Actual problems related to inorganic water compounds

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Abstract Some well known inorganic compounds have been subject to treatment for a century and to recent improvements and innovations. The occurrence, the environmental behaviour and the removal techniques of inorganic substances depend primarily on their aquatic chemistry, involving various reactions. The knowledge on speciation and its alteration is essential for process selection. Out of the more recent problems of some inorganic substances, natural, geogenic arsenic plays obviously a major role in a large number of countries. The relatively high chronic toxicity induced lower drinking water standards and activities on improved arsenic removal. Arsenic is a good example to demonstrate the chemistry principles and to derive new treatment techniques at affordable costs. A full-scale process comparison in Germany is presented, indicating the superior efficiency of a newly developed fixed-bed adsorption with a commercial granular ferric hydroxide, developed in the early 1990s. It is especially suitable for small-scale water supplies, for well-head treatment and even for decentralised removal of arsenic with low maintenance requirements.

Keywords Arsenic; granular ferric hydroxide; inorganics; speciation; trace compounds; water treatment

Introduction

Major inorganic compounds in raw waters have always received great attention in view of resource selection and adequate water treatment. Classic examples are the alkaline earth cations (hardness), dissolved salts, reduced iron and manganese, ammonia and sulfide. This paper will, however, not deal with this group of common substances, but with more recent problems of trace inorganic compounds. Some of these problems may have existed for several decades, due to natural occurrence, but recent toxicological evaluations induced significant reductions in the maximum contaminant level in drinking water. This requirement caused research and development activities on the efficiencies and optimisation of well known and established treatment options as well as on the innovation of new treatment processes.

The four sessions of this conference on inorganic compounds, found in ground waters, represent more or less the wide span of targets substances and treatment techniques. Traditional inorganics, such as ammonia, manganese, ferrous ions, hardness and dissolved salts are the topics of about half of the oral contributions. The other half is related to heavy metals and, specifically, four of them are concerned with the arsenic problem. The author was engaged for more than 10 years in arsenic research, resulting in an innovative treatment technology for naturally contaminated ground waters. Arsenic is probably nowadays one of the most important inorganic trace compound in drinking water supplies, due to its rather wide-spread occurrence in natural water bodies. It is also a very good example for demonstrating the role of water chemistry on technological solutions. Before presenting our findings on arsenic removal, a short chapter on the underlying chemical processes is included, applicable in principle to most inorganic trace compounds and water treatment processes.

The basic chemistry of inorganic trace compounds

Chemical reactions of target substances with water molecules, with dissolved inorganic and organic compounds and with surfaces of colloidal and suspended particles are
responsible for the formation of “species”. The process is thus called “speciation”. The species can be present as neutral, cationic or anionic molecules or they are solid-bound. They are basically decisive for the environmental behaviour in aquatic systems and for their removal during treatment. Depending on the chemical nature and underlying reactions, the species distribution will vary in different waters, but fairly good methods and models exist to predict species formation in water of a low organic content (avoiding complex reactions with the natural organic matter). There is, however, also a need to determine analytically the species (like arsenic(III) and arsenic(V), or chromium(III) and chromate(VI)). The redox species of a specific target compound are exhibiting quite often differing properties and removal efficiencies. The six most important types of chemical reactions are shown in Table 1 (Stumm and Morgan, 1995).

These reactions are quantified by reaction rate constants and the mass action law, however very often, multiple and coupled reactions occur, requiring iterative mathematical solutions, including corrections of constants for temperature, ionic strength and surface charge of solids. Software packages are available to solve this task, even for chemical surface complexation reactions. Some of the above reactions are, however, frequently rather slow, such as redox reactions, precipitation and surface adsorption, and need special attention in treatment plant design. An example is reduced As(III), present in reduced ground waters, but its reaction with dissolved oxygen is very slow, requiring catalytic or biological methods to speed it up for technical feasibility or other stronger and quicker oxidants must be applied (Jekel, 1994). For most heavy metals, the basic reactions in water are well known, if other dissolved inorganic compounds are involved. There is a lack of knowledge concerning the quantitative description of reactions with natural organic matter and on the surface processes of poorly defined solids, especially in multi-component adsorption. In this latter case, sorption can be quantified by experimentally derived adsorption isotherms, determined for the specific case of a water.

