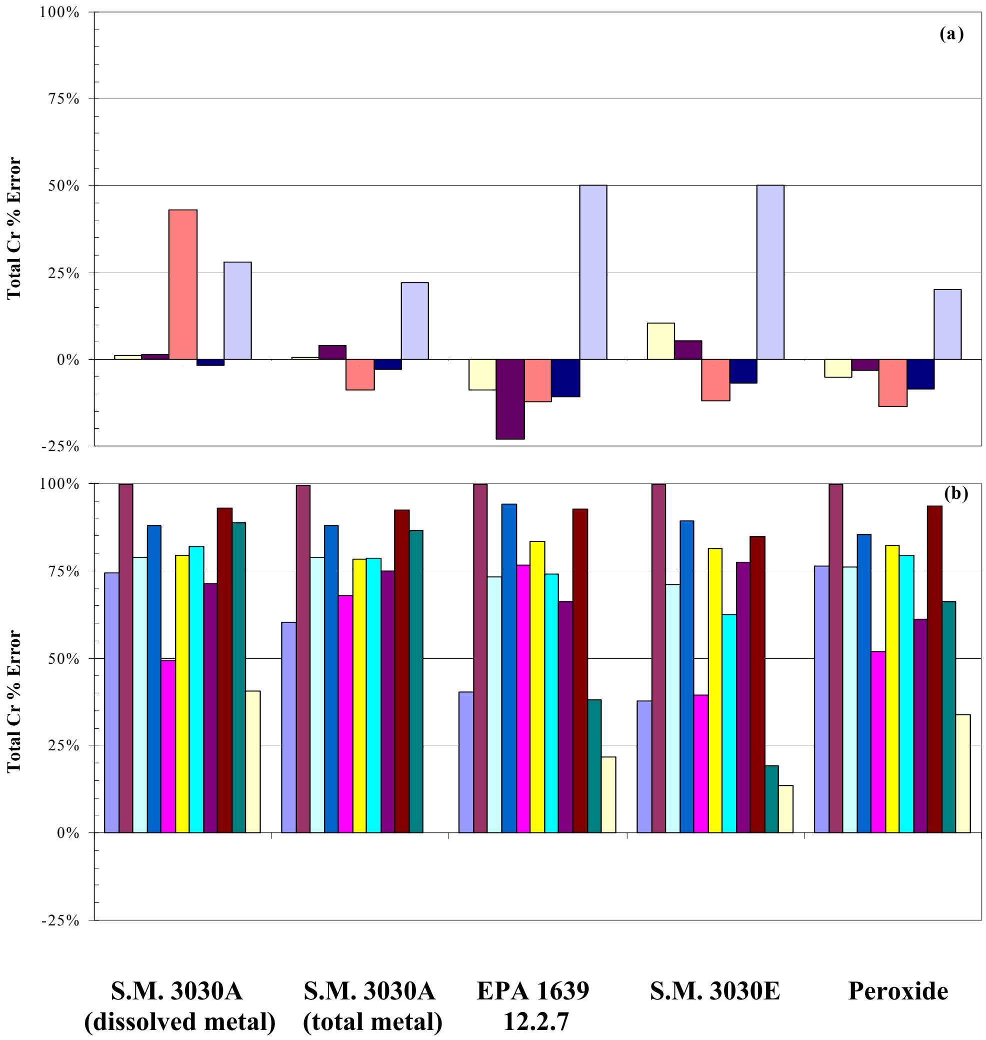

Figure 2-6. Percentage error in total chromium concentration versus digestion method. (a) Results at 5 plants with low particulate Fe (< 30 ppb); (b) Results at 11 plants with high particulate Fe (> 30 ppb).

(% Error in Total Cr calculated as (Total Cr by hydroxylamine - Total Cr) / (Total Cr by hydroxylamine)

Table 2-1. Summary of Standard and EPA Methods for Chromium Determination

Method Number	Title	Analyte	Field Treatment / Storage of Sample	Digestion Requirements, Recommended Analysis, Other Comments
S.M. 3030 A.	Preliminary Treatment of Samples: Introduction	Total Cr	acidify to pH < 2	If <1 NTU do not digest, analyze directly. If >1 NTU, digest as per S.M.3030E-K. Analyze by AAS or ICP.
S.M. 3030 A./B.	Preliminary Treatment of Samples	Total Dissolved Cr	filter sample through 0.45 μm pore dia. filter; acidify to pH < 2	analyze by AAS or ICP
S.M. 3500-Cr A.	Chromium: Introduction	Total Cr	acidify to pH < 2	analyze by AAS or ICP; requirement for digestion unclear
S.M. 3500-Cr B.	Colorimetric Method	Total Cr(VI)	adjust pH to 8 with NaOH; refrigerate	spectrophotometric determination of diphenylcarbazide Cr complex
S.M. 3500-Cr B.	Colorimetric Method	Dissolved Cr(VI)	filter sample through 0.45 μm pore dia. filter; adjust pH of filtrate to 8 with NaOH; refrigerate	spectrophotometric determination of diphenylcarbazide Cr complex
S.M. 3500-Cr C.	Ion Chromatographic Method	Dissolved Cr(VI)	filter sample through 0.45 μm pore dia. filter; adjust pH of filtrate to 9 with conc. buffer; refrigerate	analyze Cr(VI)-azide dye chromogen at 530 nm with IC
EPA 3060 A	Alkaline Digestion for Hexavalent Chromium	Total Cr(VI)	refrigerate	Add alkaline digestion reagent; heat to 90 C for 60 minutes; filter. Analyze using EPA Method 7196A after adjusting sample pH to 2. Not applied to drinking water.
EPA 1669	Sampling Ambient Water for Trace Metals at EPA Water Quality Criteria Levels	Total Cr(III)	add pH 8 iron(III) hydroxide extraction solution; filter through 0.4 μm pore dia. filter; store filter in 1 mL nitric acid	See EPA 1639 for additional details; Cr(III) is assumed to be sorbed by the iron hydroxide
		Dissolved Cr(III)	filter sample; add pH 8 iron(III) hydroxide extraction solution; filter again, store filter in 1 mL nitric acid	See EPA 1639 for additional details
		Total Cr(VI)	add 1 mL 50% NaOH per 125 mL sample	not specified
		Dissolved Cr(VI)	filter sample through 0.45 μm pore dia. filter; add 1 mL 50% NaOH per 125 mL sample	not specified

S.M. = Standard Methods; EPA = U.S. Environmental Protection Agency
AAS = atomic absorption spectroscopy; ICP = inductively coupled plasma; GFAA = graphite furnace atomic absorption

Table 2-2. Procedures Utilized in Chromium Determination QA/QC Phase

Procedure	Descriptor	Filter Sample?	Initial Treatment	Digestion	Analysis Technique	Other Comments
1	S.M. 3030-A (dissolved metal)	yes	acidify to pH 2	sit stagnant for 24 hrs	Cr(VI) on IC; total Cr on ICP-MS	Valid for dissolved Cr if turbidity < 1 NTU
2	S.M. 3030 A (total metal)	no	acidify to pH 2	sit stagnant for 24 hrs	Cr(VI) on IC; total Cr on ICP-MS	Valid for total Cr if turbidity < 1 NTU
3	EPA Method 1639 - 12.2.7	no	add 0.3 mL HNO_3 and 0.15 mL HCl to 30 mL aliquot	heat to 85 C for 2 hrs; filter through 0.45 mm pore dia. filter; acidify to 2% acid by adding 0.15 mL HNO3	total Cr on ICP-MS	Sample digestion was not performed in bottle as called for in method
4	S.M. 3030-E	no	add 0.5 mL HNO_3 to 10 mL aliquot	heat to 105 C in block heater for 2 hrs; filter through 0.45 mm pore dia. filter	total Cr on ICP-MS	Samples filtered instead of centrifuged as called for in method
5	Peroxide digestion	no	add 0.3 mL of H_2O_2 to 30 mL aliquot	sit stagnant for 24 hrs; filter through 0.45 mm pore dia. filter; acidify to 2% HNO_3	total Cr on ICP-MS	Peroxide may aid in the recovery of Cr
6	S.M. 3500-Fe B	no	add 2 mL HCl and 1 mL hydroxylamine solution (10 g NH_2OH HCl diluted to 100 mL) to 50 mL aliquot	heat to 85 C for 24 hrs; filter through 0.45 mm pore dia. filter	total Cr on ICP-MS	Sample not allowed to boil per method; iron not analyzed with phenanthroline

Table 2-3. Bottle Listing for Field Survey

Treatment before sending bottles------------------------------->					In the Field---->		Treatment in Lab----------------------------->				
Bottle	**Preservative**	**Amount of Preservative (mL)**	**Spike**	**Spike$^{\&}$ Amount (mL)**	**Sample Filtered in Field**	**Approx. Sample (mls)**	**Digestion in Lab**	**Filter Back in Lab**	**Analysis for**	**Analysis by**	**Goal**
A	Nitric Acid (pH < 2)	0.333	none		no	200	Acid@ Acid@	Yes, after digestion	Cr	GFAA ICP-MS	Total Cr
B	Nitric Acid (pH < 2)	0.167	Cr(VI)	0.1	no	100	Acid@ Acid@	Yes, after digestion	Cr	GFAA ICP-MS	Insure recovery of spike
C	12 mM Soda Ash	1.27	none		no	100	none	Yes	Cr(VI)	IC	Recoverable Cr(VI)
D	12 mM Soda Ash	1.27	Cr(VI)	0.1	no	100	none	Yes	Cr(VI)	IC	Insure recovery of spike
E	12 mM Soda Ash	0.38	none		yes, into bottle	30	none Acid@ Acid@	No No No	Cr(VI) Cr	IC GFAA ICP-MS	Soluble Cr(VI) Soluble Cr (3+6)
F	12 mM Soda Ash	0.38	Cr(III)	0.03	yes, filtered into bottle	30	none Acid@ Acid@	No No No	Cr(VI) Cr	IC GFAA ICP-MS	 Insure recovery of spike
G	100 mL of laboratory reagent-grade water with 12 mM soda ash preservative										
H	empty	(Bottle G contents filtered into Bottle H in field)					none none none	No No No	Cr(VI) Cr	IC GFAA ICP-MS	Field/Equipment Blank

Notes
@ Acid Digestion = Std. Method 3030E
& Spike will be 10 ppb Cr(VI) or 10 ppb Cr(III)

Stock Solutions
Chromium(VI) Spike Solution: 10 mg Cr(VI) / L
Chromium(III) Spike Solution: 10 mg Cr(III) / L
Soda Ash Solution: 100 g Na2CO3 / L

Table 2-4. Field Survey Data and Results

Plant ID	Water Source	pH&	Turbidity& (ntu)	Alkalinity& (mg/L)	Total Fe# (ppb)	Total Cr# (ppb)	Total Cr (3030E) (ppb)	Total Cr (no dgstn.) (ppb)	Cr(VI)@ (ppb)	Soluble Cr(VI)@ (ppb)
1	SW	7.96	34	50	1930	2.78	1.73	1.1	<0.2	<0.2
2	SW	8.02	1.44	120	70	11.72	<0.09	0.1	<0.2	<0.2
3	GW	7.9	<.5	127	<4	1.92	1.72	1.9	2.13	1.83
4	SW	7.87	5.2	66	620	1.38	0.40	0.3	<0.2	0.22
5	GW	n/r	n/r	n/r	<4	0.50	0.25	0.4	<0.2	0.36
6	GW	8.51	0.71	200	60	0.89	0.72	0.1	0.28	0.32
7	GW	7.8	0.09	n/r	<4	5.56	5.27	5.3	5.34	5.52
8	GW	7.51	n/r	n/r	<4	36.42	40.74	39.7	38.13	39.67
9	SW	7.96	3.06	43	480	0.75	0.08	0.1	0.28	0.28
10	SW	7.19	2.4	19.8	390	0.74	0.64	n/m	0.38	0.53
11	GW	7	0.4	n/r	10	8.42	9.00	8.7	9.07	9.83
12	GW	7.39	2.28	298	6960	0.16	<0.09	<0.09	<0.2	<0.2
13	SW	8.3	2.1	106	100	0.81	0.49	0.3	0.54	0.50
14	SW	8.19	7.1	82	500	1.02	0.19	0.2	0.34	0.37
15	SW	8.57	15	103	1240	2.00	0.75	0.4	<0.2	<0.2
16	SW	7.96	0.575	135	<4	0.15	<0.09	0.1	0.32	0.31
17	SW	8.0	1.88	94	190	0.80	0.18	0.2	<0.2	<0.2
18	SW	6.75	27.6	27	2060	4.33	0.66	0.3	0.21	<0.2
19	SW	7.3	7	68	260	0.32	<0.09	0.1	<0.2	<0.2
20	SW	7.4	6.1	151	180	0.22	<0.09	0.1	<0.2	<0.2
21	SW	7.4	2.7	16	100	0.19	<0.09	0.1	<0.2	<0.2

n/r = not reported; n/m = not measured

&pH, Turbidity, and Alkalinity data as reported by plant personnel

#Total metal concentration by hydroxylamine procedure as analyzed by ICP-MS

@Cr(VI) concentration analyzed by IC

CHAPTER III: PRECIPITATIVE REMOVAL OF AS, BA, B, CR, SR, AND V USING SODIUM CARBONATE

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ABSTRACT: Sodium carbonate softening at pH 10.3 is a viable method of removing the inorganic contaminants arsenic, barium, chromium, strontium, and vanadium from drinking water sources. A broad survey revealed that removals varied widely and were dependent on solution composition. Median removals of As, Ba, Cr, Sr, and V were 24%, 100%, 92%, 99%, and 60%, respectively. Linear and nonlinear empirical models were fit to crudely estimate the removal of these contaminants in the presence of other elements that are typically removed in the softening process (i.e. calcium, magnesium, silicon, iron, and aluminum). Boron was removed to a much lesser extent (median removal 2%) indicating soda ash softening is not a promising treatment option for this purpose.

