clear that for smaller systems serving less than 1,000 people, UV disinfection at 40 mW s cm^{-2} is significantly less expensive than chlorination at a dosage of 1.5 mg L^{-1}, whereas costs for the two methods are comparable for systems serving between 1,000 and 10,000 consumers.

Compared to UV disinfection, a TiO_2-photocatalyzed As(III) oxidation system would incur additional costs due to the TiO_2 media and its eventual disposal. In addition, since oxygen is needed as an electron acceptor, aeration is required if the source water has prohibitively low dissolved oxygen concentrations. Twenty-six percent of groundwater distribution systems currently use aeration, but this statistic does not distinguish between small and large facilities (McNeill and Edwards 1995). Several types of aeration devices are recommended for small systems, including open tray and diffused aeration. Both of these options have low power and maintenance requirements (1997). Moreover, since these aeration methods were designed to remove volatile organic carbon compounds, they typically saturate the treated water with air. A lower oxygen requirement for TiO_2 photocatalysis would mean these treatments could be run with lower air pressures or that even simpler aeration methods, such as cascading or running water over a corrugated surface, could be applied.

The UV intensity needed for TiO_2 photocatalysis is lower than that needed for disinfection: the applied power in these experiments was 25 mW s cm^{-2} for 365 nm. This would lower electricity and lamp replacement costs.

Despite these unknowns for how the true cost of TiO_2 photocatalysis compares to UV disinfection, the substantial cost gap between chlorination and UV disinfection for systems serving less than 1,000 people makes TiO_2/UV worth considering as a pre-oxidation step to convert As(III) to As(V). A TiO_2-based photocatalysis system has several additional benefits over chlorination. First, there are no hazardous chemicals to deal with, resulting in fewer maintenance and training requirements. Also, no disinfection byproducts are generated in water with high TOC. Although this is not likely to be a problem with most groundwaters, TiO_2 photocatalysis would mineralize much of the TOC loading in those waters that do contain significant levels of TOC. TiO_2/UV treatment could be applicable to systems in which a membrane technology is already installed, whereas chlorination causes degradation of certain membranes. Finally, TiO_2 has antibacterial properties when irradiated (Kuhn et al. 2003; Yu et al. 2003; Kim et al. 2005). Although it could not be applied as a primary disinfection method because As(V) must be removed subsequent to TiO_2 treatment, this capability would prohibit bacterial fouling that might otherwise become a concern. If disinfection is necessary, a lower dosage might be possible following TiO_2 photooxidation.

6.3 Considerations for Application of TiO_2-Photocatalyzed As(III) Oxidation

6.3.1 Further information needed

Currently unknown factors critical to evaluating the practicality of this As(III) oxidation approach include the number of bed volumes a given quantity of TiO_2 catalyst can treat before regeneration or replacement is required, the cost of the TiO_2 media, and the minimum dissolved oxygen concentration for efficient operation. The catalyst lifetime is expected to be high because the reaction efficiency does not depend on adsorbing and *retaining* As. TiO_2 is conserved in the reaction; therefore, as long as a dynamic sorption equilibrium is maintained, allowing As(III) to access the TiO_2 surface, the photocatalyst will retain optimal efficiency. However, catalyst poisoning, in which As(V) or other anions (e.g., phosphate, fluoride) saturate sorption sites and remain bound, therefore inhibiting As(III) sorption, needs to be further investigated.

Although catalyst poisoning assessments conducted in this study ran for only 84 and 144 bed volumes during the 22 and 24 hour runs of 5 mM $NaNO_3$ and synthetic groundwater, respectively, total bed volumes treated by the beads in these experiments totaled 267 and 180 (Appendix B). Beads were removed and rinsed several times with water between experiments, but this was shown to remove only a fraction of adsorbed As. No loss of As(III) oxidation efficiency was observed over these time periods. Moreover, a dark sorption period was conducted for several hours before each UV experiment to achieve equilibration of the TiO_2 surface with fixed $[As]_{diss}$. In the $NaNO_3$ matrix, As(III) was the primary adsorbate, but synthetic groundwater systems also included competitive adsorbates like phosphate, fluoride, and sulfate. Although As(III) oxidation was hindered during experiments using groundwater compared to those using $NaNO_3$, indicating that some reaction interference was occurring, the groundwater systems showed no further inhibition of As(III) photooxidation with extended use.

