Arsenic Occurrence and Innovative Technologies Development for Arsenic Pollution control in China

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Arsenic and arsenism occurrence in China

Approaches and strategies for arsenic pollution control
- What we are doing for arsenic pollution control
- Strategies for arsenic pollution control in China

Innovative technologies development in China
- Small systems for arsenic removal in distributed rural areas
- Innovative Processes available in Municipal drinking water plant

Conclusions
Population exposing to high arsenic (>50 ppb): >5 million, mainly in rural areas
More people are included as As exposure due to more strict standard for As in drinking water (<10 ppb)
As pollution distribution:
11 provinces/Autonomous Regions/Municipalities
Arsenism rate in high-As areas: 15.54%
Arsenic pollution distribution

1st Inner Mongolia
2nd Shanxi
3rd Qinghai
4th Anhui
5th Jilin
6th Xinjiang

Referenced

Ranking between provinces / Autonomous Regions / Municipalities
Among these 14 villages, 12 villages exceed 10 μg/L and 2 exceed 50 μg/L
As pollution occurs in 42 villages
Population being exposed to arsenic: 35,000
Simultaneous presence of arsenic and fluoride
## Arsenic pollution occurrences in typical provinces

<table>
<thead>
<tr>
<th>Province</th>
<th>Media and underground situations</th>
<th>areas (km²)</th>
<th>As concentration (µg/L)</th>
<th>Affected population</th>
<th>Arsenism cases</th>
</tr>
</thead>
<tbody>
<tr>
<td>Xinjiang</td>
<td>Underground &gt;100m</td>
<td>3,000</td>
<td>~850</td>
<td>100,000</td>
<td>2,000</td>
</tr>
<tr>
<td>Inner Mongolia</td>
<td>Underground 10~50m</td>
<td>1,500</td>
<td>~1860</td>
<td>1 million</td>
<td>3,000</td>
</tr>
<tr>
<td>Shanxi</td>
<td>Underground 10~70m</td>
<td>1,500</td>
<td>~1930</td>
<td>1 million</td>
<td>4,000</td>
</tr>
<tr>
<td>Jilin</td>
<td>Underground</td>
<td>67 villages</td>
<td>~207</td>
<td>60,000</td>
<td>670</td>
</tr>
<tr>
<td></td>
<td></td>
<td>22 villages</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ningxia</td>
<td>Underground</td>
<td>2,000</td>
<td>~2,000</td>
<td>25,000</td>
<td>500</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4 villages</td>
<td>~318</td>
<td>12,200</td>
<td>260</td>
</tr>
<tr>
<td>Qinghai</td>
<td>Underground</td>
<td>5 villages</td>
<td>~150</td>
<td>86,900</td>
<td>8</td>
</tr>
<tr>
<td>Anhui</td>
<td>Underground</td>
<td>5 villages</td>
<td>~143</td>
<td>60,300</td>
<td>0</td>
</tr>
<tr>
<td>Beijing</td>
<td>Underground</td>
<td>4 villages</td>
<td>~1,800</td>
<td>N.A.</td>
<td>N.A.</td>
</tr>
<tr>
<td>Taiwan district</td>
<td>Underground 100~280m</td>
<td>4 villages</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

N.A.: not available

Referenced
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Conclusions
What are doing in China...

Aiming to supply safe drinking water to people in rural areas, including arsenic control...

- Endeavors from the government predominant, constructive and effective
- Non-Governmental Organization (NGO) Efforts we are groping and striving ...
- Commercial investment and marketization rare, but being stimulated and advocated
Efforts from government

- **2000~2005**, 11.7 billion RMB from central government, 67 million people being benefited
- **2005~2006**, 2 billion RMB from central government, 11 million people being benefited
- **2007~2012**, 32 billion RMB from central government, 27.9 billion RMB from local government, 6.5 billion RMB from local residents, aiming to providing safe drinking water to 160 million people

- The perennial cost should be evaluated for residents
- The operation, maintenance and fittings replacement should be well supervised for
NGO efforts

Chinese Academy of Sciences (CAS): Technical expertise

China Foundation for Disabled Persons (CFDP): Project execution and management

Global Health and Education Foundation: Funding provision
NGO efforts

- The 1st water station installation was finished on Sep. 27th, 2007 in Shanyin County;
- The another 5 stations are expected to be finished in 2008;
- In the future, more stations...