INTRODUCTION

Inorganic elements such as arsenic, barium, boron, chromium, strontium, and vanadium are either regulated by the United States Environmental Protection Agency (US EPA) or are under consideration for possible regulation (Table 3-1). While there are proven methods for the removal of some of these contaminants, practical data on precipitative removal at high pH for a range of waters is lacking. Precipitative softening is often used at existing conventional water treatment facilities, it is often less expensive than membrane processes, and it can achieve multiple objectives. It is therefore useful to obtain preliminary insights as to how softening would perform in removing emerging contaminants. Utilities would also find a predictive tool helpful in estimating removal efficiency of each contaminant if softening was employed as a treatment process in a given water. Information on treatment and possible removal is also necessary to support cost benefit analyses of regulations.

To address these needs, water samples were collected from across the United States and preserved at high pH using sodium carbonate (soda ash). Initially, the primary reason for sample collection was to ascertain the amounts of total chromium and hexavalent chromium in U.S. source waters and therefore, high pH samples were required to maintain chromium speciation. An additional benefit to this type of sampling protocol was that it could be considered as a surrogate for precipitative softening. While it is true that most water treatment plants soften by the addition of lime, data for specific contaminants preserved with sodium carbonate at high pH might still prove useful in formulating models to predict possible removals of those contaminants. The objective of this study was to 1) survey the range of removals attained by precipitative softening via sodium carbonate, and 2) provide models for the removal of arsenic, barium, boron, chromium, strontium, and vanadium via the softening process based on this data.

The following sections contain a brief background on the current regulatory status of each contaminant examined in this study. A summary of the current understanding of each contaminant's removal via softening is also included.

Arsenic. Arsenic is classified as a human carcinogen and is currently regulated by the US EPA (Table 3-1). In natural waters arsenic primarily occurs as the arsenate (AsO_4^{3-}) or arsenite (AsO_2^-) oxyanions. McNeill and Edwards (1995) determined that arsenate removal during lime softening is dependent on the constituents that are precipitated. At facilities precipitating only calcium carbonate ($CaCO_{3\,(s)}$), arsenate removal ranged between 0 and 10%. At facilities where both calcite and $Mg(OH)_2$ precipitated, arsenate removal ranged between 60 and 95%. A study by Chen et al (2002) included year-long sampling at a lime softening plant that was experiencing reducing conditions in its raw water. Since arsenate is much easier to remove from natural waters than arsenite, the arsenite in this raw water was oxidized to arsenate by chlorination prior to the lime softening process. Only 28% of the arsenate and 11% of the magnesium was removed at this facility. These results are consistent with the idea that $Mg(OH)_2$ precipitation is required for efficient arsenate removal.

Barium. Barium is currently regulated by the US EPA (Table 3-1) but is not classified as carcinogenic. The current regulatory limit of 2 mg/L was established based on a study on human volunteers that indicated a barium dose of 10 mg/L for four weeks had no adverse effects (US EPA, 2004b).

Barium is a member of the alkaline earth group of elements and, as such, has similar chemical properties to calcium and magnesium. Barium occurs as a divalent cation (Ba^{2+}) in nature and combines with hydroxide, carbonate, and sulfate to form $Ba(OH)_{2\ (s)}$, $BaCO_{3\ (s)}$, and $BaSO_{4\ (s)}$, respectively. Solubility product constants for these compounds are listed in Table 3-2. The high solubility of barium hydroxide compared to magnesium hydroxide indicates that its formation in a traditional lime softening process would not usually be a practical way to remove barium from a water source. The low solubility of barium carbonate, however, could make it a viable means of removing dissolved barium from water provided the raw water carbonate alkalinity is high enough or there is another source of carbonate such as soda ash. Studies have shown that greater than 90% of barium was removed from a water with an alkalinity of 250 mg/L as $CaCO_3$ and containing 7.4 mg/L barium when the water was softened with lime to pH 11 (Krause and Stover, 1982).

Boron. Recently boron has come to the forefront as a possible drinking water contaminant that could be regulated in the next few years. Boron was placed on the EPA's original Contaminant Candidate List in March 1998 (US EPA, 1998). The basis for possible regulation is a 1992 EPA Drinking Water Health Advisory for boron. A lifetime human health advisory of 0.6 mg boron /L for drinking water was deemed appropriate based on findings in a study by Weir and Fisher (US EPA, 1992; Cantilli, 1991; Weir and Fisher, 1972).

Softening processes have not been proven effective for the removal of boron at reasonable chemical doses, and in fact, some evidence suggests that softening will not remove boron. A study by Nebgen et al (1973) found that lime softening only removed

12% of the 1.7 mg/L boron present in brackish water. Also, Waggott (1969) tested very high dose lime softening (263-400 mg/L as CaO) as a means of removing boron from wastewater effluent. No information was presented as to the concentrations of $CaCO_3$ or $Mg(OH)_2$ solids formed or final pH but removal was between 0-16% at all conditions tested for waters containing 1.6 mg/L B. In contrast, a magnesium-assisted lime softening process has been cited as effective in reducing B to less than 0.2 mg/L in wastewater re-use applications, although the initial boron level, chemical doses or other operational details were not provided (Idelovitch et al, 1980).

Chromium. Total chromium in drinking water is currently regulated by the US EPA (Table 3-1) but is not classified as carcinogenic. Two oxidation states of chromium exist in natural waters: Cr^{3+} and Cr^{6+}. Studies on chromium removal by lime softening indicate that removal is speciation dependent (Sorg, 1979). Lime softening during pilot plant testing resulted in greater than 97% removal of Cr(III) at pH 11 while removal of Cr(VI) was 5% at pH 9.5. A more recent study on effluent from a stainless steel manufacturer substantiates this result. Cr(VI) comprised 96% of the total chromium in the effluent and only 5% removal was obtained at pH 11.3 (Schoeman et al, 1996).

Strontium. Strontium is not currently regulated but a lifetime human health advisory of 4 mg/L has been established for drinking waters (Table 3-1). Strontium is similar to barium in that it is also an alkaline earth group element. Strontium also occurs as a divalent cation (Sr^{2+}) in nature and can combine with hydroxide, carbonate, and sulfate to form $Sr(OH)_{2(s)}$, $SrCO_{3(s)}$, and $SrSO_{4(s)}$, respectively. $Sr(OH)_2$ is slightly soluble in water while the other compounds are relatively insoluble (Table 3-2). Data for strontium removal during lime softening are not available.

Vanadium. Vanadium was placed on the EPA's original Contaminant Candidate List in March 1998 (US EPA, 1998). There is also an action level of 0.05 mg/L established in the State of California by the Department of Health Services for drinking water (Table 3-1). Vanadium can occur in any of three valence states (+3, +4, or +5) in natural or treated waters and control of its solubility has been attributed to various vanadium oxides, metal vanadates (such as calcium and magnesium), and even surface sorption to various oxide minerals (Schock and Kelly, 2002). Little data are available describing the removal of vanadium by lime softening however. Fifty seven percent of vanadium present was removed by lime softening from water with an initial concentration of 0.5 mg/L in a study by Hannah et al (1977).

The objectives of this study are to evaluate the effectiveness of soda ash softening for the removal of arsenic, barium, boron, chromium, strontium, and vanadium and to develop empirical regression models describing the observed soda ash softening. These models in turn may provide a predictive tool for estimating removal of these emerging inorganic contaminants during the soda ash softening process. The applicability of these models to the lime softening process is not evaluated in this study but similar trends should be anticipated in most natural waters.

EXPERIMENTAL PROCEDURE

Three hundred seventy three raw water samples (2/3 groundwater, 1/3 surface water) were obtained from numerous water treatment plants located across the United

States as part of a recent American Waterworks Association Research Foundation (AwwaRF) survey. This survey was initiated to obtain data on the occurrence of boron and hexavalent chromium in water supplies of the United States. Each location provided two samples of unfiltered water in high density polyethylene (HDPE) bottles. One sample was preserved at pH < 2 with nitric acid. The other sample was preserved at pH 10.3 ± 0.3 (one standard deviation) with a fixed dose of sodium carbonate. The acid-preserved sample was obtained so that a 'total' concentration of boron and chromium could be determined. The base-preserved sample was necessary so that soluble hexavalent chromium could be determined while minimizing the possibility of reduction of hexavalent chromium to trivalent chromium (Archundia et al, 1993). However, since the final pH of all samples was between 9.6 and 11.1, the filtered water results are also indicative of precipitative removal at high pH values.

The pH of each sample was measured after receipt in the laboratory with a Corning 315 pH meter. All base-preserved samples were kept in a 4 ºC constant temperature room prior to analysis.

Each acid-preserved sample was digested in the laboratory using a modified hydroxylamine hydrochloride procedure similar to Standard Methods 3500-Fe (APHA, 1998). Hyrdroxylamine hydrochloride (10% solution added as 2% v/v) and hydrochloric acid (4% v/v) are added to each sample. The sample is placed in an oven at 90 °C for 24 hours. An aliquot is taken from the sample bottle and analyzed directly by ICP-MS or ICP-ES. This procedure was determined necessary by previous work which demonstrated total chromium was not recovered as efficiently when using Standard Method 3030-E if particulate iron was present in samples (Parks et al., 2004). Analyses for total amounts of aluminum, arsenic, barium, calcium, chromium, iron, magnesium, silicon, strontium, and vanadium were conducted on an Agilent 7500C Inductively Coupled Plasma – Mass Spectrometer (ICP-MS) following EPA Method 200.8. This ICP-MS is equipped with a collision cell, which allows the use of hydrogen (H_2) and helium (He) gas to reduce polyatomic interferences. All analyte concentrations were also corrected by the appropriate internal standard. Boron concentration was measured by a JY Ultima Inductively Coupled Plasma Emission Spectrometer (ICP-ES) due to interferences on the ICP-MS. The ICP-MS had a large memory effect in that it took an inordinately long time to wash out the boron and get back to background. These concentrations are deemed 'total concentration' of contaminant.

Liquid from each base-preserved sample was passed through a 0.45 μm pore-size nylon syringe filter and then acidified with nitric acid (2% v/v). The filtered aliquots were analyzed by ICP-MS/ICP-ES as noted above. These concentrations are termed 'dissolved concentration after high pH precipitation'.

Method detection limits (MDLs) for each metal were estimated by evaluating seven replicate measurements of a blank solution. The standard deviation of the seven concentrations is multiplied by 3.14 (approximate Student's t value for 99% confidence) to obtain an estimate of the MDL. Results for the MDL estimate for arsenic, barium, chromium, boron, strontium, and vanadium in this study are shown in Table 3-3.

Laboratory ware (HDPE) was tested to determine possible interferences on removal; i.e., whether elements may sorb to or leach from container surfaces at the preservation pH values. Bottles were prepared with 100 mL of deionized water and spiked with approximately 30 ppb of either As(III), As(V), Cr(III), Cr(VI), B, Ba, Sr, or

V. Both redox states of arsenic and chromium were tested since speciation in field samples was not quantified. An initial sample was taken from each bottle and analyzed as above for each element's baseline concentration. Sodium carbonate was added to raise the pH above 10. After sitting for 4 days, samples were taken from each bottle and passed through a 0.45 μm pore-size nylon syringe filter and acidified with nitric acid (2% v/v). All samples were analyzed by ICP-MS or ICP-ES as detailed above. Little or no loss of the initial spike occurred in the bottles containing As(III), As(V), Cr(VI), B, Ba, or V. Approximately 24% of the Sr spike was lost after 4 days and over 60% of the Cr(III) spike disappeared. Based on results from the AwwaRF survey, on average 60% of Cr in the ambient water samples was in the form of Cr(VI), so even though sorption of Cr(III) is of concern, the data was modeled without considering this effect.

MODELING PROCEDURE

The 'particulate' concentration of each contaminant as well as other elements that may be removed during softening (e.g. Al, Ca, Fe, Mg, and Si) was calculated as the difference between 'total concentration' and 'dissolved concentration after soda ash softening'. Data were converted to molar values and negative concentrations (due to slight analytical error) were set equal to zero. A summary of the statistical parameters of the data used for modeling is presented in Table 3-3. A lower concentration limit at approximately 5x the MDL was set for each contaminant (except boron) to eliminate noise associated with data near the practical quantitation limit (PQL). Preliminary evaluations had demonstrated that virtually all boron was dissolved in samples, consistent with a recent review (Parks et al, 2004).

Many solids were formed during softening; however, only magnesium-, calcium-, iron-, aluminum-, and silicon-containing solids formed in appreciable amounts (average amount present in raw water prior to softening: Ca, 58 ppm; Mg, 4.2 ppm; Si, 3.7 ppm; Fe, 0.7 ppm; Al, 0.3 ppm). Therefore, only solids containing these elements are included in the models. Likewise, these models assume no interactions between solids. A conceptual illustration of the model is depicted in Figure 3-1.

Linear and nonlinear empirical regression models were developed and evaluated in this study to predict the effectiveness of soda ash softening for the removal of arsenic, barium, boron, chromium, strontium, and vanadium. Linear models are much easier to use but may not fit the data as well as nonlinear models. Comparisons between these two approaches are made in the discussion of results.

Linear Model. The linear model can be expressed mathematically as:

$$\frac{[M]_X}{[X]_{ppt}} = K_X * [M]_{sol} \tag{1}$$

where,

$[M]_X$ = molar concentration of contaminant 'M' that is sorbed to solid 'X'

$[M]_{sol}$ = molar concentration of contaminant 'M' that is dissolved

$[X]_{ppt}$ = molar concentration of 'X' that is precipitated as a solid (calculated as difference between 'total X' and 'dissolved concentration of X after soda ash softening)

K_X = sorption equilibrium constant for 'M' sorbed to 'X'.