Another consideration with potential catalyst poisoning concerns the mechanism of TiO_2-photocatalyzed As(III) oxidation. Although As(III) oxidation, like that of many organic substrates, has been shown to be dependent on adsorbed concentrations

(Ferguson et al. 2005; Xu et al. 2005), there is evidence that the primary oxidation mechanism can change in the presence of competitive adsorbates, thus minimizing catalyst inhibition or even enhancing photooxidation activity. When fluoride is added to TiO_2, it dramatically reduces As(III) sorption capacity due to strong ≡Ti-F bond formation (Ryu and Choi 2004), but hydroxyl radicals generated at the catalyst surface are consequently able to diffuse into solution and react with dissolved As(III), thus increasing the reaction rate (Minero et al. 2000b; Minero et al. 2000a; Maurino et al. 2005; Mrowetz and Selli 2005). Therefore, unlike adsorption media, which continually adsorb species until they reach sorption capacity, TiO_2 may not be adversely affected by certain competitively adsorbing species.

These findings suggest that TiO_2 is well suited to maintain photoactivity over many bed volumes. However, since water treatment technologies typically require replacement or regeneration after thousands to tens of thousands of bed volumes, longer-term studies are needed to confirm these speculations.

The cost of TiO_2 media must also be better characterized before feasibility of this application can be accurately assessed. The mixed P25/sol gel TiO_2-coated glass beads used in this study have been shown to be effective, but they are probably not financially optimal. Instead of glass beads, a less expensive, nonreactive, granular substance could be used. Similar adhesion of the sol-gel to glass and stainless steel has been demonstrated (Balasubramanian et al. 2003), suggesting that the identity of the substrate is not of great importance.

Another potential setback for the current technique is the high cost of titanium isopropoxide, the precursor to the TiO_2 sol. Industrial scale production would lower this expense, but a synthesis employing a less expensive precursor would be preferable. Depending on the specific follow-up treatment for As(V) removal, beads or an alternate substrate could potentially be coated only with a concentrated P25 slurry. Preliminary experiments conducted with P25 coated beads (Appendix C) demonstrated efficient As(III) oxidation, although this was not directly comparable to studies with P25/sol gel coated beads. The drawback with this method was the mechanical instability of the beads; shaking or other disturbances caused some of the TiO_2 to be dislodged. The media would be expected to have a shorter lifetime than the P25/sol gel coated beads because of incremental TiO_2 loss over time. However, if subsequent As(V) removal treatment is capable of filtering small quantities of dislodged TiO_2, then this simple coating technique may be the most cost effective, even if the media need to be replaced more frequently.

Finally, further studies are needed to determine the minimum amount of dissolved oxygen needed for efficient As(III) oxidation. This work considered only air-saturated solutions, but previous work concerning photooxidation of other substrates has shown a Langmuirian dependence of the reaction rate on dissolved oxygen concentrations (Bideau et al. 1991; Gruebel et al. 1995; Augugliaro et al. 1997). Thus, it is likely that a dissolved oxygen level lower than that corresponding to an air-saturated solution would still result in efficient As(III) oxidation. This information would facilitate process optimization and minimize aeration costs.

6.3.2 Reactor geometry

Given the reaction dependence on TiO_2 absorption of UV light, an annular reactor design (Figure 6.1) is optimal. This allows lamp output in all directions to be used; moreover, since the thickness of the TiO_2-treated layer is limited by UV absorption, it allows a larger volume of water to be treated per lamp. This design is already used for UV disinfection and would require only minimal adjustments of products already on the market. This design also allows for near-plug flow, thus keeping the residence time constant and eliminating the geometric artifacts observed in this study.

The excellent results observed when using sunlight as a radiation source suggest that this natural resource could be quite useful. Use of sunlight would be best applied by using a labyrinth reactor design in which the influent water follows a tortuous route through a thin bed of TiO_2 media, which is irradiated from above (Figure 6.2). This allows sufficient contact time with the TiO_2 media and also approximates plug flow conditions. Several variations on this design are possible depending on specific system needs. For example, if the system is providing water constantly, UV lamps must be available for nighttime treatment. These could be placed underneath the reactor if the reactor bed is made of a light-transmitting material or overhead if lamps do not block incident sunlight. In addition, the labyrinth reactor could either function as a closed or open system depending on whether or not the reactor was sealed on top by a light-transmitting material. In the closed system case, the water can be kept under continuous pressure and no additional security measures are needed to prevent unwanted material from entering the water. However, the open system offers passive aeration as the thin film of water flows over the TiO_2 media, thus bypassing the need for aeration of anoxic source waters. Both cases would require a larger footprint than the annular reactor setup.