### Table 1 The chemical speciation of trace inorganics based on different reactions

<table>
<thead>
<tr>
<th>Type of Reaction</th>
<th>Chemical Equation</th>
<th>Examples</th>
</tr>
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<tbody>
<tr>
<td><strong>1. Hydrolysis reactions:</strong></td>
<td>( \text{Me}^{n+} + z \text{H}<em>2\text{O} \rightarrow \text{Me}^{(OH)</em>{n-z}}^z + z \text{H}^+ )</td>
<td>( \text{Al}^{3+} \rightarrow \text{Al}^{(OH)<em>{2+}}^2 + \text{H}^+ \text{ Al}^{(OH)</em>{2+}} \text{ etc.} )</td>
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<tr>
<td><strong>2. Acid/base reactions:</strong></td>
<td>( \text{H}_3\text{MeO}_4^- \rightarrow \text{H}_2\text{MeO}_4^- + \text{H}^+ )</td>
<td>Phosphoric acid, Arsenic(V), Selenic acid(VI)</td>
</tr>
<tr>
<td><strong>3. Redox reactions:</strong></td>
<td>( \text{Me}^{(\text{red})} \rightarrow \text{Me}^{(\text{ox})} + n \cdot \text{e}^- )</td>
<td>As(III) to As(V), Se(IV) to Se(VI), Cr(III) to Cr(VI)</td>
</tr>
<tr>
<td><strong>4. Precipitation reactions:</strong></td>
<td>( \text{Me}^{n+} + \text{A}^{m-} \rightarrow \text{Me}_x\text{A}^{y-} \text{ (solid) } )</td>
<td>( \text{Al(OH)}_3, \text{ CaCO}_3, \text{ FeCO}_3 )</td>
</tr>
<tr>
<td><strong>5. Complexing reactions:</strong></td>
<td>( \text{Me}^{n+} + z \cdot \text{B}^{m-} \rightarrow \text{MeB}_{z}^{(n-z)m} \text{ (solid) } )</td>
<td>EDTA, humic and fulvic acids, phosphate</td>
</tr>
<tr>
<td><strong>6. Sorption reaction on surfaces:</strong></td>
<td>( \text{Me}^{(ads)} \rightarrow \text{Me}^{(ads)} )</td>
<td>Heavy metal cations on ferric or aluminium hydroxides; Arsenate(V) on oxides/hydroxides</td>
</tr>
</tbody>
</table>
The arsenic case

Although arsenic in raw waters (typically ground waters) has received some attention over the last 50 years (in cases of high content, exceeding previous standards of 0.05 ppm), the recent troubles are caused by the toxicological evidence of arsenic exposure and the lower arsenic standards in the range of 0.01 ppm. Germany was the first state to propose 0.01 ppm in 1989, with a lag time until 1996 for implementation (TrinkwV 1989). Later WHO and the European Union followed this step in recent years (WHO 1993, EU 1998). The US-standard is still open and subject of debate, but may arise at 5 or 10 µg/L (Frey et al., 1998). Arsenic is one of a few aqueous compounds where human toxicological data are available for large populations over several decades of consumption of high arsenic levels. The problem is the interpolation to low concentrations around the 10 µg/L. The WHO/EU-standard of 10 µg/L is more or less a compromise between the task of public health protection and technical feasibility for removal and for quality analysis (detection limit of As is in the range of 1 µg/L).

It was known that some regions of the world have high arsenic levels, such as Taiwan, Chile and the United States. Intense monitoring and toxic effect observations (like in Bangladesh) lead to the conclusion, that natural arsenic is a rather frequent problem. The author knows of cases, exceeding the new standards, in Europe (UK, Germany, Finland, Hungary, Greece, Italy, Slovak Republic), in Asia (India, Bangladesh with probably the greatest arsenic calamity, Taiwan, Thailand) and in the Americas (USA, Argentina, Chile). It would be not surprising to find more countries. In the USA, the Southwest is mostly hit, like the state of New Mexico, where 80% of the population gets drinking water exceeding 10 µg/L. A special research program is started in the USA to cope with the problem, in view of several US$ estimated to be required for treatment plants (Frey et al., 1998).

Caused by the early introduction of a lower German drinking water limit value in 1989, research was initiated in the author’s department on various aspects of arsenic analysis, arsenic(III) oxidation and adsorptive arsenic removal.