Additionally, a mass balance can be written for each contaminant:

$$[M]_{tot} = [M]_{sol} + [M]_{Mg} + [M]_{Ca} + [M]_{Fe} + [M]_{Al} + [M]_{Si} \tag{2}$$

where,

$[M]_{tot}$ = total molar concentration of contaminant 'M'

$[M]_{sol} =$ molar concentration of contaminant 'M' that is dissolved
$[M]_{Mg} =$ molar concentration of 'M' that is sorbed to the magnesium solid
$[M]_{Ca} =$ molar concentration of 'M' that is sorbed to the calcium solid
$[M]_{Fe} =$ molar concentration of 'M' that is sorbed to the iron solid
$[M]_{Al} =$ molar concentration of 'M' that is sorbed to the aluminum solid
$[M]_{Si} =$ molar concentration of 'M' that is sorbed to the silicon solid.

Substitution of the linear model expression into the mass balance yields:

$$[M]_{tot} = [M]_{sol} + [M]_{sol} * K_{Mg} * [Mg]_{ppt} + [M]_{sol} * K_{Ca} * [Ca]_{ppt} + [M]_{sol} * K_{Fe} * [Fe]_{ppt} + [M]_{sol} * K_{Al} * [Al]_{ppt} + [M]_{sol} * K_{Si} * [Si]_{ppt} \tag{3}$$

This equation can be solved as described in McNeill et al (1997) for arsenic. Data are available from the 373 water samples for each of the parameters in Equation 3 except for the five sorption equilibrium constants. As noted above, however, only data sets in which the total contaminant concentration is greater than 5 times the MDL are included. An initial value is guessed for each sorption equilibrium constant and a 'predicted' total concentration of contaminant can be calculated for each data set. This 'predicted' total concentration is compared to the actual measured total concentration and an error function was designated as:

$$Error = (Measured' TotalMetal' - Predicted' TotalMetal')^2 \tag{4}$$

The 'error' is squared in order to eliminate problems with positive and negative errors. The errors as calculated in Equation 4 are summed and Microsoft Excel Solver is used to optimize the sorption equilibrium constants by minimizing this summation of error.

Nonlinear Model. The nonlinear model is similar to the linear model but contains a power function of the contaminant dissolved concentration:

$$\frac{[M]_X}{[X]_{ppt}} = K_X * [M]_{sol}^{n_x} \tag{5}$$

The same mass balance applies (Equation 2) and the nonlinear model expression can be substituted to give:

$$\begin{aligned}[M]_{tot} = [M]_{sol} + [M]_{sol}^{n_{Mg}} * K_{Mg} * [Mg]_{ppt} + [M]_{sol}^{n_{Ca}} * K_{Ca} * [Ca]_{ppt} \\ + [M]_{sol}^{n_{Fe}} * K_{Fe} * [Fe]_{ppt} + [M]_{sol}^{n_{Al}} * K_{Al} * [Al]_{ppt} + [M]_{sol}^{n_{Si}} * K_{Si} * [Si]_{ppt}\end{aligned} \tag{6}$$

where,

n_x = degree of nonlinearity associated with solid 'X'.

The parameter fitting proceeds as above; however, now there are 10 variables that must be determined.

RESULTS AND DISCUSSION

The overall data on contaminant occurrence and contaminant removal by high pH soda ash softening are presented, followed by linear and nonlinear model results.

Occurrence. The cumulative distribution for the occurrence of various elements in raw water samples obtained during this survey (Figure 3-2) illustrates the nature of source waters tested. Median concentrations of As, Ba, B, Cr, Sr, and V were below their respective LOC values (Table 3-1). In fact, all barium and chromium concentrations were below 47 ppb and 885 ppb, respectively. Only one sample tested higher than the vanadium LOC (119 ppb) and, likewise, only one sample tested higher than the strontium LOC (6340 ppb). Approximately 5% of all samples exceeded 10 ppb arsenic, while 8% of all samples exceeded 600 ppb boron.

Softening results. Excellent removal of calcium, iron, and aluminum was achieved by the precipitative softening process (Figure 3-3). The removal of magnesium was not as good as that which would occur at a higher pH (~10.8). Silicon removal was fairly low as well. Little is known about silicon removal via precipitative softening but some researchers theorize that it is linked to magnesium removal (e.g. Roalson et al, 2003); however, no correlation between silicon and magnesium removal was apparent in this study (data not shown).

Removal of barium, chromium, and strontium via precipitative softening was excellent in most samples (median removals of 100%, 98.8% and 92.4% respectively) (Figure 3-4). Boron removals were extremely low with over 90% of all samples below 10% removal.

Linear model. Excellent fit was obtained between predictions and actual data for arsenic, boron, chromium, and vanadium using a linear model (Table 3-4). The two contaminants most easily removed, barium and strontium, could not be modeled with any degree of accuracy using this approach, possibly due to the precipitation of a barium- or strontium-containing solid (discussed later). Total concentrations of arsenic, boron, chromium, and vanadium followed equations of the form:

$$[As]_{total} = [As]_{sol} + 85*[Ca]_{ppt}*[As]_{sol} + 2700*[Fe]_{ppt}*[As]_{sol} \tag{7}$$

$$[B]_{total} = [B]_{sol} + 7.3*[Ca]_{ppt}*[B]_{sol} + 1360*[Fe]_{ppt}*[B]_{sol} \tag{8}$$

$$[Cr]_{total} = [Cr]_{sol} + 440*[Mg]_{ppt}*[Cr]_{sol} + 9100*[Fe]_{ppt}*[Cr]_{sol} \tag{9}$$

$$[V]_{total} = [V]_{sol} + 230*[Si]_{ppt}*[V]_{sol} + 1400*[Fe]_{ppt}*[V]_{sol} + 9700*[Al]_{ppt}*[V]_{sol} \tag{10}$$

where the subscripts 'total' mean 'total molar amount of contaminant in water before treatment', 'sol' means 'dissolved amount of contaminant remaining after treatment', and 'ppt' means 'total molar amount of element which precipitates as a solid during soda ash softening'.

Nonlinear model. There was also excellent agreement between predicted total metal and actual total metal for arsenic, boron, chromium, and vanadium using a nonlinear model (Table 3-4). As in the case of the linear model, neither barium nor strontium could be modeled accurately using this approach. Total concentrations of arsenic, boron, chromium, and vanadium followed equations of the form:

$$[As]_{total} = [As]_{sol} + 2.0*[Mg]_{ppt}*[As]_{sol}^{0..67} + 5.7*[Ca]_{ppt}*[As]_{sol}^{0.85} + 8.0*[Fe]_{ppt}*[As]_{sol}^{0.61} \quad (11)$$

$$[B]_{tot} = [B]_{sol} + 29*[Ca]_{ppt}*[B]_{sol}^{1.17} + 1.75*10^{6}*[Fe]_{ppt}*[B]_{sol}^{1.72} \quad (12)$$

$$[Cr]_{total} = [Cr]_{sol} + 1.1*[Mg]_{ppt}*[Cr]_{sol}^{0.60} + 0.33*[Fe]_{ppt}*[Cr]_{sol}^{0.34} + 4.72*10^{-4}*[Al]_{ppt}*[Cr]_{sol}^{0.00} \quad (13)$$

$$[V]_{total} = [V]_{sol} + 5.3*10^{-5}*[Mg]_{ppt}*[V]_{sol}^{0.00} + 3.2*10^{-4}*[Si]_{ppt}*[V]_{sol}^{0.045} + 7.5*10^{-4}*[Fe]_{ppt}*[V]_{sol}^{0.09} + 2.3*10^{-3}*[Al]_{ppt}*[V]_{sol}^{0.14} \quad (14)$$

Model application. Data from over 370 water samples indicate that soda ash softening can be a viable treatment technique for the removal of arsenic, barium, chromium, strontium, and vanadium. In actual practice the total amount of contaminant will be known and an estimate of the soluble (or dissolved) contaminant after treatment is required to evaluate the viability of available treatment options. Using the models presented in the previous sections, an estimate of the dissolved arsenic, boron, chromium, or vanadium concentrations can be ascertained and subsequently, a decision can be made on whether soda ash softening can be an effective treatment process in a given situation (see Illustrative Example). An independent data set will be needed to assess the accuracy of the above conceptual models. The linear model equations (Equations 7-10) are often accurate enough for a first approximation on the amount of removal that might be expected. When the nonlinear regression model equations are employed and multiple solids are responsible for contaminant removal, a program such as Microsoft Excel Solver may need to be employed to calculate the residual dissolved concentration.

Model verification. No bench-scale experiments were performed as part of this study. However, the models were applied to data not used in the model development. This includes data below 5 μg/L for arsenic, chromium, and vanadium. Even though these concentrations are close to the MDLs of these elements, the total concentrations predicted by each model are still in fair agreement in most cases with the total concentrations actually measured (linear model R^2 values: arsenic, 0.44; chromium, 0.19; vanadium, 0.62 and nonlinear model R^2 values: arsenic, 0.45; chromium, 0.60; vanadium, 0.27).

Barium removal. Dissolved levels of barium were below detection after soda ash treatment in over 75% of the samples examined (Figure 3-4). However, the modeling technique described in this study poorly characterizes barium removal. We speculate that much of the barium in these samples was removed by precipitation as barium carbonate. The solubility product constant for barium carbonate is 5.1e-9 (Table 3-2) and samples were softened by the addition of 12 mM sodium carbonate. Thus, at a typical pH of 10.3, less than 120 μg/L Ba^{2+} should be in the dissolved state. Final concentrations of carbonate were not measured so no definitive conclusion can be made as to the fraction of barium that precipitated as barium carbonate and the fraction that might be sorbed to other solids which formed.

Strontium removal. Dissolved levels of strontium were below detection after soda ash treatment in over 25% of the samples examined (Figure 3-4). As in the case of barium, we speculate much of the strontium was removed by precipitation of strontium carbonate or strontium sulfate. Additional removal could be the result of sorption to other solids formed in the precipitative softening process.

Boron removal. Boron was not removed to a great extent (Figure 3-4) in any of the samples in this study. The high model correlation coefficients (Table 3-4) can be attributed to the correlation between total and dissolved boron species.

Limitations of the model. Anions such as sulfate, nitrate, and phosphate were not measured but have been known to affect the sorption characteristics of many contaminants. Competition between elements may also be a factor but was not considered in these models. Traditional softening with lime may give different results depending on the alkalinity (i.e. carbonate level) in the raw water but the work presented herein provides a basis for further confirmation studies.

SUMMARY AND CONCLUSIONS

- Barium, chromium, strontium, and vanadium were removed quite effectively by soda ash softening in over half the water samples tested. Sodium carbonate was dosed at 12 mM and the resultant pH ranged from 9.6 to 11.1 (mean = 10.3).
- Due to the large amount of sodium carbonate used, barium and strontium were most likely removed during the softening process by formation of barium carbonate and

strontium carbonate. Additional barium or strontium could have been removed from solution by sorption to other solids formed during the process.

- Soda ash softening is not a viable treatment option for boron removal in most instances. The maximum removal noted in this study was 35%.
- Models accounting for the role of multiple solids in contaminant removal during softening might be used as predictive tools for estimating removal efficiencies for arsenic, boron, chromium, and vanadium dependent on water quality. In most cases, the linear models are accurate enough for a first approximation of the effectiveness of soda ash softening. Until validation data is obtained, such prediction should be considered preliminary and confirmation is necessary at bench scale.

ACKNOWLEDGEMENTS

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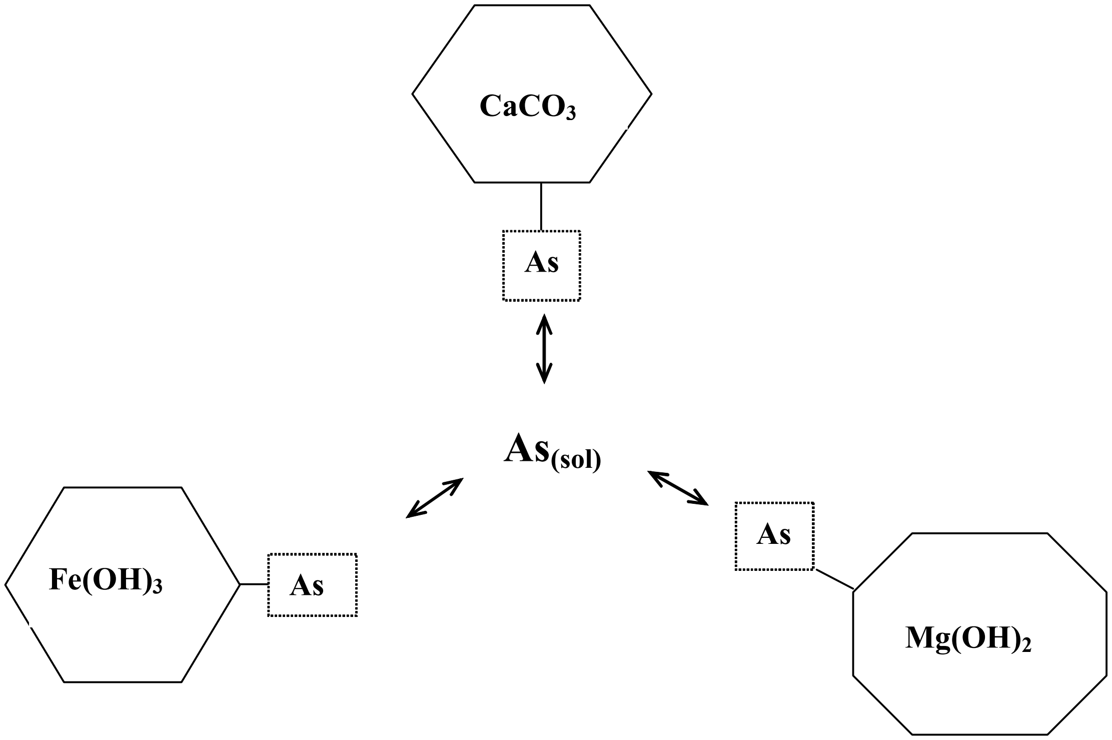

Figure 3-1. Model conceptualization of McNeill and Edwards (1997). Note that a single dissolved contaminant is in equilibrium with multiple solids.