The operational models are very important for the sustainable development of NGO efforts
Strategies for arsenic pollution control

- **Changing source water**
  - Being restricted, if absence of satisfactory and safe water source
  - Great engineering investment for water transportation systems
  - Water quality should be well evaluated except for arsenic

- **Treatment facilities installation (recommended)**
  - Without great pipeline constructions and corresponsive investment

  - Less expense required, more people benefited at the same time

- The development of technologies and systems for arsenic removal from drinking water is of critical importance in China

- Easy to handle, cost effective, being available in rural areas if being well managed
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Conclusions
2.2 Pre-Oxidation Processes

Reduced inorganic As(III) (arsenite) should be converted to As(V) (arsenate) to facilitate removal. This step is critical for achieving optimal performance of all unit processes described in this Handbook. Conversion to As(V) can be accomplished by providing an oxidizing agent at the head of any proposed arsenic removal process. Chlorine, permanganate, ozone, and Filox-R™ are highly effective for this purpose. Chlorine dioxide and monochloramine are ineffective in oxidizing As(III). Ultraviolet (UV) light, by itself, is also ineffective. However, if the water is spiked with sulfite, UV photo-oxidation shows promise for As(III) conversion (Ghurye and Clifford, 2001). Based on these considerations, only chlorine, permanganate, ozone, and Filox-R™ are discussed further in this Handbook.

USEPA, 2003
High performance

As(III) removal

Low cost
Ferric and manganese binary oxides (FMBO) Preparation

Fe$^{2+}$ stock solution → Base solution → Permanganate stock solution → Suspension of Ferric and manganese binary oxides (FMBO) → aged → filtration → dried → Power FMBO
FMBO Characterization

SEM/EDX analysis

Oxidation and adsorption abilities

<table>
<thead>
<tr>
<th>Element</th>
<th>Wt%</th>
<th>At%</th>
</tr>
</thead>
<tbody>
<tr>
<td>MnK</td>
<td>24.02</td>
<td>24.32</td>
</tr>
<tr>
<td>FeK</td>
<td>75.98</td>
<td>75.68</td>
</tr>
</tbody>
</table>

Fe:Mn \(\approx\) 3:1
<table>
<thead>
<tr>
<th>adsorbents</th>
<th>Maximal adsorption potential</th>
<th>references</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>As(III) (mmol g(^{-1}))</td>
<td>As(V) (mmol g(^{-1}))</td>
</tr>
<tr>
<td>FMBO</td>
<td>1.77 (pH4.8)</td>
<td>0.93 (pH4.8)</td>
</tr>
<tr>
<td>Manganese dioxide</td>
<td>0.13</td>
<td>0.1</td>
</tr>
<tr>
<td>Geothite</td>
<td>/</td>
<td>0.53 (pH3-3.3)</td>
</tr>
<tr>
<td>Al(_2)O(_3)/Fe(OH)(_3)</td>
<td>0.12 (pH 6.6)</td>
<td>0.49 (pH 7.2)</td>
</tr>
<tr>
<td>Fe(III)-loaded sponge</td>
<td>0.24 (pH 9.0)</td>
<td>1.83 (pH 4.5)</td>
</tr>
<tr>
<td>Fe-Mn-mineral</td>
<td>0.16 (pH 5.5)</td>
<td>0.09 (pH 5.5)</td>
</tr>
<tr>
<td>TiO(_2)</td>
<td>0.43 (pH 7.0)</td>
<td>0.55 (pH 7.0)</td>
</tr>
</tbody>
</table>

Proposed Mechanisms for As(III)

1st Step: As(III) adsorption onto FMBO surfaces

\[
\text{As(III)}(\text{aq}) + (-\text{S}_{\text{Fe-Mn}}) \rightarrow \text{As(III)} - \text{S}_{\text{Fe-Mn}} \quad (1)
\]

2nd step: As(III) oxidation with manganese oxides

\[
2\text{MnO}_2 + \text{H}_3\text{AsO}_3 + \text{H}_2\text{O} \rightarrow 2\text{MnOOH}^* + \text{H}_2\text{AsO}_4^- + \text{H}^+ \quad (2)
\]
\[
2\text{MnOOH}^* + \text{H}_3\text{AsO}_3 + 3\text{H}^+ \rightarrow 2\text{Mn}^{2+} + \text{H}_2\text{AsO}_4^- + 2\text{H}_2\text{O} \quad (3)
\]

Arsenic species transformation and Manganese dioxides reductive dissolution

3rd step: As(V) adsorbing onto ferric oxides sites

\[
\text{As(III)} - \text{S}_{\text{Fe-Mn}} + \text{As(V)}(\text{aq}) \rightarrow \text{As(V)} - \text{S}_{\text{Fe-Mn}} + \text{As(III)}(\text{aq}) \quad (4)
\]

The reductive dissolution of manganese oxides changes the surface characteristics of adsorbents, promotes the formation of active sites available for arsenic adsorption, and facilitates arsenic removal.