The standard reduction has affected some 300 small to medium-sized water utilities in Germany who withdraw groundwater containing arsenic of geogenic origin. With the aim of providing the water utilities efficient and reliable methods for arsenic removal, the Dept. of Water Quality Control of TU Berlin investigated existing water purification methods for their suitability and performed research projects on possible improvements and new alternatives. Since all the methods can only remove As(V) effectively, and fail to remove As(III) (Jekel, 1994), oxidation methods were also investigated and developed. Effective oxidation could be achieved by including solid manganese dioxide in a packed filter bed (Driehaus et al., 1995). In addition it could be shown that rapid biological oxidation of As(III) in a filter bed is possible and indeed technically not complicated (Seith and Jekel, 1997). Within the scope of this work, an analytical method was developed for the reliable differentiation between As(III) and As(V) on the basis of hydride generation atomic spectrometry (Driehaus and Jekel, 1997).

An established and well known method for arsenic removal of drinking water is the coagulation with a ferric salt. In this case the arsenic is attached to the formed ferric hydroxide flocs. These are then removed by rapid filtration. An alternative is the use of a ferrous salt as coagulant. In this case oxidation by means of dissolved oxygen to ferric ions is necessary as a first step. For smaller water supplies, the fixed–bed adsorption processes are more appropriate. The adsorbent can be activated alumina in a absorber column, although this is not ideal for arsenic adsorption. Granulated ferric hydroxide (GFH) has been developed as a new adsorbent at the TU Berlin for the removal of arsenic (Driehaus et al., 1998), offering the potential as a very effective, simple and reliable method for the arsenic removal with very high capacities.
A case study on full-scale treatment for arsenic removal

At a water utility which faced an arsenic problem typical for many parts of Germany, a water treatment demonstration plant was installed, in which the various methods could be improved and compared with each other in a full scale operation. The investigation included also a case-related estimation of costs for each applied removal technique.

The treatment plant for arsenic removal was set up in the Stadtoldendorf water works (Lower Saxony). The supply area lies in the sandstone area of the “Solling”, where geogenic arsenic is found in the groundwater. Groundwater at approx. 600,000 m³ per year is extracted from three deep wells. The characteristic parameters of the oxygen-rich raw water were as follows:

- Turbidity: 0.45 FNU
- Arsenic: 21 µg As(V)/L, no AsIII
- pH: 7.9
- Orthophosphate: 50 µg PO₄-P/L
- Calcium: 50 mg/L
- Fluoride: 50 µg/L
- Hydrogen carbonate: 2.3 mmol/L
- Silicate: 15 mg Si/L

The treatment plant, designed for a maximum flow rate of 2,450 m³/day, was equipped with four identical pressure filter units in parallel. The layout is shown in Figure 1. The filters had an area of 5.31 m² each. They are designed to be operated with a filter rate of 4–12 m/h.

Two filter containers (F1 and F3) were set up for the coagulation with iron salts, with a two-layer filter filled with 0.7 m sand (grain size 0.63–1 mm) and anthracite (0.8–1.6 mm). Ferric chloride and ferrous sulfate solutions were used as coagulation agents. Filter 2 were filled with 5 m³ of the new adsorbent GFH (Supplier: GEH Wasserchemie, Osnabrück), filter 4 was filled with 11 m³ activated alumina. The option was available to dose acid and alkaline solution at the in- and outlet of the adsorber units. All filters could be backwashed with water, the coagulation filters could also be washed by air scour.

Results

Coagulation with iron salts

In order to optimize the coagulation/flocculation with iron salts, the degree of removal of arsenic was determined as a function of iron dose. The results are shown in Figure 2. The level of removal increased rapidly with the increase in dose. For a dose of 1 g/m³ a
reduction of 90% could be achieved. In order to ensure that the control value of 5 µg/L is complied with, allowing a safety margin below the limit value of 10 µg/L in case of operational variations, it is necessary to have a removal rate of 75%. In each case, this requires an iron dose of at least 0.6 g/m³, but no difference exists between ferric and ferrous salt.

Coagulation can only be used successfully if the solids can be separated out reliably and if most of the coagulant is also removed. The residual concentration of iron in the treated water is determined by the solubility of the coagulation products, which is largely dependent on the pH of the water. In the case presented here, the pH of 7.9 was in the optimum range for the complete precipitation of the iron, thus the levels of dissolved iron in the filtrates for both coagulants lay well below 3 µg/L.