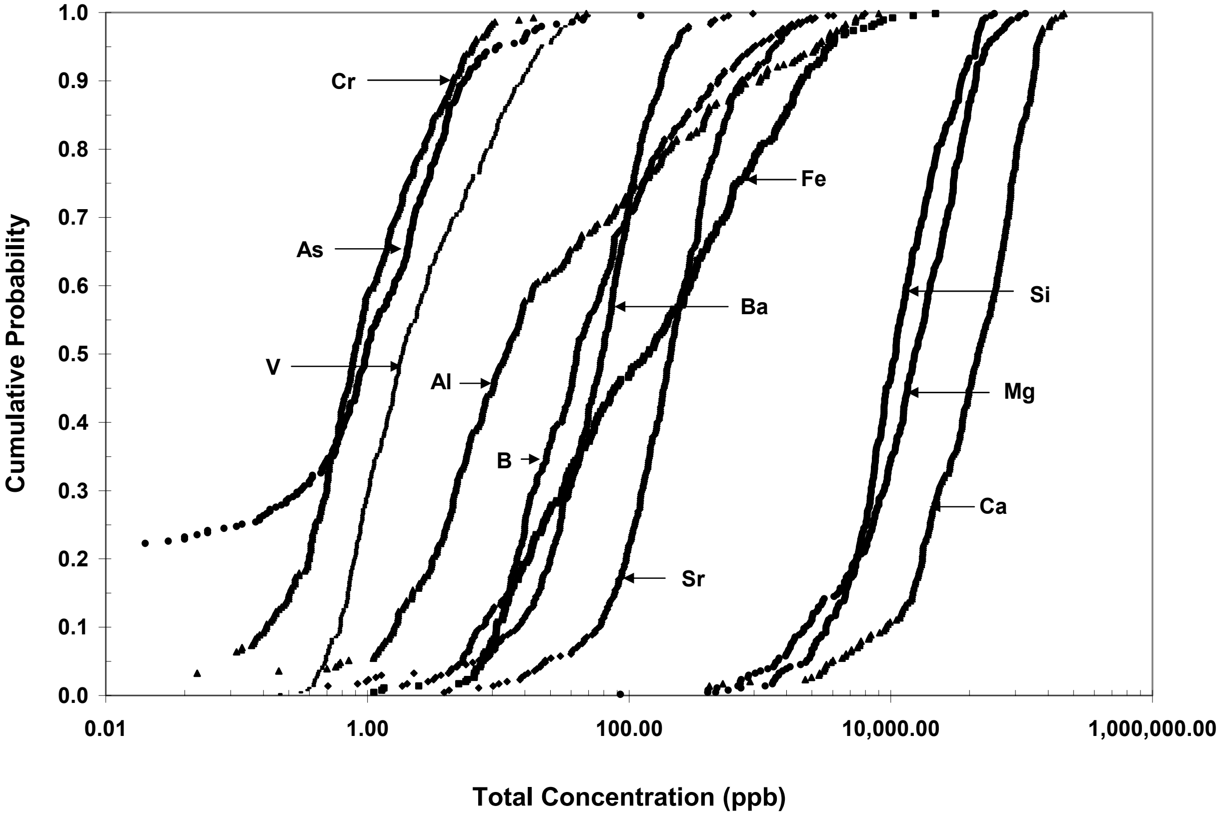

Figure 3-2. Occurrence data from AwwaRF raw water survey. Samples obtained from source waters to 373 water treatment facilities across the United States. 2/3 of the samples were groundwater sources; 1/3 were surface water sources.

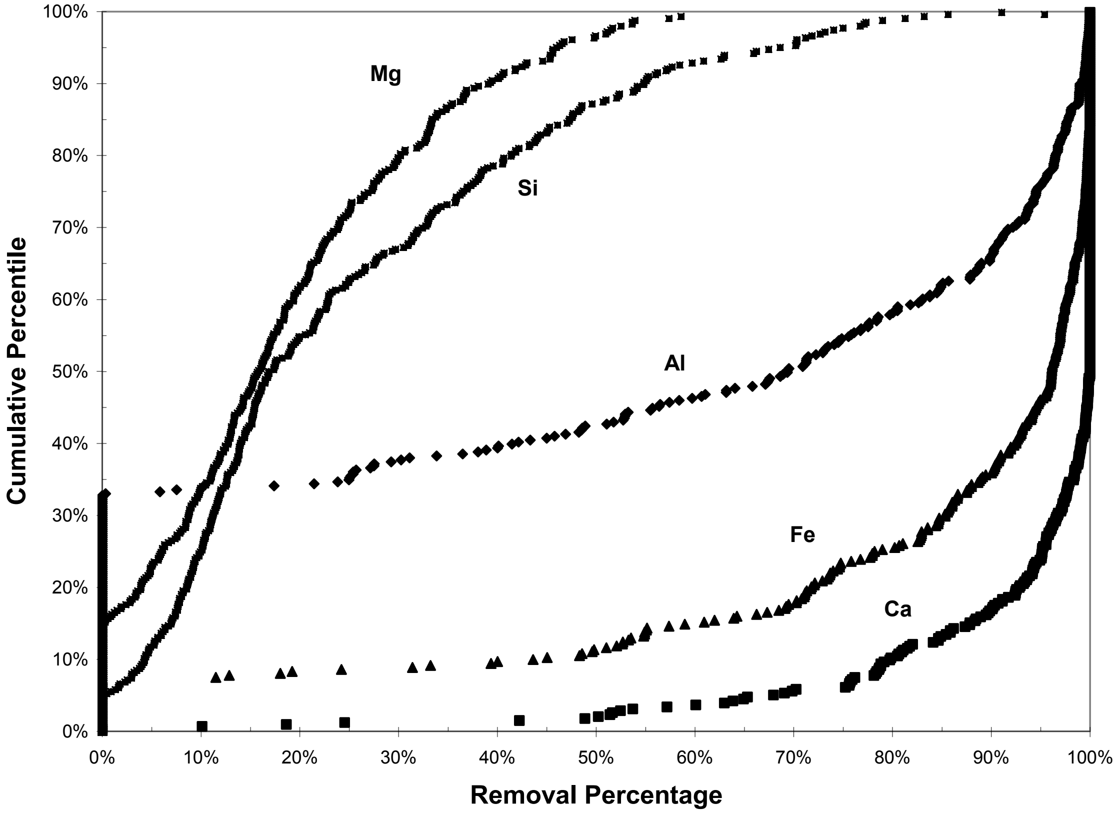

Figure 3-3. Cumulative distribution of solids removal by soda ash softening. Average pH = 10.3; pH range 9.6 – 11.1.

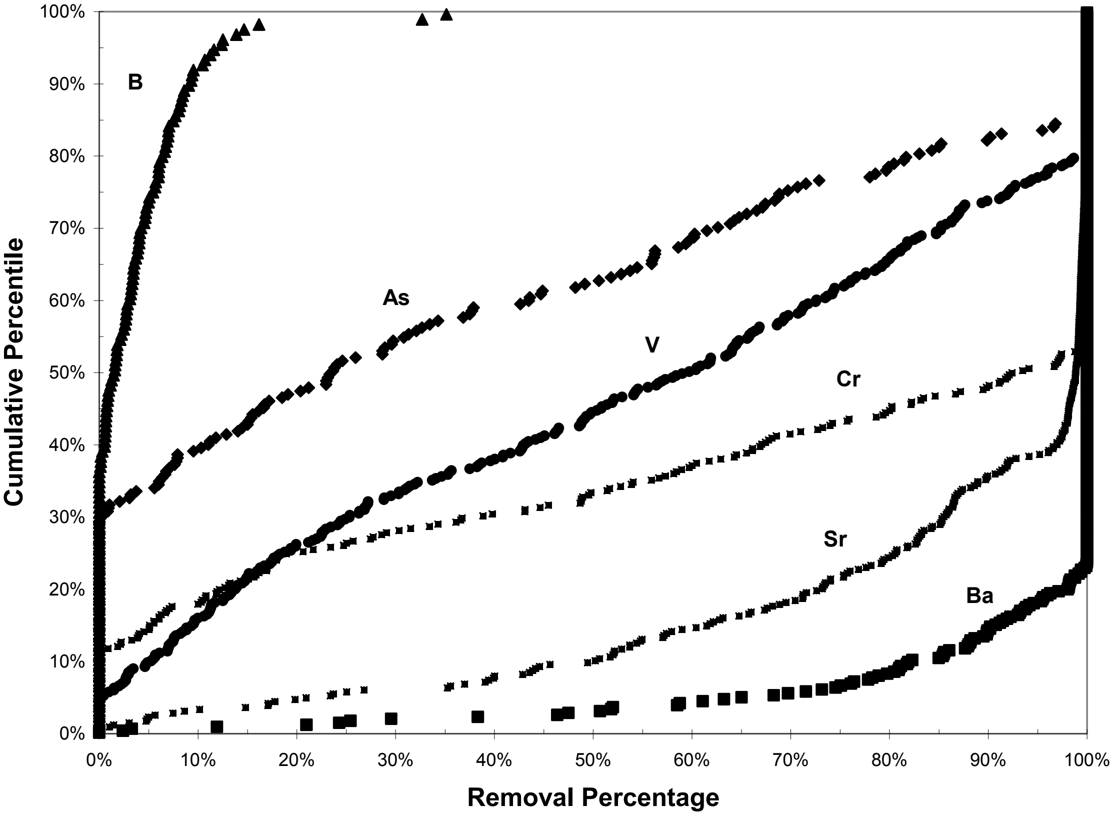

Figure 3-4. Cumulative distribution of contaminant removal by soda ash softening. Average pH = 10.3; pH range 9.6 – 11.1.

Illustrative Example

Raw water characteristics:

Chromium =	40	ppb	7.69E-07	M
Magnesium =	48	ppm	1.97E-03	M
Iron =	0.2	ppm	3.69E-06	M
Aluminum =	0.04	ppm	1.40E-06	M

Calculate expected treated water chromium concentration,
assuming water is softened with soda ash at pH 10.3.

Using linear model,

$$[\mathrm{Cr}]_{tot} = [\mathrm{Cr}]_{sol} + 440*[\mathrm{Mg}]_{ppt}*[\mathrm{Cr}]_{sol} + 9100*[\mathrm{Fe}]_{ppt}*[\mathrm{Cr}]_{sol}$$

Rearranging equation,

$$[\mathrm{Cr}]_{sol} = [\mathrm{Cr}]_{tot} / \{1 + 440*[\mathrm{Mg}]_{ppt} + 9100*[\mathrm{Fe}]_{ppt}\}$$

Substituting raw water concentrations,

$[\mathrm{Cr}]_{sol} = 21.1$ ppb

Using nonlinear model,

$$[\mathrm{Cr}]_{tot} = [\mathrm{Cr}]_{sol} + 1.1*[\mathrm{Mg}]_{ppt}*[\mathrm{Cr}]_{sol}^{0.60} + 0.33*[\mathrm{Fe}]_{ppt}*[\mathrm{Cr}]_{sol}^{0.34} + 4.7*10^{-4}*[\mathrm{Al}]_{ppt}*[\mathrm{Cr}]_{sol}^{0}$$

Solving for $[\mathrm{Cr}]_{sol}$ using Microsoft Excel Solver,

$[\mathrm{Cr}]_{sol} = 22.4$ ppb

Note: These compare to an actual value of 20.5 ppb obtained from survey.

Percentage removal would be as follows:

Actual sample = 51%
Predicted by linear model = 53%
Predicted by nonlinear model = 56%

Table 3-1. Levels of Concern for Selected Contaminants

Contaminant	Level of Concern (mg/L)	Reason	Reference
Arsenic	0.01	USEPA National Primary Drinking Water Regulatory limit	US EPA, 2002
Chromium	0.1	USEPA National Primary Drinking Water Regulatory limit	US EPA, 2002
Barium	2	USEPA National Primary Drinking Water Regulatory limit	US EPA, 2002
Boron	0.6	Noncancer Lifetime Health Advisory; included on 1998 CCL	US EPA, 1998
Vanadium	0.05	California DHS action level; included on 1998 CCL	US EPA, 1998
Strontium	4	Noncancer Lifetime Health Advisory	US EPA, 2004c

USEPA = United States Environmental Protection Agency
CCL = EPA Contaminant Candidate List
California DHS = California Department of Health Services

Table 3-2. Selected Solubility Product Constants

Compound	**Formula**	**Ksp**
barium hydroxide	$Ba(OH)_2$	5.0E-03
barium carbonate	$BaCO_3$	5.1E-09
barium sulfate	$BaSO_4$	1.1E-10
magnesium hydroxide	$Mg(OH)_2$	1.8E-11
calcium carbonate	$CaCO_3$	2.8E-09
strontium hydroxide	$Sr(OH)_2$	slightly soluble
strontium carbonate	$SrCO_3$	1.1E-10
strontium sulfate	$SrSO_4$	3.2E-07

Ref: Dean, 1987

Table 3-3. Contaminant Data Statistical Parameters

Contaminant	MDL (ppb)	Lower Limit* of Modeled Data (ppb)	Mean* of Modeled Data (ppb)	Median* of Modeled Data (ppb)	Highest* Concentration (ppb)	Number of Samples Included in Model
Arsenic	2.1	5	17.7	9.5	123	39
Chromium	0.6	5	10.6	7.6	47	41
Barium	1.8	10	56.5	31.7	884	145
Boron	1.6	50	373	147	3321	141
Vanadium	0.8	5	15.5	11.5	118	118
Strontium	12.6	50	467	242	6343	264

** initial total concentration*

Table 3-4. Model Correlation Coefficients

Contaminant	Number of Samples Included in Model	Linear Model Correlation Coefficient (R^2)	Nonlinear Model Correlation Coefficient (R^2)
Arsenic	39	0.988	0.989
Boron	141	0.995	0.995
Chromium	41	0.89	0.96
Vanadium	118	0.94	0.98

CHAPTER IV: BORON REMOVAL VIA FORMATION OF MAGNESIUM SILICATE SOLIDS DURING PRECIPITATIVE SOFTENING

Jeffrey L. Parks and Marc Edwards

ABSTRACT: Precipitative softening is an option to remove silicon and boron from natural waters. Silicon is removed from hard waters by precipitative softening when the molar ratio of Mg:Si is less than 6:1 by the formation of an amorphous magnesium silicate. This solid has an apparent solubility product constant of $10^{-25.66}$ and is stoichiometrically similar to the mineral forsterite, Mg_2SiO_4. Boron removal is consistent with sorption to this amorphous magnesium silicate. Boron removal can be roughly described by a Freundlich isotherm: $\frac{B_{sorb}}{Mg_2SiO_{4(s)}} = 21 * B_{sol}^{0.51}$.