But engineering

How to develop innovative technologies, based on FMBO, available for small systems and large scale drinking water plants?
1st: Innovative Processes for small systems

In Situ Coating and Embedded Regeneration

Porous carrier

Active species (FMBO) in situ coating

arsenic adsorption

In Situ Coating and Embedded Regeneration
In Situ Coating and Embedded Regeneration

Feasible in engineering, easy to be auto-controlled

KMnO$_4$ + NaOH

FeSO$_4$

Repeated several times
Coated on porous materials:

- Coated on diatomite
- Coated on zeolite
Bench scale continuous tests

**Initial As (As(III) and As(V)) = 100 μg/L, pH = 7.0, EBCT = 5 min**

- Better potential of removing As(III) than As(V) is also observed
- Adsorbents regeneration increases capacity for arsenic
## Adsorbents characteristics

<table>
<thead>
<tr>
<th>sample</th>
<th>Surface area (m² g⁻¹)</th>
<th>Pore volume (mL g⁻¹)</th>
<th>Average pore diameter (Å)</th>
<th>Fe and Mn content (mg g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Plain DE</td>
<td>7.09</td>
<td>0.005</td>
<td>18.13</td>
<td>0.0</td>
</tr>
<tr>
<td>cA-I</td>
<td>8.66</td>
<td>0.013</td>
<td>58.25</td>
<td>10.58</td>
</tr>
<tr>
<td>cA-II</td>
<td>10.73</td>
<td>0.015</td>
<td>61.57</td>
<td>16.40</td>
</tr>
<tr>
<td>cA-III</td>
<td>12.51</td>
<td>0.021</td>
<td>65.74</td>
<td>22.61</td>
</tr>
<tr>
<td>cA-IV</td>
<td>16.23</td>
<td>0.021</td>
<td>69.53</td>
<td>29.74</td>
</tr>
</tbody>
</table>

Embedded regeneration increase BET surface area and Fe/Mn content, which are valuable for arsenic removal.
Field tests in suburb of Beijing

Objectives of field tests

- Different kinds of carrier as manganese ore, diatomite, zeolite, geothite, gravel sand, aluminum oxides… (carrier optimization)
- Filtrating rate and EBCT (operational parameter optimization)
- Adsorbents regeneration
- Evaluation of aqueous Fe$^{2+}$ and Mn$^{2+}$ removal and dissolution

14 months fields tests for arsenic removal capacity evaluation and parameters optimization
Design of small systems processes

- FMBO adsorption
- Sand filtration + FMBO adsorption
- (oxidation) + Micro-flocculation + FMBO adsorption
- (oxidation) + Micro-flocculation + Sand filtration
- (oxidation) + Micro-flocculation + Sand filtration + FMBO adsorption
- ...

Removal of Fe(II), Mn(II), As(III), As(V)
Engineering demonstration (1000m³/d)

2007
Beiwu Town, Shunyi District, Beijing

2008
Shunyi District, Beijing; Shanyin, Shangxi Province
Fe and Mn concentration in the effluent are lower than that in the influent, indicating the potential for Fe and Mn removal.

Mn are not observed to dissolve from FMBO during As adsorption, possibly ascribing to adsorption of Mn(II) onto FMBO.

Adsorbents regeneration optimization is crucial for Mn(II) dissolution control for the process.
Based on processes of typical large scale plants:

Firstly, FMBO is enhanced to be coated onto surfaces of filtering media;

Secondly, FMBO is in situ formed and introduced into the systems, acting as both oxidants and adsorbents;

Thirdly, the in situ formed FMBO is on-line coated onto filter media for surfaces refreshing.

In the end, the adsorbed arsenic is excluded.

- Avoid great reconstruction for existing plants, if being required for facilitating arsenic removal.
- Easy, high effective and low expense for practice.
Cases analysis in Zhengzhou city

Underground wells scattering in Zhengzhou City

As occurrence in Wells for Dongzhou Plant

As occurrence in Wells for Shifo Plant

Arsenic species analysis:
As(III) ratio varies from 54.6%~100%
Source: water aeration filtration disinfection distribution systems

- 14.2 ppb
- 11.0 ppb (22.5%)

Shifo Plant (100,000 m³/d)  Dongzhou Plant (200,000 m³/d)

Accounting for 30% of drinking water in Zhengzhou City

- Not satisfactory As removal achieved, exceeding newly issued standard in China (10ppb)
- 2.5 million people are potentially exposing to arsenic
- Difficulty in large-scale reconstruction due to capital shortage and less sites available
Cases analysis—processes reconstruction

Source
- water
- aeration
- filtration
- disinfection
- distribution systems

1. FMBO introduction during source water transportation

2. FMBO in situ coated onto filter media and on-line refreshed, without adsorbents regeneration

3. Filter media optimization, avoid water loss increase due to FMBO introduction

Advantages:
- Without large scale reconstruction
- and high investment
Conclusions

- Arsenic occurrence in drinking water is relatively serious in China, especially in rural areas.

- Much efforts are being devoted for arsenic pollution control in drinking water, the installation of water treatment facilities are less expensive and more effective in comparing to changing source water.

- The development of innovative technologies available in rural areas are crucial for arsenic control in China.

- We are devoting to developing innovative technologies for arsenism control in China.
Acknowledgement

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Thank you for your attention and constructive advices!