However, because of the differing mechanisms for the formation of flocs/particles, a very considerable difference in separation was found. The oxidation of ferrous to ferric ions takes place gradually in oxygen-rich aqueous solution, thus the hydroxide flocs are mostly formed within the filter bed. This leads to the production of flocs on the filter grains which are smaller and more dense than the ferric flocs and with better surface adhesion properties. The main difference in the separation of the flocs shows in Figure 3, which

![Figure 2](https://iwaponline.com/ws/article-pdf/2/1/1/408575/1.pdf)  
Figure 2  Removal of arsenic as a function of the dosages of Fe(III) and Fe(II)

![Figure 3](https://iwaponline.com/ws/article-pdf/2/1/1/408575/1.pdf)  
Figure 3  Total iron concentration against filter depth for Fe(III) and Fe(II) (filter rate: 7.7 m/h)
presents the decrease of the iron concentration through the filter bed towards the end of a filter run. In the case of ferrous ions the iron concentration drops very quickly, even though more than 10 kg of iron has been removed (after 11,900 m³ of treated water). The flocs are completely removed within the first 0.5 m of the filter layer. For ferric ions the iron concentration is reduced more gradually through the filter bed. After 4.3 kg of separated iron and 4,600 m³ flow of treated water, however, the filtration capacity is exhausted and flocs may break through.

Although the flocs with ferrous salt are separated mainly in the upper layers of the filter, there is surprisingly a lower pressure loss. In the case of ferric salt the head loss increases linearly with the amount of iron separated. At the breakthrough point (4.3 kg of separated iron) the head loss peaks at 330 mbar. In the case of ferrous salt the pressure loss for 4.3 kg of separated iron is only 150 mbar. The head loss increases with the mass of iron separated, until at 10 kg of iron the head loss is approximately 520 mbar.

**Adsorption techniques**

**Activated alumina**

The adsorption on activated alumina proved to be the least suitable for large-scale applications. Owing to inadequate information, errors were made when filling the filters with activated alumina and the granular material solidified and could no longer be used. Investigations showed that the reason was the high alkalinity of the used commercial activated alumina, which gave rise to cement-like reactions on contact with water. Large amounts of water would be necessary to wash out the alkalinity (ca. 300 bed volumes), which represents a further obstacle to its use. As a result of these problems, no further tests were carried out with the activated alumina, which in any case does not adsorb arsenic opti-

**Granulated ferric hydroxide**

Granulated ferric hydroxide (GFH) is a weakly crystalline b-FeOOH produced by conditi-

<table>
<thead>
<tr>
<th>β-FeOOH</th>
<th>52–57%</th>
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<tbody>
<tr>
<td>Iron density</td>
<td>about 0.38 kg/L</td>
</tr>
<tr>
<td>Water content</td>
<td>43–48%</td>
</tr>
<tr>
<td>Grain density</td>
<td>1.59 kg/L</td>
</tr>
<tr>
<td>Packing density</td>
<td>1.29–1.29 kg/L</td>
</tr>
<tr>
<td>Particle porosity</td>
<td>72–77%</td>
</tr>
<tr>
<td>Porosity of the bed</td>
<td>22–28%</td>
</tr>
<tr>
<td>Specific surface</td>
<td>250–300 m²/g</td>
</tr>
</tbody>
</table>
Apart from arsenic, other anions also adsorbed on the surface of the GFH. This results in a reduction in arsenic adsorption. In comparison with arsenic the breakthrough of silicate and fluoride occurs quite early; after approximately 6,000 bed-volumes only 10% are still removed. The main competitor, like in coagulation with iron salts, is orthophosphate. The adsorption of phosphate and arsenate(V) during operation is shown in Figure 4.

Although phosphate is present in relatively high concentrations in the raw water (molar ratio P/As = 5:1), the breakthrough occurs slightly earlier than for arsenic. This demonstrates the higher affinity for the arsenate(V). It is possible to estimate that at least 80,000 bed-volumes of water can be treated before the limit value of 10 µg/L is reached. The average loading of the GFH is then about 1.3 g As per litre GFH corresponding to a GFH-consumption of approx. 13 mL/m³. By using 2 GFH adsorber units in parallel with shifted start-up points, 100,000 bed volumes can be reached (mixing of filtrates guarantee the 5 µg/L). In the operational phase with acidified influent the arsenic concentration decreases drastically from about 7 to 2 µg/L. Measurements in different bed depth indicate, that breakthrough will then occur after a three-fold filter run time (above 240,000 bed volumes).