INTRODUCTION

It is becoming increasingly important to remove silicon and boron from natural waters for a variety of reasons. Although there are no published adverse health effects from the consumption of silicon, its removal is sometimes desirable to prevent fouling of reverse osmosis membranes and clogging of pipes (Gill, 1993; Sheikholeslami and Tan, 1999; Price et al, 1997).

Recently boron has come to the forefront as a possible drinking water contaminant that could be regulated in the next few years (EPA, 2003). The basis for possible regulation is a 1992 EPA Drinking Water Health Advisory for boron. A lifetime human health advisory of 0.6 mg boron /L for drinking water was deemed appropriate based on findings in a study on male beagles by Weir and Fisher (EPA, 1992; Cantilli, 1991; Weir and Fisher, 1972). Boron removal from irrigation waters is also important for many crops. Boron toxicity may occur in boron-rich soils or in soils that have been exposed to boron-contaminated irrigation waters or the excess application of boron-rich fertilizers, sewage sludge, and fly ashes (Nable et al., 1997). Some plants are more sensitive to boron than others. Sensitive plants cannot tolerate irrigation waters with as little as 0.3 mg/L boron while other plants may be able to survive where 4 mg/L boron irrigation water is used (Keren and Bingham, 1985).

There are several theories regarding the removal of silicon during the softening process. While most researchers agree that silicon removal increases as magnesium removal increases (e.g. Roalson et al., 2003), the removal mechanism is unclear. The prevailing theory is that silicon sorbs to the surfaces of magnesium hydroxide formed during precipitative softening (Faust and Aly, 1998; Idelovitch and Wachs, 1983). Other possibilities include the formation of the smectite mineral, montmorillonite (Harder, 1972); the formation of the calcium-magnesium silicate mineral, tremolite (Roalson et al., 2003); or the formation of a magnesium silicate mineral such as kerolite, sepiolite (Stoessell, 1988) or forsterite (Faust and Aly, 1998).

Little is known about the removal of boron during the softening process as well. Since only a small fraction of boron is normally removed (< 10%) via precipitative softening there has been little reason to study the mechanism of this removal (Parks and Edwards, 2005). As in the case with silicon, many researchers believe the boron sorbs to the surface of magnesium hydroxide or becomes incorporated into the crystalline structure of magnesium hydroxide formed during the softening process (Rhoades et al., 1970). Results from Recepoglu and Beker (1991) demonstrate that 30% of geothermal waste water boron (28.5 mg/L) can be removed from water containing 135 mg/L silicon by the addition of MgO. Their results indicate that an 8:1 molar ratio of Mg:Si is necessary to achieve this removal at pH values of 9.1 and 10.5 (Recepoglu and Beker, 1991).

The objective of this study was to determine the practical mode of removal for both silicon and boron when water is treated by a precipitative softening process. In addition, models were developed to estimate the amount of silicon and boron removed from natural waters.

EXPERIMENTAL MATERIALS AND METHODS

During a recent survey conducted by Virginia Tech, samples of treated and untreated water were obtained from water treatment plants around the United States that employed a variety of treatment processes. In several instances, samples were also obtained from various locations throughout the treatment process as well. While most of the boron removal data was typical of that found in the literature, the treatment plant in Ames, Iowa was removing approximately 50-60% of the boron in its influent water via lime softening. Many jar tests were conducted using actual influent water from this treatment plant as well as water prepared in our laboratory to determine the mechanism by which boron was being removed. These jar tests are described in detail in the following paragraphs.

Unless stated otherwise all bench tests were conducted using a six-place jar tester[1] and were designed to simulate precipitative softening at the laboratory scale. For tests with synthetic water, each jar was filled with approximately one liter of deionized water. Calcium, magnesium, and silicon were added as necessary using reagent grade stock solutions of calcium chloride (20,000 mg/L as Ca), magnesium chloride (10,000 mg/L as Mg), and sodium silicate (16,667 mg/L as Si). Boron was added as necessary using a high purity boric acid solution (1,000 mg/L as B). Ionic strength was held constant (0.01 ± 0.003) by adding crystalline sodium chloride as needed. Ames water was used as received with no additional calcium, magnesium, silicon, or boron added. The pH of each solution was raised using a 5 N sodium hydroxide solution. This solution was prepared fresh each day to minimize contamination with atmospheric carbonate. All chemicals were rapid mixed at 150 rpm for several seconds. The mixing speed was then slowed to 30 rpm for 30 minutes of flocculation. pH was monitored and adjusted as needed during the flocculation period. Solutions were decanted and filtered through a 0.45 µm pore size nylon membrane filter after 30 minutes of quiescent settling. Details of each experimental protocol are given below.

The Role of Magnesium. It has long been known that magnesium is involved in the removal mechanism of silicon during precipitative softening. However, no strong data has been collected as to whether adsorption or co-precipitation is responsible. Jar tests were conducted in which silicon was added to water containing magnesium ions prior to the formation of a magnesium-containing solid (designated 'in situ') and after the formation of a magnesium-containing solid (designated 'pre-formed').

In the 'in situ' experiment, approximately 50 mg/L magnesium, 12 mg/L silicon, and 100 µg/L boron were added to one jar (similar concentrations to those measured in Ames). The pH was raised to 11.0 and the solution was mixed at 30 rpm for 50 minutes. A sample was withdrawn, filtered through a 0.45 µm pore size nylon syringe filter, and then analyzed for magnesium, silicon, and boron.

In the 'preformed' experiments, approximately 50 mg/L magnesium was added to each of three jars. The pH was raised to 11.0 in each and the solutions were mixed at 30 rpm. Approximately 12 mg/L silicon and 100 µg/L boron were added to each jar after 25, 25, and 40 minutes, respectively. After an additional 20, 40, and 25 minutes respectively, samples were withdrawn from each jar, filtered through a 0.45 µm pore size nylon syringe filter, and then analyzed for magnesium, silicon, and boron.

Effect of pH and Silicon on Boron Removal. Jar tests were conducted to determine the effect of pH on the removal of boron from water that contained appreciable levels of magnesium and silicon. Duplicate jar tests were conducted without silicon to establish its essentiality. Approximately 50 mg/L magnesium, 15 mg/L silicon, and 1000 μg/L boron were added to three one liter jars. Carbon dioxide was bubbled through each solution prior to silicon addition to insure initial pH level was approximately 7. Three additional jars were prepared in an identical manner except silicon was not added. pH was raised with 5N sodium hydroxide as described above, except samples were taken from each jar at pH values of 10, 10.2, 10.4, 10.6, 10.8, 11, 11.3, and 11.6. The pH was allowed to stabilize at these values for 10 minutes before samples were withdrawn.

Effect of Magnesium and Silicon Concentration on Solid Formation. A series of jar tests were performed varying both initial magnesium and silicon concentrations. All tests were performed at pH 10.8 and sodium chloride was added to each jar to reduce variability that might be introduced if ionic strength was allowed to vary widely. Initial concentrations of magnesium included 0, 2, 5, 10, 20, and 50 mg/L while initial concentrations of silicon were 0, 2, 5, 10, and 25 mg/L. All jar tests were conducted per the protocol described above.

Analytical Methods. Calcium, magnesium, silicon, and boron concentrations were measured by a JY Ultima^2 inductively coupled plasma with emission spectroscopy (ICP-ES) in accordance with *Standard Methods* (1998). Inorganic carbon was measured with a

Sievers 800 Portable Total Organic Carbon Analyzer[3]. Conductivity was measured with a YSI Model 32 Conductance Meter[4]. Ionic strength was estimated using the relationship derived by Russell (1976):

$$\mu = 1.6 \times 10^{-5} \times \text{specific conductance } (\mu\text{mho/cm}) \qquad (1)$$

Activity coefficients were estimated using the Güntleberg approximation of the Debye-Hückel theory (Snoeyink and Jenkins, 1980):

$$-\log \gamma = (0.5 \times Z^2 \times \mu^{1/2}) / (1 + \mu^{1/2}) \qquad (2)$$

where,

γ = activity coefficient

Z = charge of the ion

μ = ionic strength.

Surfaces of some solids formed were analyzed at 20 kilovolts with an IXRF energy dispersive spectrometer (EDS) that was connected to a Leo 1550 field emission scanning electron microscope (FE-SEM). All samples were plated with gold palladium at a thickness of 20 nm prior to surface analysis. Sample sites were chosen at random based upon inspection with the SEM. EDS can detect elements with atomic numbers greater than and including carbon so boron could not be evaluated using this method.

X-ray diffractograms were performed on a Scintag XDS 7000 unit on several of the precipitated solids obtained in the jar tests using CuKα radiation. Patterns were step scanned from 2 to 70 degrees at a step scan rate of 0.02 Deg/min using a 0.075° step and a counting time of 4 seconds.

RESULTS AND DISCUSSION

After describing results of preliminary experiments establishing the mode of removal for both silicon and boron from solution during precipitative softening, a model is developed to estimate the formation of a magnesium silicate solid and the residual soluble magnesium and silicon concentrations. A model is then developed to estimate the amount of boron that can be removed from solution when this magnesium silicate solid forms.

Ames Iowa Water Treatment. Samples were collected from various locations in the lime softening process employed in the Ames Iowa water treatment plant. Approximately 50 – 60 % of the influent boron was removed from the raw water (Table 4-1). This anomalously high removal led us to look more closely at the specifics of the lime softening process employed at Ames as well as the composition of their influent water.

Isolation of the particular mechanism of boron removal proved to be difficult. Ames raw water contained approximately 110 mg/L calcium, 33 mg/L magnesium, 7 mg/L iron, 12 mg/L silicon, and 130 μg/L boron. Samples of this water were obtained along with a sample of the lime used in Ames. Jar tests conducted using Ames water and Ames lime did give similar results. At a final pH of 10.8 56% of the original boron was removed as well as 42% of the calcium, 56% of the magnesium, 37% of the silicon and all of the iron. Similar results were also obtained when Ames water was used in conjunction with reagent grade lime. These results eliminate operational procedures at the treatment plant as the cause for the excess boron removal and indicate that water chemistry must be critical in obtaining significant boron removal. The ‘after mixing’ results (Table 4-1) also indicate that a large amount of boron is incorporated into solids formed during this process (‘Total’ boron much greater than ‘Soluble’ boron in this sample). The following sections detail the results of our investigation in isolating the constituent(s) in the Ames water responsible for this enhanced boron removal.

The Role of Calcium. Silicon and boron removal proved to be unaffected by the presence of calcium. A set of side-by-side jar tests with deionized water containing 100 μg/L boron, 12 mg/L silicon, and 33 mg/L magnesium showed that 68% of boron and 54% of silicon could be removed by softening with or without 110 mg/L calcium. Additionally, a second side-by-side test with 0 and 110 mg/L calcium indicated that no boron or silicon was removed if magnesium was absent from the initial water (data not shown).

The Role of Magnesium. Silicon removal during precipitative softening is highly influenced by magnesium. Although this result has been discussed in past research (e.g. Faust and Aly, 1998; Idelovitch and Wachs, 1983; Roalson et al., 2003), the mechanism by which silicon is removed has not been defined. In this study we performed tests to check two hypotheses: (1) silicon is sorbed to the surface of magnesium hydroxide formed during precipitative softening, or (2) silicon is precipitated by magnesium during precipitative softening. Jar tests demonstrate that silicon co-precipitates with magnesium at high pH. Approximately 80% of the original silicon is removed when both silicon and magnesium are present prior to pH elevation (Table 4-2). However, if magnesium hydroxide is allowed to form at high pH for 25 minutes and then silicon is introduced, then less than 5% of the silicon is removed from solution (indicating sorption to magnesium hydroxide surfaces is only a minor factor in silicon removal).