Despite the energy savings, systems taking advantage of natural sunlight are unlikely to be used in the United States or other countries where electricity is readily available. This could, however, be of use in developing nations, particularly if it could be combined with a low cost As(V) adsorbent. Its competitiveness with GFH and other iron-based adsorbents would depend on whether the nation in question can produce its own treatment media and the relative shipping costs of TiO_2 media and GFH.

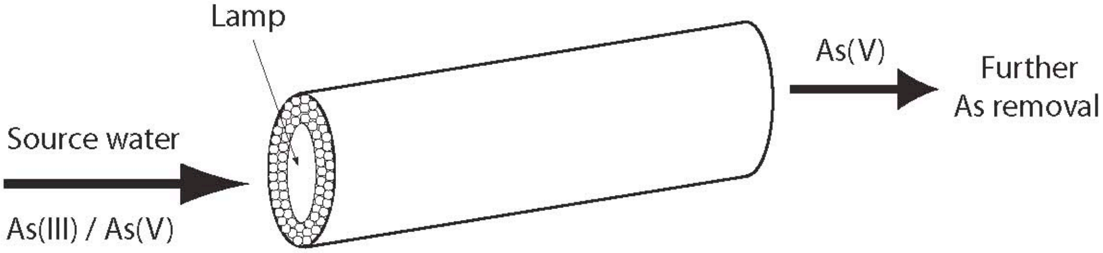

Figure 6.1. Schematic of annular reactor.

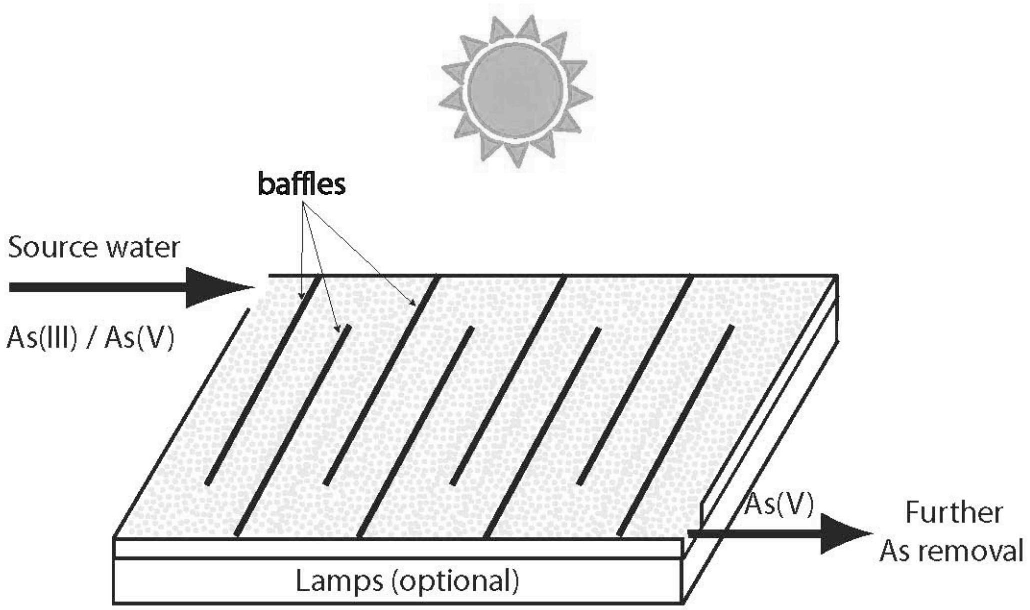

Figure 6.2. Schematic of labyrinth reactor.

6.4 Conclusions

TiO_2-photocatalyzed As(III) oxidation may prove to be a practical and cost-effective pre-oxidation step for U.S. drinking water facilities that meet the following criteria:

(1) Source water contains a substantial fraction of As(III)

(2) System serves less than 10,000 people

(3) A water treatment system is currently in place but it is not effective for As(III) removal (e.g., C/F, AA, etc.)

(4) Chlorination is not currently used, even for disinfection; or adding chlorine earlier in the pipeline would have undesirable consequences

(5) Source water does not have high Fe/Mn levels

Although only a fraction of U.S. water distribution systems meet these criteria, this technology has potential to be the best choice for certain systems. In addition, potential exists for application abroad, either at wellheads or at small drinking water treatment facilities.