Since the GFH adsorber also operates as a particle filter, turbidity of the raw water is also completely eliminated. There is a gradual increase in the head loss of the adsorber bed. In order to avoid excessive mechanical stress on GFH, 500 mbar should not be exceeded. After approximately 8,000 bed-volumes the adsorber bed was backwashed with water only at 30 m/h; backwash water consumption was approximately 0.13%.

Economic comparison
The costs of the arsenic removal consist of the investment for the treatment plant and the investment for a sludge settling tank (only coagulation methods) as well as of the consumption costs for chemicals respectively GFH, backwash water, disposal of the residuals and maintenance of the plant.

The compilation of the investments were calculated on the basis of the project documents of the executing firms. According to the expected life span of the components the periods of amortization were selected to be 2, 5, 10 and 20 years. Credit interests were included. It is assumed that the credit period is equal to the amortization period. Within this time, a linear credit repayment takes place. The credit interests are distributed evenly over the entire period (static calculation). An interest rate is estimated at 7% per year.

The consumption costs were calculated under the following conditions:
• production of 600,000 m$^3$ drinking water per year (1,640 m$^3$/day);
• the plant operates with two filter units (flow rate 41 m$^3$/h each);
• the dosage of Fe (III) or Fe (II) amounts to 0.6 g Fe/m$^3$;
• disposal of the sludge after a sedimentation by a waste handling enterprise;
• the treatment capacity of the GFH amounts in case A to 70,000 bed volumes (conservative estimation) and case B 100,000 bed volumes (2 adsorber with shifted start-up point);
• the GFH price includes the disposal; discharge of the backwash water into the public sewer system;
• calculation of the costs for backwash water on the basis of the internal supply price for pure water;
• constant telemetric monitoring of the plant;
• Fe(III) requires regular maintenance every 3 days, because of possible floc breakthrough; Fe(II) only every 5 days; unscheduled maintenance, which cause higher cost, is necessary for both coagulant every 20 days;
• regular maintenance for GFH adsorption every 10 days; 2 arsenic analyses monthly.

Table 3 shows the calculated costs with the percentages for the examined treatment techniques. With the treatment capacity of 100,000 bed volumes (case B), the GFH adsorption proved to be the most economical technique. Even in the unfavorable case A (70,000 bed volumes) the costs are only slightly higher than for the Fe(II) coagulation. Owing to the high sludge disposal costs the Fe(III) coagulation is the most expensive in comparison.

**Conclusion**

All the methods for the removal of arsenic tested in this investigation are able to ensure the compliance with the limit value for drinking water of 10 µg As/L. However, there are differences between the methods in terms of operational handling, monitoring and maintenance, as well as in technical and economic aspects.

Considering first the two methods involving coagulation, the use of ferrous salt has advantages over the use of ferric ions. These advantages are the result of the mechanism of formation of the iron hydroxide flocs with ferrous ion dosing and their properties in filtration:

• The better filtration properties with ferrous ions avoid breakthrough of flocs, offering better operational reliability.
• The separation of the flocs leads to a lower head loss in the case of ferrous salt.

The GFH process is a new method of arsenic removal which proved to be very successful. Even with an unfavourable pH near 8 and competing phosphate it was possible to ensure compliance with the drinking water standard for more than 70,000 bed volumes. Apart from initial minor alterations to the pH, the water was not affected negatively in any
way, nor were there any hygienic problems. Phosphate was adsorbed but to a lesser extent than arsenic and a low turbidity was also completely eliminated.

The GFH process was the easiest to operate. In comparison with the coagulation methods it offered very high operational reliability, with minimum needs for labour input. It is a simple process technology, requiring lower levels of investment in a plant. The operation and monitoring of a GFH adsorber can be executed by untrained personnel. The cost comparison shows that the GFH adsorption can be the most economical method, if a lifetime above 72,000 bed volumes is achieved. This depends on the raw water characteristic, essentially on the pH-value, the competing phosphate level and the operation mode of the plant.

In a plant with 2 adsorber in operation and a shifted start-up point, more than 100,000 bed volumes can be achieved. A pH-value of about 7 could even be favourable for an adsorber life of 240,000 bed volumes and more. Furthermore, GFH is a feasible option for decentralized treatment at individual affected water extraction points (well-head treatment) or even in point-of-entry and point-of-use systems.

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References