Boron is also removed much more efficiently when magnesium and silicon co-precipitate. Approximately 70% of an initial boron dose is removed from solution in this instance, as opposed to less than 10% removal when magnesium was precipitated as $Mg(OH)_2$ prior to silicon addition (Table 4-2).

pH Effect. Magnesium and silicon removal improved as the pH was increased. Boron removal was negligible below pH 10.4 and reached a maximum at pH 10.8 (Figure 4-1). Above pH 10.8 boron removal began to decrease. In duplicate solutions without silicon, boron removal was ≤ 10% at all pH levels tested. This is additional evidence supporting the hypothesis that boron is sorbing to a magnesium silicate solid. Boron removal at higher pH values may decrease because hydroxide ion, carbonate ion, or $SiO_2(OH)_2^{2-}$ may out-compete the borate anion for surface sites on the magnesium silicate solid. An alternate explanation may be that the borate anion is repulsed by a negative surface charge, however no PZC measurements were performed to verify the surface charge of the solids formed.

Evidence of the Formation of Two Types of Amorphous Solids. Jar tests were conducted with various concentrations of magnesium and silicon at pH 10.8. The pH of 10.8 was selected since it was the optimum pH for boron removal (and hence the optimum pH for magnesium silicate formation) during the previous experiment. After completion of the jar test protocol all solutions were passed through a 0.45 μm pore size nylon membrane filter using a vacuum pump. All solutions were very difficult to filter; i.e. up to a couple of hours were required to filter one liter of solution. The solids collected, however, were quite different. In solutions with little or no silicon, the solids were white and shiny. The solids collected from solutions containing very high magnesium and silicon were gel-like and dull grayish-white in color. The initial water-saturated filter cake was approximately 6 mm thick. After air-drying over night these solids dried up and hardened (Figure 4-2). Scanning electron micrographs (SEM) were taken of both solids (Figure 4-3). The solids with little or no silicon were 'platy' (Figure 4-3a) while those with a large amount of silicon were 'clumpy' (Figure 4-3b). Additionally, energy dispersive spectroscopy (EDS) was employed on these solids and the elemental analysis of the 'clumpy' material indicated a 1.86 (± 0.19):1 molar ratio of magnesium to silicon. This is roughly consistent with a predicted stoichiometry based on measurements of magnesium and silicon removed.

X-ray diffractograms indicated that this magnesium silicate solid was largely amorphous as would be expected for solids formed in this manner (Figure 4-4). Allowing the solids to age for two months showed a substantial increase in crystallinity (Figure 4-4) but no match for the pattern has been found at the present time.

Solubility Product Constant for Amorphous Magnesium Hydroxide. Jar tests were conducted with various amounts of magnesium in the absence of silicon. Inorganic carbon was measured and in all cases the solubility of magnesite (Table 4-3) was not exceeded. The average solubility product constant of the amorphous magnesium hydroxide solid formed during precipitate softening and one hour aging in the absence of silicon is $10^{-10.53}$ (data not shown).

Solubility Product Constant for Amorphous Magnesium Silicate. Likewise, jar tests were conducted with a large amount of silicon (approx. 25 mg/L) and various amounts of magnesium. As stated above, these solids had an approximate molar ratio of Mg:Si of 2:1. A molecular formula of Mg_2SiO_4 can describe this solid and is consistent with the mineral forsterite. Forsterite has a solubility product constant of $10^{-26.9}$ (Nordstrom and Munoz, 1994) while the slightly more soluble solid formed during these tests has an average K_{sp} of $10^{-25.66}$. These equilibrium relationships are shown graphically in Figure 4-5 alongside other magnesium- and silicon-containing minerals.

Model for Silicon Removal during Precipitative Softening. Final concentration data from a series of jar tests with varying amounts of magnesium and silicon are shown alongside the equilibrium saturation curves for the amorphous solids described above (Figure 4-6). The concentrations shown are for the Mg^{2+} and $Si(OH)_4$ species only and do not include other soluble magnesium and silicon complexes (listed in Table 4-2). Our model for predicting silicon (and magnesium) removals during practical conditions present during precipitative softening is set forth below:

Step 1 – The ion activity product (IAP) for both amorphous magnesium silicate and amorphous magnesium hydroxide were calculated.

(a) - If the amorphous magnesium silicate IAP exceeded its solubility product constant ($10^{-25.66}$), then this solid was assumed to form. Skip to Step 2. [IAP = $\{Mg^{2+}\}^2$ x $\{Si(OH)_4\}$ x $\{OH^-\}^4$]

(b) - If the amorphous magnesium hydroxide IAP exceeded its solubility product constant ($10^{-10.53}$), then this solid was assumed to form. Skip to Step 3. [IAP = $\{Mg^{2+}\}$ x $\{OH^-\}^2$]

(c) - If neither solubility product constant was exceeded then the equilibrium magnesium and silicon concentrations will equal the initial concentrations since no solid formed. Finished.

Step 2 – If amorphous magnesium silicate was forming, a value for the equilibrium silicon concentration was calculated that satisfied both the silicon mass balance in Equation (1) and the magnesium mass balance in Equation (2).

$$\text{Total Si} = [Si(OH)_4] + [SiO(OH)_3^-] + [SiO_2(OH)_2^{2-}] + [\text{am-}Mg_2SiO_{4(s)}] \quad (1)$$

$$\text{Total Mg} = [Mg^{2+}] + [MgOH^+] + [MgCO_3^0] + 2 \text{ x } [\text{am-}Mg_2SiO_{4(s)}] \quad (2)$$

(in this case [Mg^{2+}] can be calculated from the pK of am-$Mg_2SiO_{4(s)}$)

Step 3 – If amorphous magnesium hydroxide was forming instead of amorphous magnesium silicate, the equilibrium silicon concentration will equal the initial silicon concentration. The equilibrium magnesium concentration was calculated from the pK expression for am-$Mg(OH)_2$.

This model's prediction of equilibrium silicon is excellent (Figure 4-7a); however, care must be observed when interpreting the magnesium equilibrium data (Figure 4-7b). There is a transition zone where neither the magnesium hydroxide nor the magnesium silicate equilibrium is satisfied. This transition appears to occur when the initial Mg:Si molar ratio is greater than 6:1. The final equilibrium magnesium concentration in this situation is difficult to predict. One possible explanation is that both solids (magnesium hydroxide and magnesium silicate) may be forming at this high Mg:Si ratio. This should not be considered a serious shortcoming of the model however, since the initial silicon concentration would have to be quite low for this situation to occur (and if that was the case, silicon removal would probably not be a concern anyway). The final equilibrium silicon concentration in this situation is predicted well by this model in any case, most likely because the equilibrium curve in the transition zone is very steep (i.e. there is only a small change in silicon concentration over a large range of magnesium concentrations).

Model for Boron Removal during Precipitative Softening. As described in previous sections, boron appears to be removed from water via sorption to an amorphous magnesium silicate of similar composition to forsterite. Jar tests conducted with various amounts of magnesium, silicon, and boron (Figure 4-8) indicate that a Freundlich isotherm provides a good model to predict boron removal in these situations:

$$\frac{B_{sorb}}{Mg_2SiO_{4(s)}} = 21 * B_{sol}^{0.51} \tag{3}$$

where,

B_{sorb} = boron removed from solution by sorption to magnesium silicate solid (M)

$Mg_2SiO_{4(s)}$ = magnesium silicate solid formed during precipitative softening (M)

B_{sol} = soluble boron remaining in solution (M).

The correlation ($R^2 = 0.86$) is surprisingly good considering one of the terms in the Freundlich fit ($Mg_2SiO_{4(s)}$) is modeled by the previously described procedure.

Solid Formation Kinetics. Several jar tests were allowed to proceed for a time period of two weeks. Further removal of both magnesium and silicon occurred over the entire period, indicating that distinct silicon-containing solids are forming instead of the currently accepted theory that silicon is sorbing to a magnesium hydroxide solid. Aging of a magnesium-only solid into a more crystalline form should result in a release of silicon to the water as surface area available for sorption decreased.

One jar test containing magnesium, silicon, and boron was conducted over a period of 45 days. Results show that soluble boron reaches a minimum in 1 – 4 hours and then begins to slowly rise (Figure 4-9). During the same time period, magnesium and silicon continue to slowly decrease. These results can be explained by the increasing crystallinity of the amorphous magnesium silicate solid as it ages, resulting in less surface area and therefore fewer surface sites for boron sorption. This is additional evidence that a magnesium silicate solid is removing boron via sorption onto its surface.

Model Use. These models can be used to get a first approximation on the degree of silicon and/or boron removal that can be expected if softening is employed as a treatment process. Our data show that significant silicon and boron removal only occur if the amorphous magnesium silicate described in this manuscript is formed. This solid only appears to form if the Mg:Si molar ratio in the raw water is less than 6:1. Once it is determined that this solid will form the model can be employed. Typically one will know the softening pH, total magnesium, total silicon, total boron, and total carbonate in the raw water. Final softened concentrations can be estimated for $[Mg^{2+}]$, $[MgOH^{+}]$, $[MgCO_3^{0}]$, $[Si(OH)_4]$, $[SiO(OH)_3^{-}]$, $[SiO_2(OH)_2^{2-}]$, $[HCO_3^{-}]$, $[CO_3^{2-}]$, $[B]_{sol}$, $[B]_{sorb}$, and $[am\text{-}Mg_2SiO_4]_{(s)}$ by solving a system of 11 equations. These equations include 4 mass balances (magnesium, silicon, boron, and carbon), 1 sorption isotherm (for boron), 1 solubility product constant (for amorphous magnesium silicate), and 5 equilibrium expressions (located in Table 4-3).

Implications of Research. Boron removal from natural waters can be enhanced by formation of a magnesium silicate solid during softening. If necessary, supplemental magnesium and/or silicon (depending on which is limiting) could be added to water prior to softening to form higher concentrations of this solid. pH adjustment to 10.8 is also necessary.

In seawater the average concentrations of magnesium, silicon, and boron are 1290 mg/L, 2.9 mg/L, and 4.5 mg/L respectively. Preliminary experiments indicate that softening with sodium hydroxide or sodium silicate can result in similar boron removals (59 vs. 56%); however, only ¼ the amount of base is necessary to achieve this removal using sodium silicate (11.5 mmol/L Na_2SiO_2 vs 43 mmol/L NaOH). Due to the multitude of constituents in seawater, the high levels of total dissolved solids, or some other factor inherent to seawater, boron removal cannot be modeled effectively using the methods described in this study. Although the large amounts of sludge that form often precludes precipitative softening as the treatment of choice for seawater, silicon addition can still enhance boron removal in subsequent treatment in certain situations.

Anions such as sulfate, nitrate, and phosphate were not included in our synthetic waters but have been known to affect the sorption characteristics of many contaminants. Traditional softening with lime may give different results depending on the alkalinity (i.e. carbonate level) in the raw water but the work presented herein provides a conceptual basis for further confirmation studies.

CONCLUSIONS

- A model has been developed that can accurately predict silicon removal during precipitative softening. Silicon removal is consistent with co-precipitation by magnesium and not by sorption to magnesium hydroxide solids.

- Boron is removed from solution by sorption to the amorphous magnesium silicate formed during precipitative softening. Its removal was consistent with a Freundlich isotherm.

- Boron desorbs from the magnesium silicate solid after long periods of time, most likely due to a decrease in surface area due to a higher degree of crystallinity associated with a more aged solid.

- Total retention time should be less than 4 hours for water after magnesium silicate flocs are formed to prevent boron from desorbing into the treated water.

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[1] Phipps and Bird, Richmond, VA

[2] Horiba Jobin Yvon, Inc., Edison, NJ

[3] Sievers Instruments, Inc., Denver, CO

[4] YSI, Inc., Yellow Springs, OH

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Table 4-1. Ames Iowa water treatment plant sampling results.

Sample Location	Soluble					Total				
	Boron (ppb)	Calcium (mg/L)	Iron (mg/L)	Magnesium (mg/L)	Silicon (mg/L)	Boron (ppb)	Calcium (mg/L)	Iron (mg/L)	Magnesium (mg/L)	Silicon (mg/L)
Raw water	73.6	108.8	6.9	32.8	12.4	70.2	99.5	7.0	32.7	13.0
Backwash water	30.7	57.7	0.0	2.5	4.2	32.1	93.7	1.1	5.1	5.7
After mixing	32.2	59.8	0.0	2.4	4.5	131.5	637.3	17.9	80.9	29.1
After clarification	31.1	59.8	0.0	1.9	4.3	32.5	57.8	0.0	2.2	4.5
After recarbonation	30.5	59.5	0.0	1.8	4.3	32.1	57.8	0.1	2.0	4.4
After fluoride	36.7	59.3	0.0	1.8	4.5	32.5	58.6	0.0	1.9	4.7
% Removal	50.2%	45.5%	100.0%	94.4%	63.4%	53.7%	41.1%	100.0%	94.0%	63.5%

Table 4-2. Influence of ‘preformed’ versus ‘in-situ’ magnesium precipitation on silicon and boron removal.

Condition	Mg Elapsed Time* (min)	Si Elapsed Time* (min)	Final Mg Conc. (mg/L)	Final Si Conc. (mg/L)	Final B Conc. (ppb)	Si Removal (%)	B Removal (%)
'Preformed' Mg precipitation	65	20	0.3	12.2	94.8	0.0%	5.2%
	65	40	1.0	11.5	94.2	3.9%	5.8%
	50	25	0.2	11.7	90.2	2.5%	9.8%
'In-situ' Mg precipitation	50	50	4.4	2.4	30.8	79.9%	69.2%

Approximately 50 mg/L magnesium, 12 mg/L silicon, and 100 µg/L boron initially dosed.
pH maintained at 11.0 throughout test
B = boron; Mg = magnesium; Si = silicon
** Elapsed time between chemical addition and sample collection*

Table 4-3. Equilibria for the Mg-Si-CO_3-H_2O system (partial list)

Species	Equilibrium Equation	pK	Reference
solids			
Amorphous Silica	$SiO_2 + 2H_2O = Si(OH)_4$	2.7	Faust and Aly, 1998
Brucite	$Mg(OH)_2 = Mg^{2+} + 2OH^-$	11.16	Nordstrom and Munoz, 1994
Enstatite	$MgSiO_3 = Mg^{2+} + H_4SiO_4 + 2(OH^-)$	16.6	Nordstrom and Munoz, 1994
Forsterite	$Mg_2SiO_4 + 4H_2O = 2Mg^{2+} + Si(OH)_4 + 4(OH^-)$	26.9	Nordstrom and Munoz, 1994
Kerolite	$Mg_3Si_4O_{10}(OH)_2 \cdot H_2O + 9H_2O = 3Mg^{2+} + 4Si(OH)_4 + 6(OH^-)$	58.21	Stoessell, 1988
Magnesite	$MgCO_3 = Mg^{2+} + CO_3^{2-}$	7.46	Stumm and Morgan, 1996
Talc	$Mg_3Si_4O_{10}(OH)_2 = 3Mg^{2+} + 4H_4SiO_4 + 6(OH^-)$	62.8	Nordstrom and Munoz, 1994
dissolved			
Mg^{2+}			
$MgOH^+$	$Mg^{2+} + H_2O = MgOH^+ + H^+$	11.44	Stumm and Morgan, 1996
$MgCO_3^0$	$Mg^{2+} + CO_3^{2-} = MgCO_3^0$	-2.98	Stumm and Morgan, 1996
$Si(OH)_4$			
$SiO(OH)_3^-$	$Si(OH)_4 = H^+ + SiO(OH)_3^-$	9.46	Faust and Aly, 1998
$SiO_2(OH)_2^{2-}$	$SiO(OH)_3^- = H^+ + SiO_2(OH)_2^{2-}$	12.56	Faust and Aly, 1998
CO_3^{2-}			
HCO_3^-	$HCO_3^- = CO_3^{2-} + H^+$	10.33	Nordstrom and Munoz, 1994

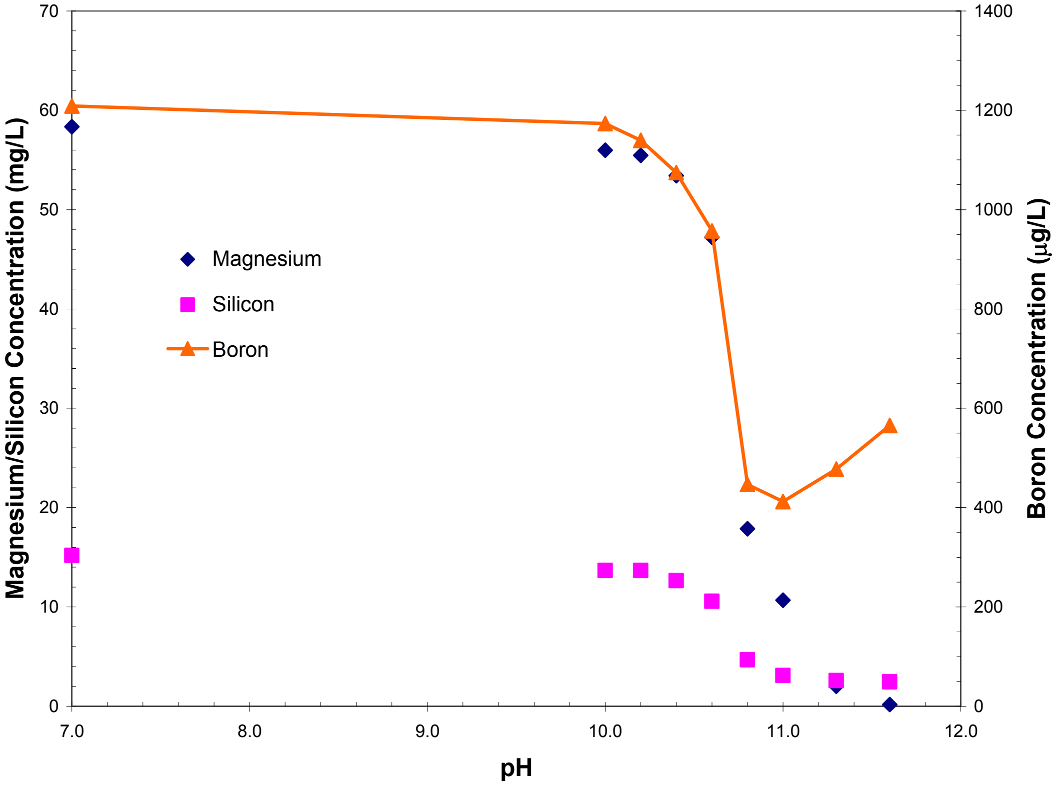

Figure 4-1. Magnesium, silicon, and boron removal as a function of pH. pH was raised by addition of 5N sodium hydroxide.

Figure 4-2. Air-dried filtered solid from pH 10.8 solution which originally contained 50 mg/L magnesium and 25 mg/L silicon.

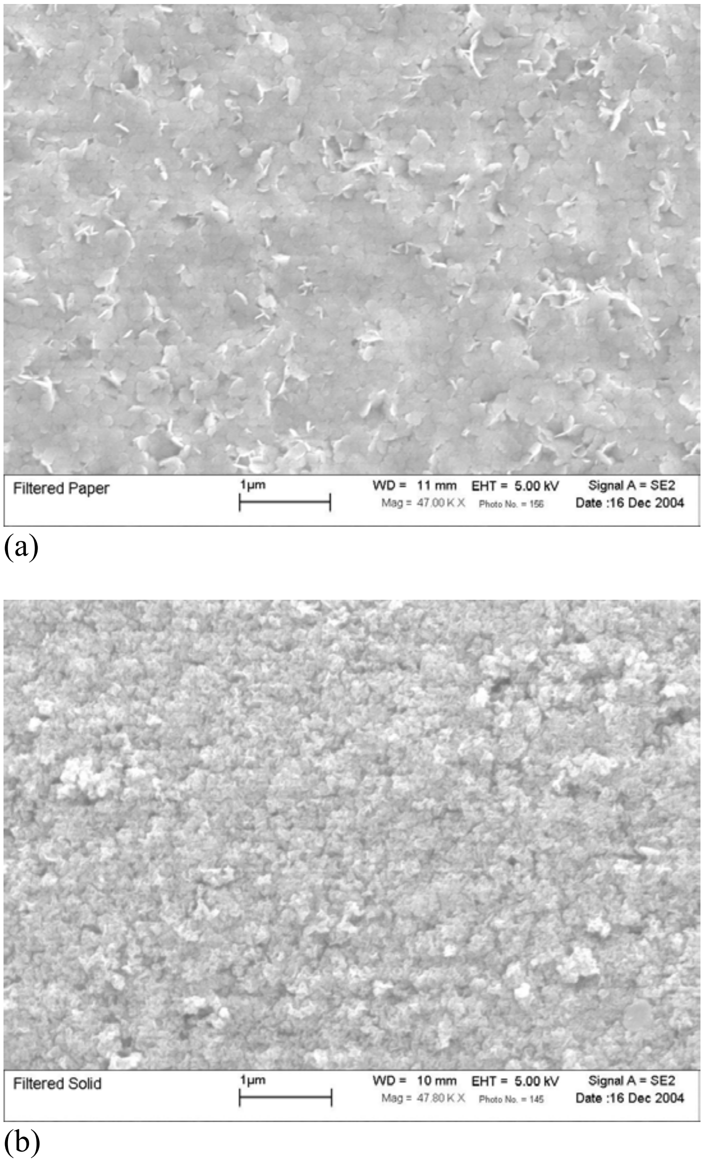

Figure 4-3. Scanning electron micrographs of (a) solid formed from solution containing only magnesium at pH 10.8, and (b) solid formed from solution containing magnesium and silicon at pH 10.8. Magnification 47,000x.

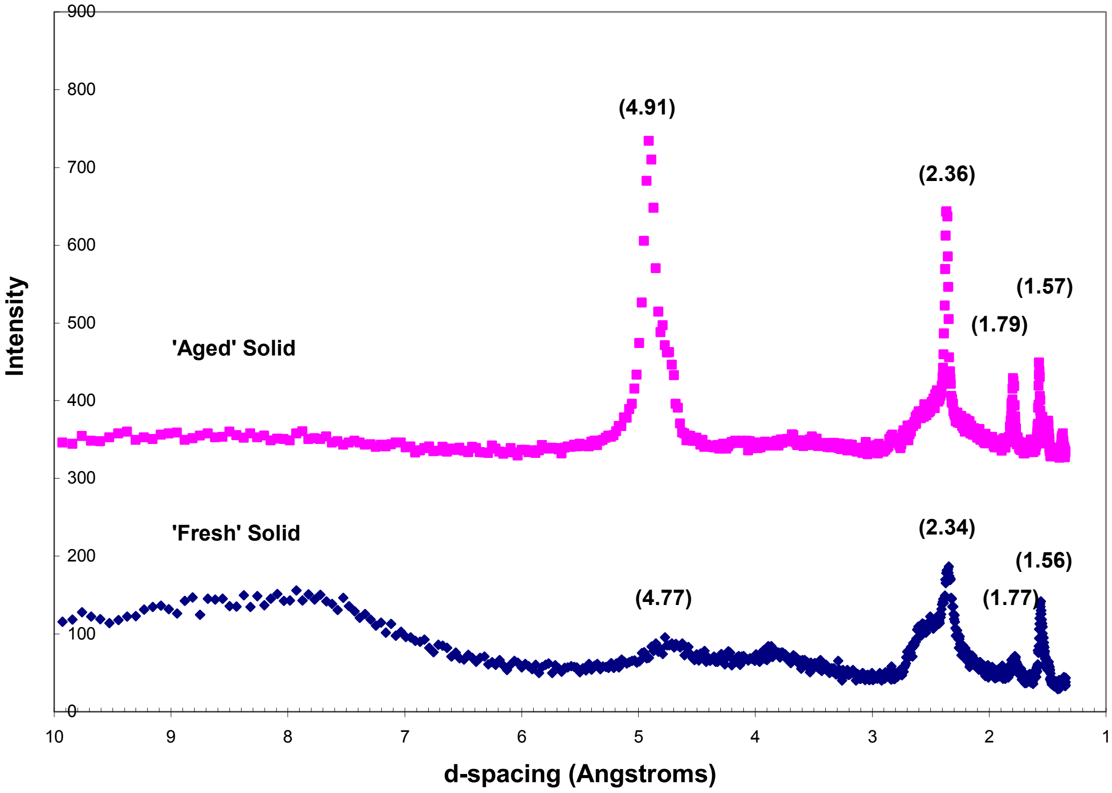

Figure 4-4. X-ray diffractograms for fresh and aged solids formed during jar test. Initial concentrations of magnesium and silicon were 30 mg/L and 12 mg/L, respectively. Solution maintained at pH 10.8.

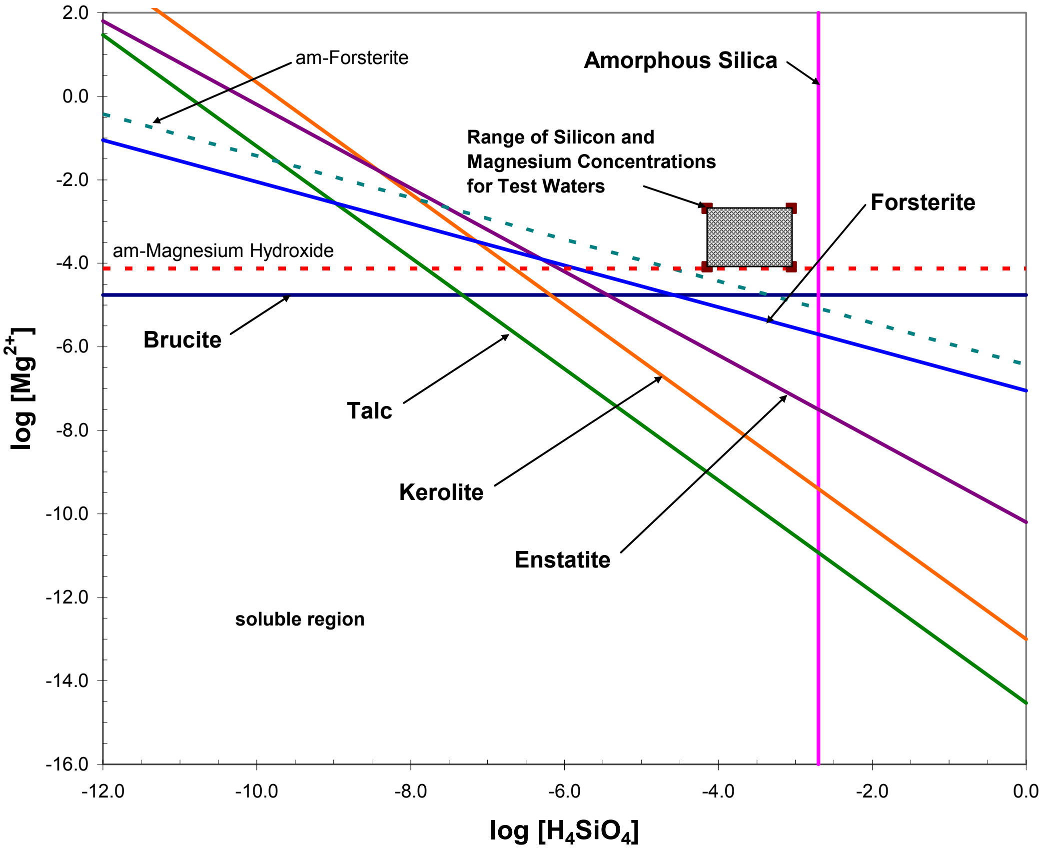

Figure 4-5. Stability diagram for Mg-Si-H_2O system at pH 10.8. Hatched area denotes region of typical magnesium (2-50 mg/L) and silicon (2-25 mg/L) concentrations in natural waters. Dashed lines indicate quasi-equilibrium determined in this study.

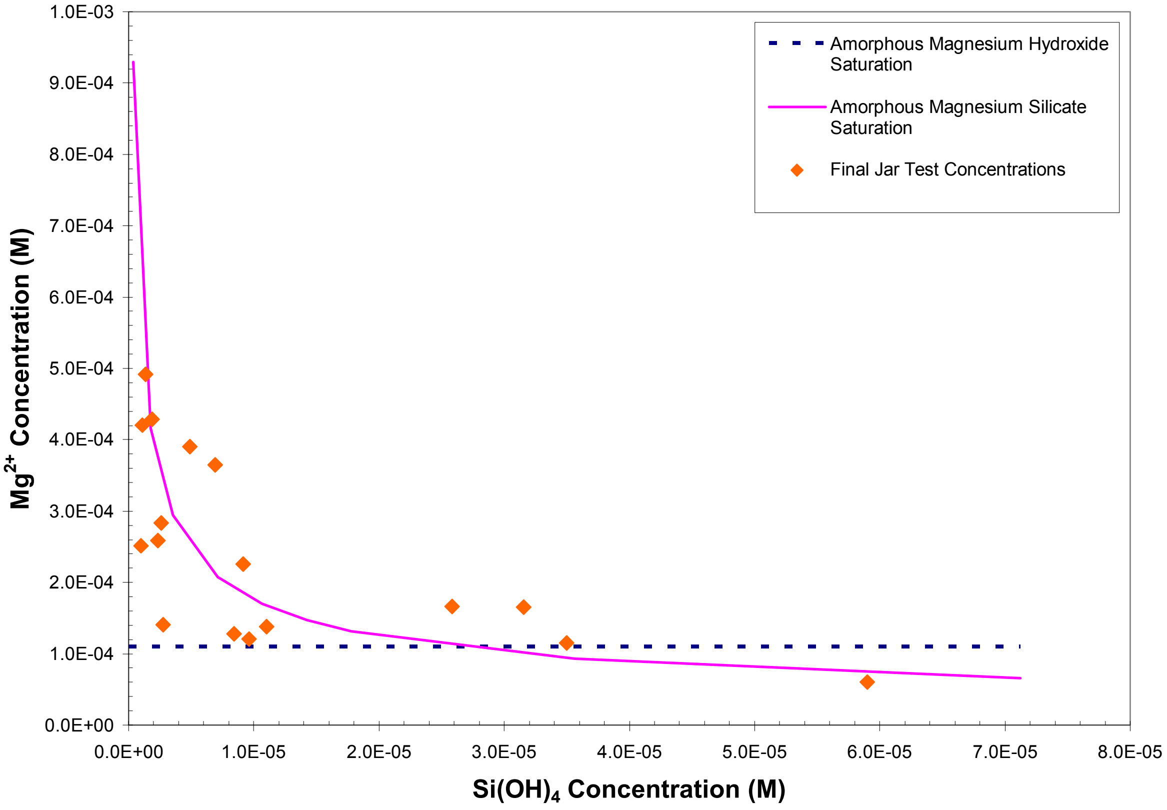

Figure 4-6. Concentration data for 1 hour jar tests at pH 10.8. Data shows that formation of a metastable magnesium silicate solid can explain why magnesium concentration does not fall on the magnesium hydroxide equilibrium curve.

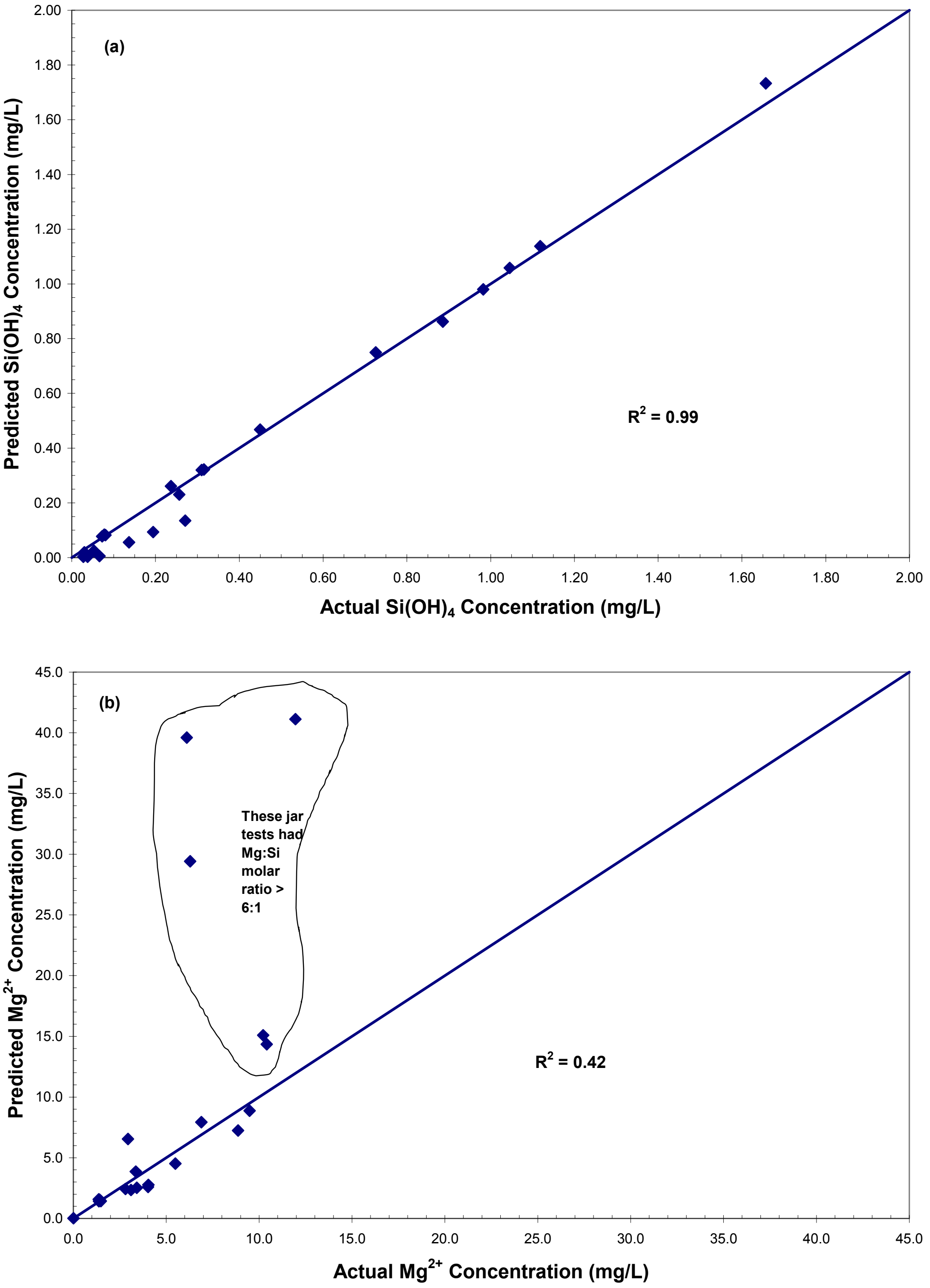

Figure 4-7. Comparison of model predictions and actual results for (a) silicon and (b) magnesium final concentrations. The 45° line represents perfect agreement between predicted and actual values.

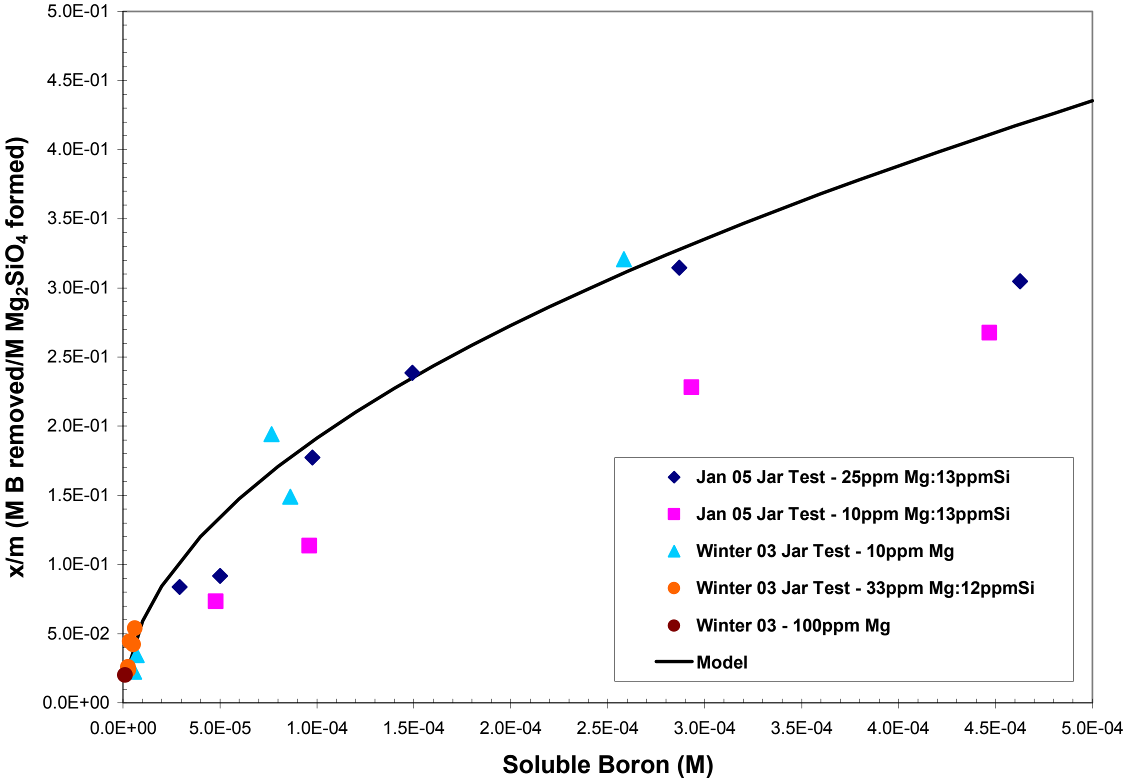

Figure 4-8. Isotherm for boron removal by sorption to Mg_2SiO_4 formed during precipitative softening.

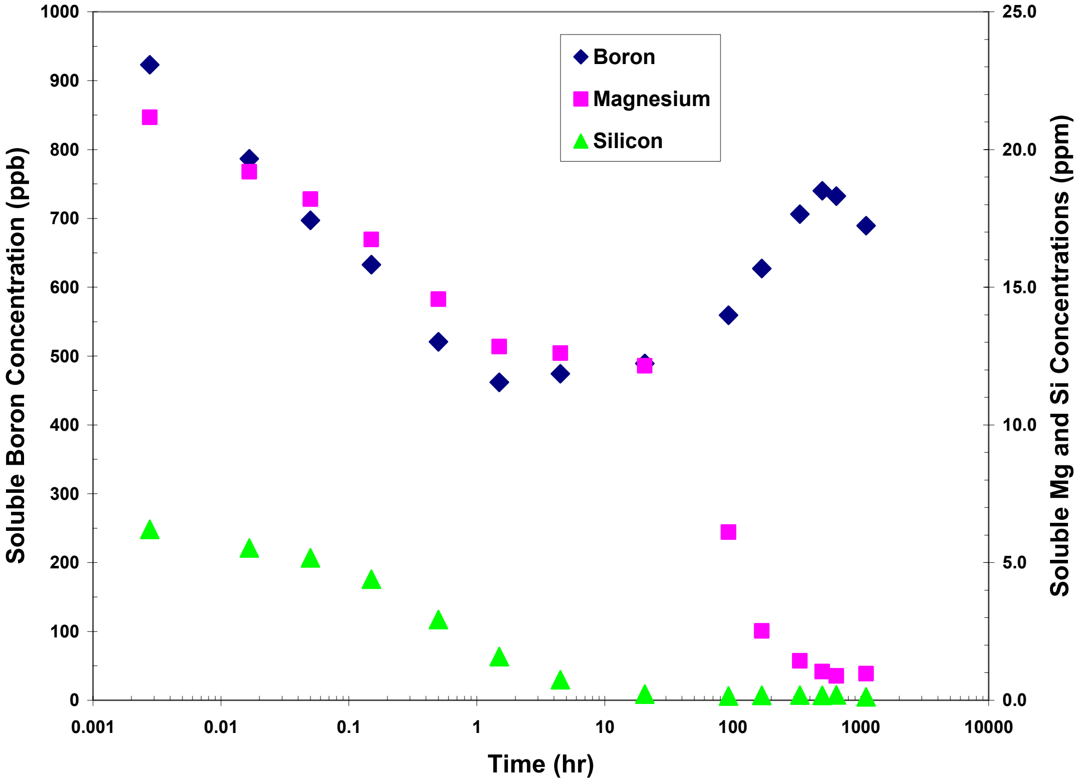

Figure 4-9. Soluble concentration data from prolonged jar test at pH 10.8. Initial magnesium, silicon, and boron were 53 mg/L, 14 mg/L, and 1160 μg/L respectively.

VITA

Jeffrey L. Parks was born in North Wilkesboro, North Carolina on February 4, 1963. He graduated from East Forsyth Senior High School in 1981. Upon graduation he enrolled in North Carolina State University and earned a Bachelor's degree in 1985 in Chemical Engineering and received his Professional Engineering license in 1991. After working in the filtration industry for fourteen years as a product engineer he began work on his Master's degree in Environmental Engineering at Virginia Polytechnic Institute and State University in August 2000. Jeffrey completed his Master's degree in September 2001 and immediately began his doctoral work on boron and chromium.